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Formation of high electrical-resistivity thin surface layer on carbonyl-iron powder (CIP) and thermal stability of nanocrystalline structure and vortex magnetic structure of CIP

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This study focuses on the carbonyl-iron powder (CIP) used in the metal composite bulk magnetic core for high-efficient/light-weight SiC/GaN power device MHz switching dc-dc converter, where the fine CIP with a mean diameter of 1.1 μm is used to suppress the MHz band eddy current inside the CIP body. When applying the CIP to composite core together with the resin matrix, high electrical resistivity layer must be formed on the CIP-surface in order to suppress the overlapped eddy current between adjacent CIPs. In this study, tens nm thick silica (SiO_2) was successfully deposited on the CIP-surface by using hydrolysis of TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$). Also tens nm thick oxidized layer of the CIP-surface was successfully formed by using CIP annealing in dry air. The SiC/GaN power device can operate at ambient temperature over 200 degree-C, and the composite magnetic core is required to operate at such ambient temperature. The as-made CIP had small coercivity below 800 A/m (10 Oe) due to its nanocrystalline-structure and had a single vortex magnetic structure. From the experimental results, both nanocrystalline and single vortex magnetic structure were maintained after heat-exposure of 250 degree-C, and the powder coercivity after same heat-exposure was nearly same as that of the as-made CIP. Therefore, the CIP with thermally stable nanocrystalline-structure and vortex magnetic state was considered to be heat-resistant magnetic powder used in the iron-based composite core for SiC/GaN power electronics. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4944705>]

I. INTRODUCTION

Recently, the wide band-gap SiC/GaN power devices have been applying for high-efficient power electronics systems such as dc-dc converter and dc-ac inverter due to their low on-resistance, fast switching speed and possible operation at ambient temperature over 200 degree-C.^{1,2} The power conversion frequency can be increased beyond 1 MHz to miniaturize the power electronics systems by using SiC/GaN power device, where the power inductor and transformer, used in the SiC/GaN based power electronics operating at 200 degree-C over ambient temperature, must have small power-loss in the MHz band and thermally stable electrical property when exposing it to such high ambient temperature.

The authors are currently developing a heat-resistant iron-based metal composite bulk magnetic core for SiC/GaN power device MHz switching dc-dc converter. The iron-based metal composite magnetic core consists of 1.1 μm diameter carbonyl-iron powder (CIP) and heat-resistant resin. Such the fine CIP is used to suppress the MHz band eddy current inside the CIP body.

However, to suppress the power loss of the magnetic core at MHz band, the CIP should have high electrical-resistivity surface layer to decrease the over-lapped eddy current between adjacent CIPs in the composite core. In this study, two kinds of high electrical-resistivity thin layer to suppress the over-lapped eddy current were investigated. One was silica (SiO₂) thin layer on the CIP-surface, which was deposited by using Stöber method.³ Another one was oxidized thin layer of the CIP-surface, which was formed through annealing in dry air.

Also thermal stabilities of the crystalline-structure and magnetic domain structure of the CIP were investigated through the heat-exposure at different temperature from 200-400 degree-C in vacuum in order to clarify a possibility of the heat-resistant iron-based composite magnetic core. In addition, an influence of the heat-exposure on the powder coercivity was also discussed.

II. AS-MADE CARBONYL-IRON POWDER (CIP)

The carbonyl-iron powder (CIP) for iron-based metal composite bulk magnetic core was produced through thermal decomposition of iron-pentacarbonyl (Fe(CO)₅) distilled previously to high purity.⁴ Typical specifications of the as-made CIP are summarized in TABLE I. The as-made CIP had an onion-skin structure⁴ due to the spherical iron layers on a nucleus in the Fe-particle growth.

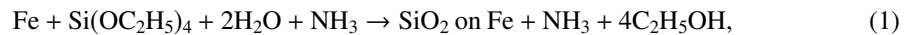
M. Koeda *et al.*⁵ reported that the as-made CIP had a nanocrystalline-structure and single vortex magnetic structure. Such the fine-grain nanostructure causes small crystalline magnetic anisotropy,⁶ and the single vortex magnetic structure causes small magneto static energy.

III. EXPERIMENTAL PROCEDURE

A. Formation of high-electrical resistivity thin surface layer on carbonyl-iron powder (CIP)

1. Formation of silica (SiO₂) thin layer on CIP

Silica (SiO₂) thin layer was deposited on the CIP-surface by using Stöber method.³ The chemical reaction of the silica formation is described as follows;



where NH₃ is a catalyst for hydrolysis and polycondensation reaction of the TEOS (Si(OC₂H₅)₄). The silica formation was done under applying ultrasonic wave at 60 degree-C.

2. Surface oxidization of CIP

The oxidized thin layer of the CIP-surface was formed through annealing in dry air using a muffle furnace. The CIPs were put in a SUS304 tray so that CIPs dispersed well, and then annealed in the muffle furnace at temperature of 180-280 degree-C for 6 hours.

B. Heat exposure of carbonyl-iron powder (CIP)

To evaluate an influence of the heat-exposure on the CIP, the CIP was annealed in vacuum at temperature of 200-400 degree-C for 1 hour. The crystalline structure and magnetic structure of the

TABLE I. Typical specifications of as-made carbonyl-iron powder.

Composition wt.%	Fe content ; up to 97.8% C ; 1.0% _{max.} , N ; 0.9% _{max.} , O ; 0.5% _{max.}	in Ref. 4
Mean diameter	1.1 μm	in Ref. 4
Saturation magnetization	200 emu/g	measured using VSM
Coercive force	below 800 A/m (10 Oe),	measured using coercivity-meter

TABLE II. Two kinds condition of silica deposition on CIP.

No.	CIP	C ₂ H ₅ OH	TEOS ; Si(OC ₂ H ₅) ₄	NH ₃
1	7 g	2500 ml	7.5 ml	148.5 ml
2	50 g		16.2 ml	

Temperature; 60 degrees-C, Time; 4 hours, C₂H₅OH; solvent for CIP.

annealed CIP were investigated. An influence of the formation process of the oxidized layer of the CIP-surface on its crystalline structure and vortex magnetic structure was also investigated.

C. Evaluation methods

TEM (Transmission Electron Microscopy) and FE-SEM (Field Emission Scanning Electron Microscopy) were used to observe the high resistivity thin layer on the CIP. The crystalline structure was investigated using powder XRD (X-ray Diffraction) and TEM. The magnetic structure was observed using Electron beam holography. In order to evaluate oxidized layer of the CIP-surface, XPS (X-ray Photoelectron Spectroscopy) was used. The powder coercivity was measured using coercivity-meter.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Formation of high-electrical resistivity thin surface layer on carbonyl-iron powder (CIP)

1. Formation of silica (SiO₂) thin layer on CIP

Two kinds condition of the silica deposition on the CIP-surface are summarized in TABLE II, No.1 is TEOS-rich condition of 1.07 ml-TEOS/1 g-CIP and No.2 is TEOS-poor condition of 0.32 ml- TEOS/1 g-CIP.

FIG. 1 shows the cross-sectional SEM images of the silica (SiO₂) thin layer deposited on the CIP-surface. In case of the TEOS-rich silica deposition, not only 40-60 nm thick silica layer on the CIP-surface but also silica nanoparticle was observed. On the other hand, in case of the TEOS-poor condition, 20-40 nm thick silica layer was deposited on the CIP-surface without silica nanoparticles. From the EDX spectra shown in FIG. 2, large peaks of “Si” and “O” were observed in the CIP-surface (symbol “A” in FIG. 1(b)). Therefore, the silica thin layer was successfully deposited on the CIP-surface through TEOS-poor condition.

2. Surface oxidization of CIP

Although not shown here, surface-oxidized layer thickness of the CIP increased with increasing annealing temperature. FIG. 3 shows the relationship between surface-oxidized layer thickness of

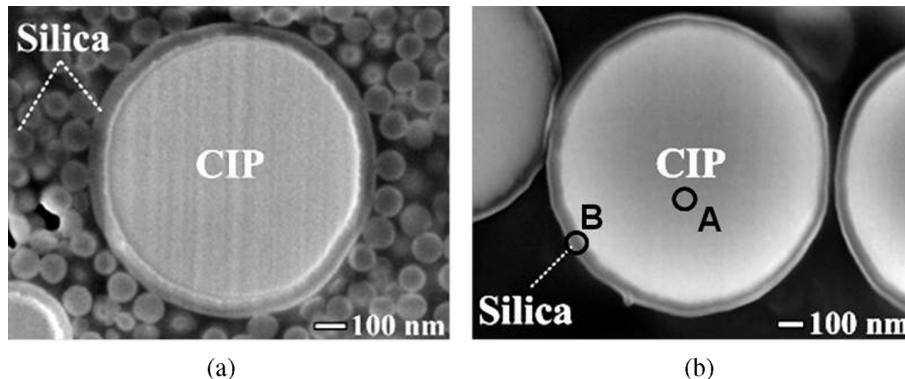


FIG. 1. Cross-sectional SEM images of silica deposited on CIP by using Stöber method.³

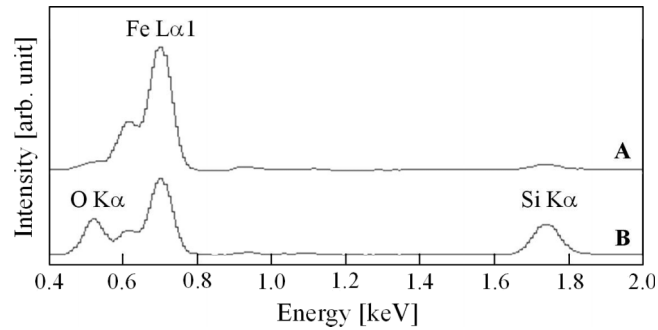


FIG. 2. EDX analysis for CIP body (region A) and silica layer (region B) in silica coated CIP by TEOS-poor condition.

the CIP and annealing time when temperature of 240 degree-C. The surface-oxidized layer thickness was evaluated from the SEM observation. As shown in FIG. 3, the interface between oxidized layer and CIP body was clearly observed. The average surface oxidized layer thickness slightly increased at the annealing time more than 6 hours, and it showed a tendency to be saturated at the annealing time around 10 hours. It was considered that the oxygen became hard to diffuse into the CIP body with increasing annealing time. From the experimental results, tens nm thick oxidized layer was obtained by annealing in dry air within 2 hours.

FIG. 4 shows the powder XRD pattern of the CIP annealed in dry air at different temperature of 200, 240, and 280 degree-C. In any case of annealing temperature, α -Fe peaks of (110) and (200) from the CIP body were observed. With increasing annealing temperature, in addition to α -Fe peaks, strong peaks of the magnetite Fe_3O_4 appeared and weak peaks of the hematite Fe_2O_3 were observed. Therefore, the surface-oxidized layer of the CIP was considered to be consisted of a mixture of the magnetite Fe_3O_4 and hematite Fe_2O_3 .

FIG. 5 shows the XPS spectra of the surface-oxidized CIP and as-made CIP. It was found that the as-made CIP had very thin native oxide of the magnetite Fe_3O_4 , which was not observed in the powder XRD because of very thin native oxide. FIG. 5 exhibited that the hematite Fe_2O_3 was formed with increasing annealing temperature, which was also confirmed in the powder XRD pattern shown in FIG. 4. Therefore, it was considered that the oxidized layer of the CIP consisted

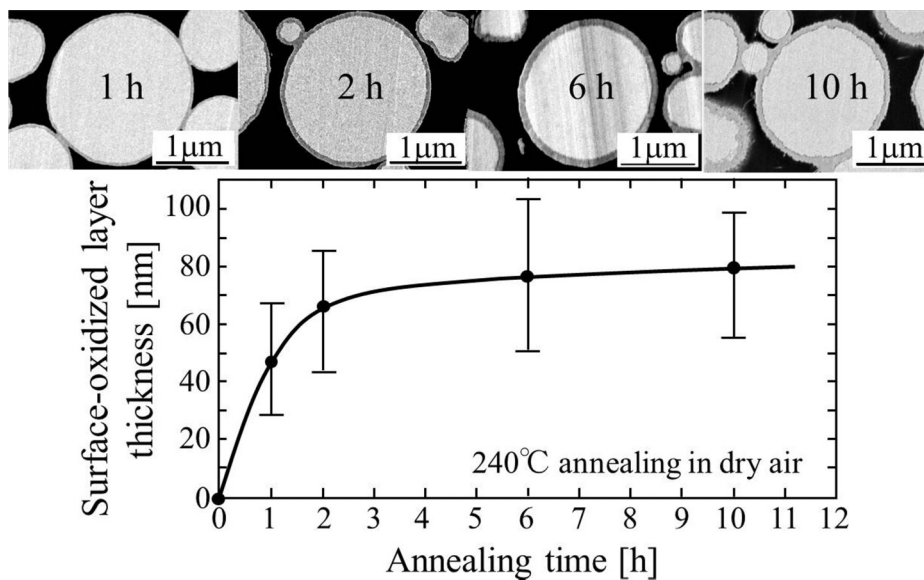


FIG. 3. Relationship between surface-oxidized layer thickness of CIP annealed in dry air at 240 degree-C and annealing time.

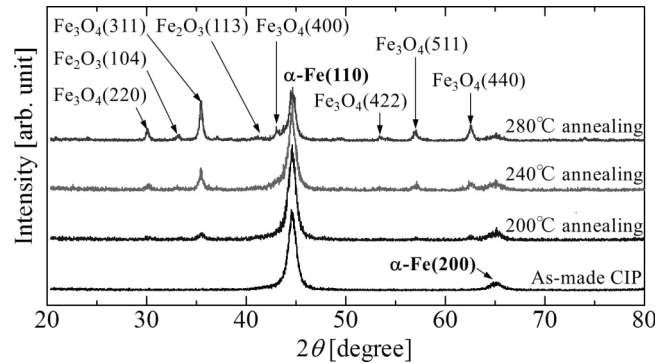


FIG. 4. Powder XRD pattern of CIP annealed in dry air at different temperature for 6 hours.

of very thin Fe_2O_3 at the vicinity of the oxidized layer surface and the magnetite Fe_3O_4 inside the oxidized layer.

Both silica thin layer on the CIP and the surface-oxidized CIP will contribute to increase volume resistivity of the iron-based metal composite bulk magnetic core even in the closely-packed CIP composite core.

B. Heat exposure of carbonyl-iron powder (CIP)

The CIP was annealed in vacuum at temperature of 200–400 degree-C for 1 hour to evaluate an influence of the heat-exposure on the nanocrystalline and vortex magnetic structure of the CIP.

1. Nanocrystalline structure

FIG. 6 shows the powder XRD pattern of the CIP annealed in vacuum at different temperature from 200–400 degree-C. Both $\text{Fe}(110)$ peak intensity and its FWHM were nearly constant at the annealing temperature less than 250 degrees-C, and then the intensity increased strongly and FWHM became sharp at the temperature above 300 degree-C. An average grain size of the CIP vs. annealing temperature is shown in FIG. 7, where the average grain size was estimated using Sherrer's formula.⁷ In FIG. 7, small grain size of 9–10 nm was stable under the heat-exposure up to 250 degree-C. From the TEM observation, the grain size increased with increasing annealing temperature over 300 degree-C because of rapid grain growth.

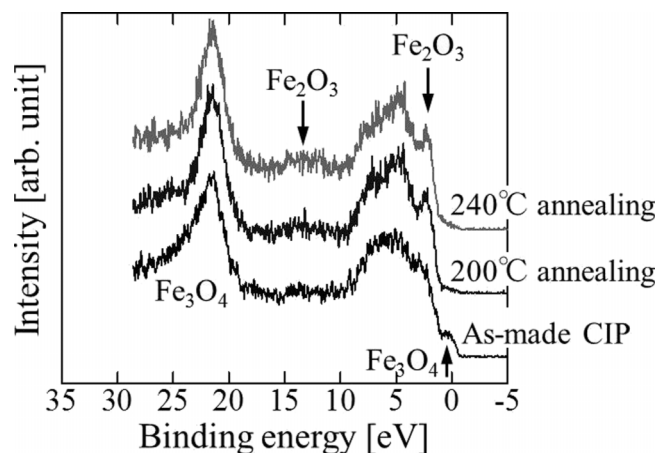


FIG. 5. XPS spectra of surface-oxidized CIP and as-made CIP, some arrows mean the specific peaks of Fe_3O_4 and Fe_2O_3 .

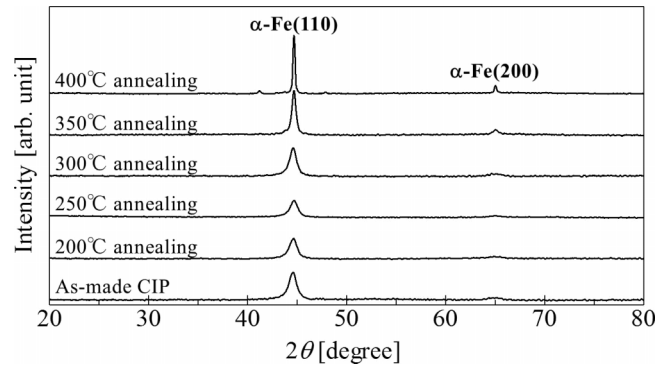


FIG. 6. Powder XRD pattern of CIP annealed in vacuum at different temperature.

2. Powder coercivity

FIG. 8 shows the powder coercivity of the CIP annealed in vacuum. The powder coercivity increased rapidly at 300 degrees-C. The grain size (D) dependence of the powder coercivity was close to D^6 at around 10 nm grain size smaller than the exchange length L_{ex} , where the exchange length L_{ex} of the CIP was estimated to be about 22 nm using the following equation,⁶

$$L_{ex} = \sqrt{A/K_1}, \quad (2)$$

where A is the exchange stiffness and K_1 is the crystalline magnetic anisotropy, in case of Fe, $A = 2.0 \times 10^{-11}$ J/m and $K_1 = 4.2 \times 10^4$ J/m³. Therefore, the increase of powder coercivity by heat-exposure at around 300 degree-C was considered to be owing to the grain growth and the increase of the crystalline magnetic anisotropy.

From the experimental results, the nanocrystalline-structure of the CIP was maintained after heat-exposure below 250 degree-C, and the small powder coercivity was also maintained after same heat-exposure condition.

3. Vortex magnetic structure

FIG. 9 shows the TEM and Electron beam holography images of the CIP annealed in vacuum at 300 degree-C for 1 hour. The powder XRD pattern shown in FIG. 7 exhibited the CIP had a fine grain even when annealing in vacuum at 300 degree-C. However, TEM image in FIG. 9(a) revealed that the annealed CIP had not only fine grains but also large grains. In the Electron beam holography image of FIG. 9(b), the multi-domain structure was observed and plural magnetic vortex states also

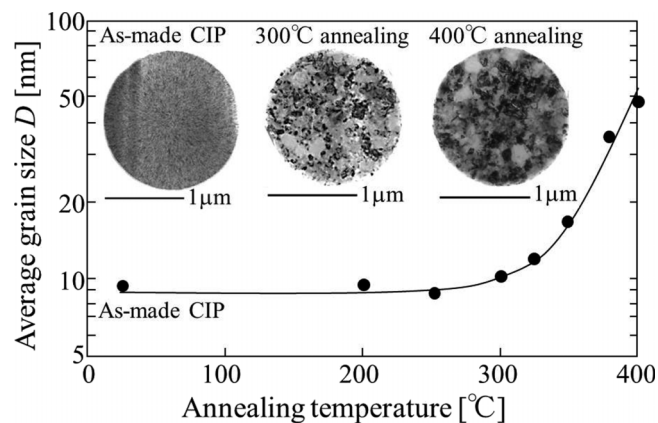


FIG. 7. Average grain size of CIP annealed in vacuum vs. annealing temperature.

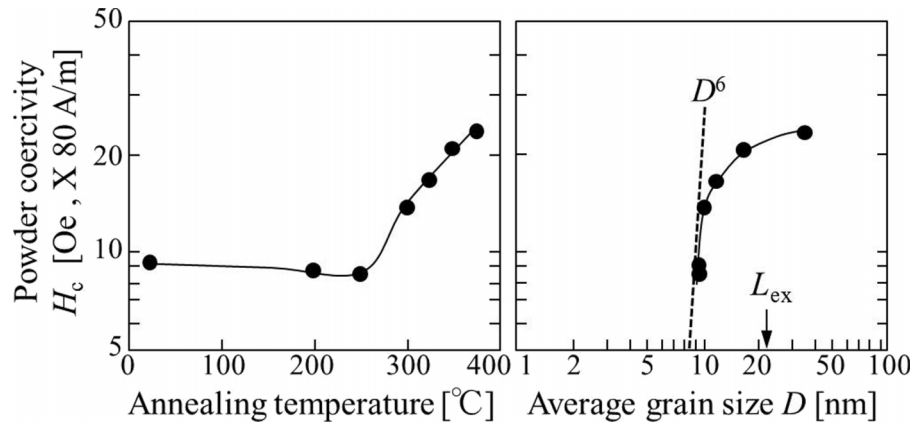


FIG. 8. Annealing temperature and grain size dependences of powder coercivity of CIP annealed in vacuum.

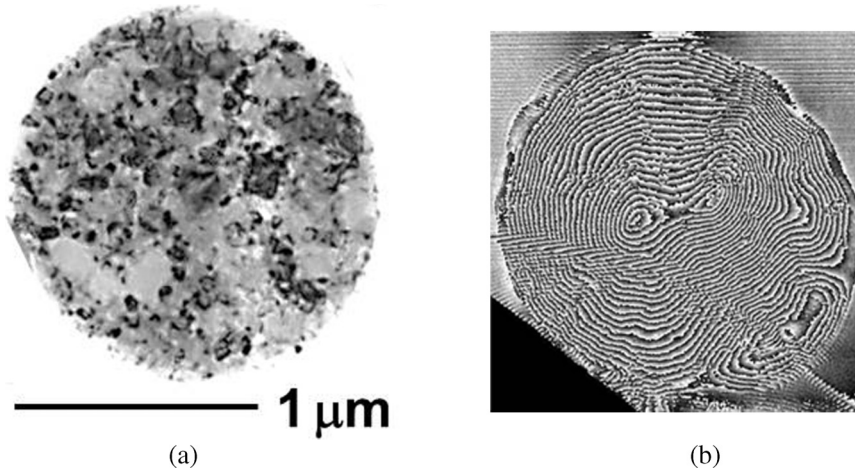


FIG. 9. (a) TEM and (b) Electron beam holography images of CIP annealed in vacuum at 300 degree-C for 1 hour.

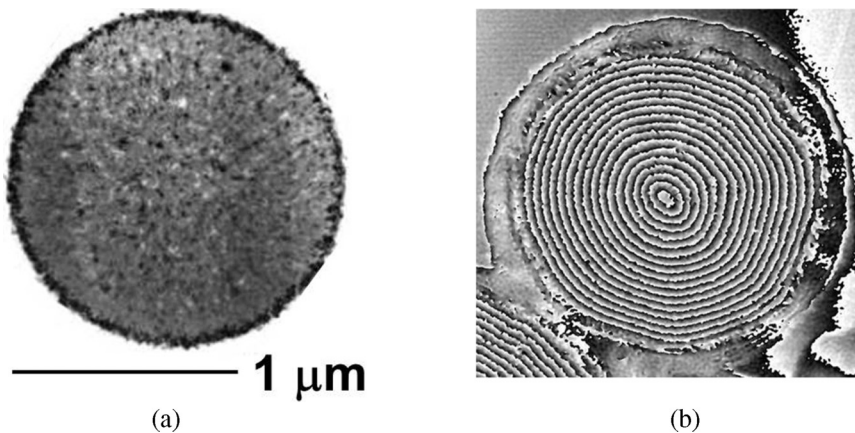


FIG. 10. (a) TEM and (b) Electron beam holography images of CIP annealed in dry air at 240 degree-C for 6 hours.

appeared. Since the as-made CIP had a single vortex magnetic structure⁵, the origin of the plural magnetic vortex states was considered to be owing to the local grain growth by heat-exposure at 300 degree-C. Therefore, thermal stability of the single vortex magnetic structure was dependent strongly on the thermal stability of the nanocrystalline-structure.

C. Vortex magnetic structure of surface-oxidized CIP

There is a possibility of change in the vortex magnetic structure through the surface-oxidation of the CIP. FIG. 10 shows the TEM and Electron beam holography images of the CIP annealed in dry air at 240 degree-C for 6 hours. The nanocrystalline-structure inside the CIP body was maintained even when the CIP-surface was oxidized in dry air, and the single vortex magnetic structure was clearly observed as well as the as-made CIP.

Although not shown here in detail, the CIP annealed in dry air at 240 degree-C had three times larger powder coercivity than that of the CIP annealed in vacuum, which was considered to be owing to the increase of the internal stress by adding the surface oxide layer. The CIP annealed in dry air at 200 degree-C for 6 hours had about 30 nm thick surface-oxidized layer and small powder coercivity of about 800 A/m (10 Oe).

V. CONCLUSION

In order to suppress the eddy current loss of the carbonyl-iron powder (CIP) based composite magnetic core for SiC/GaN power device MHz operation power electronics, both tens nm thick silica (SiO₂) and oxidized layer were successfully formed on the CIP-surface to reduce the overlapped eddy current between adjacent CIPs in the composite core. The CIP annealed in dry air had the surface-oxidized layer consisting of the hematite Fe₂O₃ at the vicinity of the surface of the oxidized layer and the magnetite Fe₃O₄ inside the oxidized layer. In addition, to realize the heat resistant composite magnetic core for high temperature operation SiC/GaN power electronics, thermal stabilities of the nanocrystalline-structure and single vortex magnetic structure of the CIP were investigated. From the experimental results, both nanocrystalline and single vortex magnetic structure were maintained after heat-exposure below 250 degree-C, and the small powder coercivity was also maintained after same heat-exposure condition.

ACKNOWLEDGEMENTS

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