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2005

Yan, Q. Y., Gambino, R. J., Sampath, S. & Huang, Q. (2005). Neutron diffraction and ferromagnetic resonance studies on plasma-sprayed MnZn ferrite films. *Journal of Applied Physics*, 97(3).

<https://hdl.handle.net/10356/95499>

<https://doi.org/10.1063/1.1831551>

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Neutron diffraction and ferromagnetic resonance studies on plasma-sprayed MnZn ferrite films

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(Received 2 July 2004; accepted 15 October 2004; published online 30 December 2004)

The magnetic properties of MnZn ferrites are affected by the plasma spray process. It is found that improvements can be made by annealing the ferrite films at 500 °C–800 °C. The annealing induced magnetic property changes are studied by neutron diffraction and ferromagnetic resonance techniques. The increase of the saturation magnetization is attributed to the cation ordering within the spinel lattice, which increases the magnetic moment per ferrite formula. The refinements on the neutron diffraction data suggest that the redistribution of the cation during annealing neither starts from a fully disordered state nor ends to a fully ordered state. The decrease of the coercivity is analyzed with the domain wall pinning model. The measurements on the magnetostriction and residual stress indicate that coercive mechanisms arising from the magnetoelastic energy term are not dominant in these ferrite films. The decrease of the coercivity for annealed ferrite films is mainly attributed to the decrease of the effective anisotropic field, which may result from the homogenization of the film composition and the reduction of the microstructural discontinuity (e.g., cracks, voids, and splat boundaries). © 2005 American Institute of Physics.

[DOI: 10.1063/1.1831551]

I. INTRODUCTION

MnZn ferrites (MZF) have been widely used in electronic applications. The conventional ceramic sintering method,¹ used to fabricate ferrite pieces, presents difficulties in performing the required miniaturization for the complex-geometrical devices. To solve these problems, fabrication techniques for making thin film–thick film devices have been applied on ferrite systems, e.g., pulse laser deposition (PLD),² sputtering,³ and plasma spray.⁴ Among these techniques, plasma spraying of ferrites has certain advantages that are suitable for industrial applications, including (1) bulk productivity: It can easily deposit large area samples with varied thickness (50 μm–2 mm), (2) low substrate temperature (<200 °C), (3) simple process: No need for vacuum or special gas (oxygen, nitrogen) environments, (4) cost efficiency. However, the magnetic properties of the as-sprayed MnZn ferrite films are partially degraded (coercivity is 120–130 Oe) compare to that of sintered MnZn ferrites (coercivity is less than 10 Oe). Although plasma spraying of planar inductors has been demonstrated to be a possible route for applications in industry,⁵ the high coercivity induced hysteresis loss may counteract the advantages.

The magnetic properties of the plasma-sprayed MnZn ferrites improve greatly after heat treatment. By varying the annealing temperature between 500 °C and 800 °C, the coercivity at ambient temperature can be decreased to less than 10 Oe while the saturation magnetization, M_s , increases concurrently. Although the annealing temperature (500–800 °C) is still not acceptable for applications such as integration with semiconductor components, it is much lower than the firing temperature of ceramic paste process (1300 °C)⁶ or

the annealing temperature of the sputtered ferrite films.⁷ Detachment of the ferrite films from some substrates (alumina, silicon) is observed during the heat treatment due to thermal expansion mismatch. This problem can be solved by choosing the suitable substrates, such as magnesium–yttrium stabilized zirconia (commercial available Mg-PSZ or Y-PSZ).

The annealing temperature of 500–800 °C is much lower than the conventional sintering temperature (~1300 °C) of MnZn ferrites, which can help to make plasma spraying of ferrites a useful tool for the industrial applications. The scope of the paper is to investigate the annealing induced magnetic property changes of plasma-sprayed MnZn ferrite films and to understand the mechanisms, which may give useful ideas to improve the engineering process of other magnetic material systems. For MnZn ferrites, the value of M_s is determined by the difference of the number of unpaired spins between the tetrahedral (*A*) sites and octahedral (*B*) sites.⁸ Thus the distribution of the cation in the *A* sites and *B* sites may affect the value of the M_s , which is examined by neutron diffraction in this work. The micro-magnetic theory of coercivity based on domain wall pinning model⁹ describes that the coercivity is closely related to the defects such as grain boundaries, precipitates, surface roughness which can pin the wall motion.¹⁰ In this model the value of coercivity is given by $h_c = 2H_c/H_k$,⁹ where h_c is the reduced coercive force that has been numerically calculated by Paul for various conditions,¹¹ H_c is the coercivity and H_k is the effective anisotropy field. Here the effective anisotropy field may include factors such as crystalline anisotropy terms, magneto-elastic terms¹⁰ and surface effects.¹² In this study, the effective anisotropy field of

plasma-sprayed MnZn ferrites is examined by ferromagnetic resonance. The magnetostriction and residual stress of the ferrite films are also measured. These data are used to explain the coercivity changes of the plasma-sprayed MnZn ferrite films on annealing.

II. EXPERIMENT

A. Synthesis

MnZn ferrite powder (Steward FLP-1510, average particle size: 25 μm) with the nominal composition of $\text{Mn}_{0.52}\text{Zn}_{0.48}\text{Fe}_2\text{O}_4$ was plasma sprayed onto various substrates, e.g., titanium, aluminum, alumina, and magnesium–yttrium stabilized zirconia (commercial available Mg-PSZ or Y-PSZ). The types of substrates have no obvious effects on the properties of ferrite films. The current and voltage was fixed at 500 A and 55 V, respectively. The stand-off distance (the distance between the exit of the nozzle and the substrate) was set to be 120 mm. The thickness of the ferrite films were in the range of 120–150 μm . Free-standing films were made by peeling off the films from the substrates. The as-sprayed films were annealed in air and vacuum at different temperature (500 °C and 800 °C) for up to 180 min. The pressure of the chamber was $\sim 10^{-6}$ Torr during the vacuum annealing.

B. Characterizations

Phases present in the starting powder and in the ferrite films before and after annealing were identified with XRD patterns obtained on a SCINTAG/PAD-V diffractometer using Cu $K\alpha$ radiation. The density of the free standing ferrite films was measured by using a helium pycnometer, which is converted to porosity based on the theoretical x-ray density.¹³ Scanning electron microscopy (LEO 1550 with a field emission gun) was used to examine the morphology of the MZF films before and after annealing. The average molar ratio of the metallic elements in the ferrite films was measured by energy dispersive x-ray spectroscopy (EDS). The hysteresis loops of the ferrite films were assessed with a Quantum Design MPMS SQUID magnetometer at 5 K and ambient temperature in a field range from –5000 to 5000 Oe. The ferromagnetic resonance (FMR) of free standing ferrite films was measured at 9.5 GHz with the static magnetic field applied both parallel ($H_{\parallel}$) and perpendicular ($H_{\perp}$) to film plane.

The magnetostriction of the MnZn ferrite films was measured by using the laser deflection method.¹⁴ Bimorph cantilever samples in rectangular shape, 3 cm $\times$ 2 cm, with ferrite films on nonmagnetic titanium substrates were subjected to a uniform magnetic field area produced by a pair of Helmholtz coils. The magnitude of the magnetic field was controlled by adjusting the current sent into the Helmholtz coil. The magnetic field was measured by a Bell gauss meter 7010. As the magnetic field increases, the magnetized ferrite films expanded–contracted, creating a stress on the substrates which caused the substrates and films to bend. The cantilever sample was clamped on one end and a He–Ne laser beam was reflected off the free end. A UDT SLC-5D linear position sensor¹⁵ was placed at 1.5 meters away from the cantilever samples, which monitored the reflected beam position changes and was capable of detecting beam displacement of

2 μm . The sensor output current was sent to a position-to-voltage converter, which produced an output voltage linearly proportional to the beam position. The output voltage was measured using a HP 34401A digital multimeter. Thus the smallest detectable sample deflection was ~ 40 nm. The measurement was carried out at ambient temperature. Due to the limited space between the two Helmholtz coils, the cantilever samples were fixed with their surfaces perpendicular to the applied DC field. The deflection of the sample, Y , was converted to the in-plane strain by using the Stoney equation $e = Y t_s^2 E_s (1 - \nu_f) / 2 t_f L^2 E_f (1 - \nu_s)$,¹⁰ where t_s and t_f are the thickness of the substrate and film, respectively, E_s and E_f are the modulus of the substrate and film, respectively, ν_s and ν_f are the Poisson ratio of the substrate and film, respectively, Y the deflection of the sample at distance L from the clamped end. The values of E_s , E_f , ν_s , and ν_f were taken from the literature^{13,16} measured on bulk titanium and MnZn ferrites. According to the formula $e = \frac{3}{2} \lambda_s (\cos^2 \theta - \frac{1}{3})$,¹⁰ where λ_s is the saturation magnetostriction and e is the strain measured at an angle θ relative to the saturation magnetization direction, the strain measured in this experiment was perpendicular to the direction of the magnetization with $\theta = 90^\circ$. Thus the saturation magnetostriction was deduced to be $\lambda_s = 2e_{\perp}$.

The stress level in these ferrite films was determined by means of x-ray diffraction, which was based on the measurements of changes in crystalline lattice spacing.¹⁷ From a set of lattice spacing in different orientations, an elastic strain tensor was constructed, which was then converted to a stress tensor using Hooke's law. The in-plane stress was measured at points away from free edges, and stress in the direction perpendicular to the film surface was assumed to be zero.¹⁸ The x-ray measurements were performed on a Bruker GADDS micro-diffractometer with Cu $K\alpha$ radiation. The in plane stress was determined by using “ $\sin^2 \psi$ ” method¹⁷ with a fixed 2θ at 89° [MnZn ferrite Bragg peak (731)] and seven ψ orientations ranging from –45° to 45°.

C. Neutron diffraction and fitting

The site distribution of cation in MnZn ferrites is difficult to measure using XRD due to the similar x-ray scattering factors of Mn, Fe, and Zn. The neutron-scattering lengths of these atoms are of great difference. Thus the site distribution of cation in these plasma-sprayed MnZn ferrite films is examined by neutron diffraction. The free standing ferrite films were used to prepare for the neutron diffraction samples. Half of the films were annealed at 500 °C in air for 120 min. Both as-sprayed and annealed films were ground to fine powder. The neutron powder diffraction experiments were carried out at the NIST Center for Neutron Research. The neutron powder diffraction profiles were obtained in the BT-1 high-resolution powder diffractometer. A Cu (311) monochromator was employed to produce a neutron beam of the wavelength of 1.5403 Å. The diffraction intensity data were collected in the 2θ range of 5°–165° with steps of 0.05° at the ambient temperature.

GSAS program¹⁹ was employed in the crystalline and magnetic structure refinements. As both tetrahedral sites and

FIG. 1. XRD patterns of (1) initial powder, (2) as-sprayed MnZn ferrite films, (3) ferrite films annealed at 500 °C for 120 min and (4) ferrite films annealed at 800 °C for 120 min.

octahedral sites in the spinel lattice of MnZn ferrites may be occupied by three metal elements: Fe, Mn, and Zn, the site occupancy of these three elements can not be determined without other information. However, the fitting of the neutron diffraction data allowed for extrapolating the effective scattering length of the A sites and B sites which is defined as $b_{\text{eff}} = b_{\text{Fe}}X_{\text{Fe}} + b_{\text{Mn}}X_{\text{Mn}} + b_{\text{Zn}}(1 - X_{\text{Fe}} - X_{\text{Mn}})$, where X is the site occupancy of the element and b the neutron diffraction length (e.g., $b_{\text{Fe}} = 9.45$ fm, $b_{\text{Mn}} = -3.73$ fm, and $b_{\text{Zn}} = 5.68$ fm). The changes of the value of b_{eff} after annealing were considered to be associated with the ordering of the cation distribution in the spinel lattice which changed the element site occupancy X .

III. RESULTS AND DISCUSSION

The x-ray diffraction (XRD) patterns of the initial powder and ferrite films (as-sprayed and annealed) are presented in Fig. 1. It is noted that the initial powder is a pure spinel phase while wustite FeO forms in the as-sprayed films [see pattern (2)] under conditions of oxygen loss during the spray. The wustite FeO is a metastable phase under 560 °C²⁰ and its formation may result from the rapid quenching of the MZF molten droplets. After annealing the MZF films at 500 °C in air for 120 min, the wustite peaks disappear and peaks from hematite Fe₂O₃ are observed in pattern (3), indicating an oxidation process taking place concurrent with the annihilation of the metastable wustite phase. It can be seen that pattern (4) shows no significant difference from pattern (3) except that the intensity of the hematite peaks is higher, suggesting more Fe²⁺ is oxidized to Fe³⁺ in ferrite films after annealing at higher temperature.

The SEM images of the microstructure of as-sprayed and annealed MZF are shown in Fig. 2. The as-sprayed MZF coatings are constructed of layers of splats.²¹ The diameters of these splats are in the range of 15–150 μm and the thickness is ~1 μm. Each splat is comprised of well-crystallized columnar grains as shown in Fig. 2(a). These columnar grains grow perpendicular to the substrate along the temperature gradient during the rapid solidification. The average diameter of these columnar grains is ~200 nm as shown in Fig. 2(b). After annealing the ferrite films at 500 °C in air for 120 min, it is found that these columnar grains refine to equal-axis shaped grains with average size of 200 nm as seen

FIG. 2. SEM images of plasma-sprayed MnZn ferrite films. (a) Cross section view of as-sprayed films shows the columnar grains. (b) Top view of as-sprayed films shows that the diameter of the columnar grains is around 200 nm. (c) After annealing the ferrite films at 500 °C in air for 120 min, the columnar grains change to equal-axis shaped grains with average diameter 200 nm. (d) After annealing the ferrite films at 800 °C in air for 120 min, the size of the grain increases to ~500 nm. The horizontal lines in (a) are splat boundaries.

in Fig. 2(c). This is a polygonization²² process possibly driven by the elastic mismatch within the columnar grains due to the rapid crystal growth during the quenching stage. Similar instability has been reported in the rapid dendritic grown μ -cordierite upon annealing at 1450 °C.²² It is seen in Fig. 2(c) that the grain boundary phase grows thicker during this annealing process. According to the above phase analysis on the XRD patterns, the grain boundary phase in the annealed MZF is deduced to be hematite Fe₂O₃. After annealing at 800 °C, these equal-axis grains grow to around 500 nm as shown in Fig. 2(d).

Figure 3 shows the hysteresis loops of ferrite films before and after annealing measured at ambient temperature. The corresponding values of M_s and H_c are summarized in Table I, where the unit of M_s is converted from “emu/g” to “emu/cc” with an independent measurement of the density. It is seen that the magnetic properties of free standing ferrite films show no obvious difference from that of ferrite films on titanium substrates. The values of saturation magnetization

FIG. 3. Hysteresis loops of plasma-sprayed MnZn ferrite films measured at ambient temperature.

increase after annealing the ferrite films at 500 °C in air for 120 min. Increasing the annealing temperature to 800 °C or extending the annealing time does not change the saturation magnetization. For the same annealing time, the coercivity of the ferrite films is further decreased from 80 to 10 Oe by increasing the annealing temperature from 500 °C to 800 °C. For the same annealing temperature, extending the annealing time from 120 to 180 min. show no obvious effects on the coercivity. The coercivity dependence on the particle size is theoretically predicted to be a convex curve,¹⁰ where the maximum of H_c occurs in the single-domain radius, r_c . For poly-crystalline MnZn ferrite samples with grain sizes between 0.3 and 3 μm , it is reported that the domain size is identical to the grain size.²³ Thus the grain sizes of the plasma-sprayed MnZn ferrite is less or equal to the domain size in both as-sprayed and annealed cases. Increasing the grain size from 200 to 500 nm may either increase or keep the values of the coercivity the same. Therefore, the decrease of the coercivity as observed in Fig. 3 cannot be attributed to the slightly grain growth as observed in Fig. 2. For ferrite films that are annealed in vacuum at 800 °C for 120 min, the coercivity is 48 Oe which indicates that oxygen may be important to modify the magnetic properties of the ferrite films during annealing.

The increase of the saturation magnetization after annealing is considered to be associated with the redistribution of cation in *A* sites and *B* sites within the spinel lattice. The extreme high temperature and rapid quenching conditions achieved in the plasma spray process may allow retention to room temperature of the random cation site distribution characteristic of MZF at high temperature. The annealing process

TABLE I. Magnetic properties of MnZn ferrite films after annealing in air. T_{annl} is the annealing temperature, t_{annl} the annealing time.

T_{annl} (°C)	t_{annl} (min)	M_s (emu/cc)	H_c (Oe)
As-sprayed	0	205 ^a	130 ^a
		210 ^b	128 ^b
500	120	358 ^a	80 ^a
		362 ^b	80 ^b
500	180	364 ^a	78 ^a
800	120	377 ^a	10 ^a
800	180	375 ^a	8 ^a

^aFree standing films.

^bFerrite films on titanium substrates.

FIG. 4. The neutron diffraction data of plasma-sprayed MnZn ferrites (a) as-sprayed, (b) annealed at 500 °C in air for 120 min. The cross dots are the measured data and the solid line is the fit to the data. The difference line beneath the fitted data shows the excellent agreement of the model to the data.

may redistribute the cations to their equilibrium position in the spinel lattice. Similar results have been reported in rapidly quenched Co ferrite.²⁴ Neutron diffraction patterns with Rietveld refinements,¹⁹ as shown in Fig. 4, have been employed to analyze the ordering of cation distribution in the plasma-sprayed MnZn ferrites during annealing. The average molar ratio of the metallic elements of the samples required for the Rietveld refinement is Zn:Mn:Fe=9:21:70, which is measured by using EDS. The molar ratio between the MnZn ferrite and the wustite FeO in the as-sprayed ferrites is 9:1 determined by the fitting of the neutron data. Thus the chemistry formula of the MnZn ferrite is calculated to be $\text{Mn}_{0.67}\text{Zn}_{0.27}\text{Fe}_{2.06}\text{O}_4$. Based on this composition, assuming at 0 K that the spins in *A* sites are perfectly antiparallel to the spins in *B* sites, the magnetic moment per unit formula for a fully disordered cation distribution with Mn, Zn, and Fe evenly distributed in the *A* sites and *B* sites is calculated to be 4.53 μ_B , which increases to 6.29 μ_B for a fully ordered cation distribution with Zn and Mn favoring the *A* sites. However, calculation based on the values of saturation magnetization of the ferrite films measured by the SQUID at 5 K gives that the magnetic moment per formula unit increases from 3.03 to 4.59 μ_B after annealing, which is beyond the range of 4.53–6.29 μ_B . This suggests that the spins in *A* sites and *B* sites may not be perfectly antiparallel aligned, in which case the interaction between the *A*–*A* or *B*–*B* sites cannot be fully neglected comparing to that between the *A*–*B* sites.⁸ The refinement on the neutron data gives that b_{eff} of *A* sites and *B* sites are 3.8 and 7.1 fm, respectively, for as-sprayed MnZn ferrites while the values change to 2.0 and 8.3 fm for samples annealed at 500 °C in air for 120 min. For a MnZn ferrite with the composition of

FIG. 5. Field induced strain (magnetostriction) in the plasma-sprayed MnZn ferrite films before and after annealing at 500 °C in air for 120 min. The ferrite films are on titanium substrates. The magnetic field is applied in the direction perpendicular to the film surface while the strain is measured in the direction parallel to the film plane.

$\text{Mn}_{0.67}\text{Zn}_{0.27}\text{Fe}_{2.06}\text{O}_4$, the calculated values of b_{eff} for a fully disordered cation distribution are 6.19 fm for both *A* and *B* sites while the values change to -0.33 fm for *A* sites and 9.45 fm for *B* sites for a fully ordered cation distribution. Therefore, the Rietveld refinement results suggest that the distribution of the cation become more ordered after annealing the ferrite samples. However, the ordering of the cation during annealing neither starts from a fully disordered state nor ends to a fully ordered state. It shall be noted in Table I that the values of M_s saturate after annealing the ferrite at 500 °C for 120 min which indicates that extending the annealing time or increasing the annealing temperature cannot result in further ordering of the cation distribution.

The field induced strain (magnetostriction) measured in the direction perpendicular to the applied magnetic field is presented in Fig. 5. According to $e = \frac{3}{2}\lambda_s(\cos^2\theta - \frac{1}{3})^{10}$ with $\theta = 90^\circ$, the saturation magnetostriction is calculated to be 5.25×10^{-6} and 4.57×10^{-6} for as-sprayed and annealed MnZn ferrite films, respectively. These values are comparable to that of bulk ferrites with similar composition.²⁵ The value of λ_s is sensitive to the composition of the MnZn ferrites. The excessive Fe^{2+} in the MnZn ferrite may help to reduce the overall magnetostriction of the ferrite films.²⁶ To analyze the magnetoelastic contribution to the values of coercivity, the stress in the ferrite films has to be determined besides the data of the saturation magnetostriction.

Due to the limited penetration depth of the x-ray, only the surface stress in the plasma-sprayed MnZn ferrite films has been examined and is shown in Table II. It is found that there is compress stress in the surface of ferrite films on titanium substrate and tensile stress in both surfaces of free-standing ferrite films. The compress stress in the ferrite films on titanium substrate may result from the difference in ther-

TABLE II. Surface stress in plasma-sprayed MnZn ferrite films.

Samples	As-sprayed (on Ti sub)	Annealed ^a (on Ti sub)	As-sprayed (free-standing)	Annealed ^a (free-standing)
Stress (MPa)	-200 ± 30	-280 ± 30	80 ± 30^b 95 ± 30^c	40 ± 20^b 45 ± 20^c

^aAnnealed at 500 °C in air for 120 min.

^bTop surface.

^cBottom surface.

TABLE III. FMR results of ferrite films at room temperature.

T_{annl} (°C)	t_{annl} (min)	$H_{\perp}$ (kOe)	$H_{\parallel}$ (kOe)	H_k (Oe)	$\Delta H_{\perp}$ ^c (kOe)	$\Delta H_{\parallel}$ (kOe)	h_c
As-sprayed	0	5.97	1.52	720	2.30	1.67	0.36
500	120	8.10	1.77	340	1.57	1.16	0.47
800	120	8.37	1.88	72	0.76	0.53	0.28

^a T_{annl} is the annealing temperature.

^b t_{annl} the annealing time.

^c ΔH the line width.

mal expansion coefficients (TEC) between the ferrite films and titanium substrates. Lower TEC of the ferrites leads to compress thermal stress in the ferrite films while higher TEC of the titanium substrates introduce tensile thermal stress in the substrate.¹⁸ When the film is detached, the net force imposed on it by the substrate is removed. The tensile stress in both surfaces of the free-standing films may be balanced by the compression in the central part. This type of stress profile may originate from nonlinearity of stress distribution before substrate detachment.²⁷ It is seen in Table II that the compress stress in the ferrite films on titanium substrate increases after annealing the samples at 500 °C in air for 120 min while the tensile stress in the free standing ferrite films decreases after the same annealing process. Though the stress profiles are different between ferrite films in free standing form and those on titanium substrate, there is not much difference in the coercivity of these two types of samples as listed in Table I. This suggests that the coercive mechanisms arising from the magnetoelastic energy term is not dominant in these ferrite films. One possible explanation is that the variation of the stress, $\Delta\sigma$, within the film plane is small. The contribution of the magnetoelastic term to the energy barrier that pins the domain wall movement is proportional to $\frac{3}{2}\lambda_s\Delta\sigma$.¹⁰ Thus domain wall can move within the film plane without much pinning effect from the magnetoelastic energy barrier. The residual stress profile in plasma-sprayed NiCrAlY on a steel substrate¹⁸ studied by using neutron diffraction shows that the residual stress in the *x*- and *y*-axis of the film plane are similar, which to a certain extent confirms that $\Delta\sigma$ is small in plasma-sprayed films.

The coercivity in a magnetic material system with sharp defects is described by the micro-magnetic theory¹¹ as $H_c = h_c H_k/2$, where h_c is the reduced coercive force that depends on the defect size and defect properties in the magnetic material system, H_k is the effective anisotropy field. There are two types of sharp defects in the plasma-sprayed MnZn ferrites: (1) the secondary phases (FeO and Fe_2O_3) and (2) the structural discontinuity including cracks, splat boundaries and voids. Both may pin the domain wall motion. The values of H_k can be calculated from the equation $H_k = 4\pi M_s - (H_{\perp} + H_{\parallel}/2 - (H_{\parallel}(H_{\perp} + 5H_{\parallel}/4))^{1/2})$,¹² where $H_{\perp}$ and $H_{\parallel}$ are the perpendicular and parallel resonance fields in the ferromagnetic resonance measurements. Table III summarizes the FMR results with calculated values of H_k and h_c . It is seen that, after annealing the samples, the values of H_k decrease by an order of magnitude while the change of h_c is much less. The significant decrease of the anisotropic field may have multi origins which are discussed below: (1) Crystalline

FIG. 6. SEM images of cross section view of MnZn ferrite films, (a) as-sprayed, (b) 800 °C annealing in air for 120 min and (c) 800 °C annealing in vacuum for 120 min. The splat boundaries and cracks observed in (a) and (c) are greatly reduced in (b).

anisotropy. The crystalline anisotropy constant of MnZn ferrites is composition-dependent.²⁶ It is noted in previous study²⁸ that the as-sprayed MnZn ferrite films have a nonhomogeneous compositional profile. Zinc volatilization during the high-temperature spraying process creates local manganese rich region in the as-sprayed ferrite films. The films composition becomes more homogeneous after annealing due to cation diffusion. Zinc ferrite and manganese ferrite have opposite signs of the crystalline anisotropy.²⁶ The overall crystalline anisotropy constant of the ferrite can be decreased by adding zinc into manganese ferrite, e.g., MnFe_2O_4 has a crystalline anisotropy constant of -28×10^3 while it decreases to -3.8×10^3 for $\text{Mn}_{0.45}\text{Zn}_{0.55}\text{Fe}_2\text{O}_4$.²⁶ Thus the homogenization of film composition during annealing can reduce the local anisotropy²⁹ which contributes to decrease the effective anisotropic field. (2) Microstructural changes. It is shown in Fig. 6 that the splat boundaries and cracks are highly reduced in ferrite films that are annealing at 800 °C in air. These structural discontinuities in ferrite films annealed at 800 °C in vacuum are still as evident as those in

the as-sprayed ferrite films. The structural changes observed in Fig. 6(b) may result from the phase transition $\text{FeO} \rightarrow \text{Fe}_2\text{O}_3$, in which the molar volume of Fe_2O_3 is 20% higher than that of FeO .¹⁶ The extra surface inside the ferrite films due to the cracks, porosity, or splat boundaries may introduce magneto static anisotropy,¹⁰ which is another contribution to the local anisotropy. The decrease of the microstructural discontinuity may effectively decrease the value of H_k . (3) Magnetoelastic effects. It has been analyzed above that the magneto elastic effects on the coercivity may not be significant in these ferrite samples. By comparing the coercivity of ferrite films that are annealed in air and vacuum, the coercivity change (about $130 - 10 = 120$ Oe) during annealing in air due to above factors may be separated quantitatively. If assume that change of the crystalline anisotropy is the major factor that changes the coercivity of the vacuum annealed ferrite films, about 80 Oe of the coercivity change is due to the homogenization of the film composition. Thus the rest change of ~ 40 Oe is attributed to the microstructural change of the films. The line width $\Delta H_{\parallel}$ and $\Delta H_{\perp}$ show a downward trend after annealing the ferrite films as listed in Table III. The mechanism for ΔH is proposed to be the inhomogeneous broadening due to the variations in local magnetic anisotropy.³⁰ Therefore, the decrease of ΔH is in agreement with the decrease of H_k . According to Paul's model,¹¹ the value of h_c increases with the increase of the defect size and finally saturates. Although it is seen in Fig. 6 the microstructural discontinuities are greatly reduced in the annealing ferrite films, the x-ray data shows that the amount of the secondary phase in the ferrite films increases after annealing at 800 °C. Thus the change of the size of the sharp defects may be limited in the annealed ferrite samples, which results in slightly decrease of the h_c .

IV. CONCLUSION

The magnetic properties of plasma-sprayed MnZn ferrites have been studied. It is found that improvements can be made by annealing the ferrite films at 500 °C–800 °C. The saturation magnetization increases from 200 to 380 emu/cc, which is a result of cation ordering confirmed by neutron diffraction. The coercivity decreases from 130 to 10 Oe after annealing at 800 °C for 120 min, which is analyzed with the domain wall pinning model $H_c = h_c H_k / 2$. The stress measurements on the ferrite films indicate that the contribution of the magneto-elastic energy on the coercivity is small. The FMR results show that the effective anisotropy field decreases significantly after the annealing process, which may results from the homogenization of the film composition and reduction of structural discontinuity. The values of h_c change slightly after annealing, which may be a combined result of the reduction of the microstructural discontinuity (e.g., cracks, voids, and splat boundaries) and the increase of the amount of secondary phase in the ferrite films.

ACKNOWLEDGMENTS

The authors want to thank for Professor C. Vittoria and Dr. X. Zuo in Northeastern University for their invaluable assistance in the FMR measurements and proofreading of the

manuscript. The authors also want to thank G. A. Bancke for making ferrite samples. This work is supported by MRSEC program of National Science Foundation under award DMR-0080021.

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