Preparation and Characterization of Fe-Based Amorphous Soft Magnetic Flakes for High Performance Magnetodielectric Inductors

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Flake-shaped FeSi-P alloy particles with high aspect ratio were prepared by ball milling 25-μm spherical amorphous powders that boasted one of the world’s highest saturation magnetic flux densities at 1.5 T, and ultra-low coercivity below 0.5 Oe. We demonstrate that the aspect ratio of the flakes, as well as the magnetic properties, can be control by the milling parameters, such as milling time, speed, and the composition of the milling balls. The balls-to-powder ratio was varied between 2.6 - 10, balls diameter between 3 - 10 mm, and milling time between 1 - 25 hours. To avoid oxygen exposure, the powders were handled in argon atmosphere in a glove box, milled in toluene, and subsequently dried in vacuum. The maximum aspect ratio of the flakes exceeded 10 MHz.

We demonstrate that after the milling, the coercivity \( H_c \) increased from 0.5 Oe to 39.0 Oe, and the saturation flux density \( B_s \) decreased from 1.5 T to 1.3 T. The flakes were subsequently annealed in flowing argon for 1 hour between 300 – 450 °C. The coercivity and saturation density initially improved with temperature, and respectively reached 18.8 Oe and 1.4 T at 375 °C. The crystallization occurred at higher temperatures, and magnetic properties gradually declined.

Index Terms — alloys, cores, flakes, inductors, magnetodielectric

I. INTRODUCTION

THE RAPID growth of semiconductor-based communication and computational platforms has made power and thermal management challenges a great concern, especially with the shifting of operational frequencies to higher bands. High performance inductors provide substantial size reduction and effective thermal energy management by reducing generated heat. A path undertaken here includes the development of high saturation induction, high permeability, soft magnetic flakes. Suspended in a low loss RF thermoset, such flakes can be used in composite inductors [1, 2] operating up to and beyond 200 MHz.

Applications with significant market impact include onboard inductors, power converters, filters, etc., and can be especially important to enabling scaling of silicon based voltage regulators, where miniaturization is driven by Moore’s law. Fully Integrated Voltage Regulators (FIVR) will also experience greater efficiency and performance.

Iron powder cores are commercially available and perform with permeability values up to and beyond 100, but only at frequencies below 500 KHz. Core loss limits higher frequency operations due to Eddy currents and related conduction losses. Ferrite cores with engineered grain boundary regions exhibit ultra-low loss [3], high saturation magnetic flux density \( B_s \), and high permeability, and may operate up to frequencies exceeding 10 MHz. Although embedded flake composites have been studied in the literature, no commercial products have been identified. Compared to spherical powders, flake-shaped particles with high aspect ratio allow to increase the permeability and natural resonance frequency, exceed the Snoek limit [4], and reduce Eddy current loss.

20-25 μm spherical amorphous FeSi-P soft magnetic powder used in this work was supplied by Carpenter Technology Corporation and boasted one of the world’s highest magnetizations at 1.5 T, as compared to FeSiAl (1.2 T) [5] and NiZn ferrite (0.31T @ 10kHz) [6]. The powder is produced via gas atomization. This process allows for consistent powder quality, and offers a number of advantages, such as high purity, tight chemistry tolerances, and highly spherical shape. Simultaneously, it results in wide particle size distributions [7].

Herein, we demonstrate that these spherical particles can be efficiently turned into flakes by ball milling [8]. The shape and aspect ratio [9] of the flakes can be control by adjusting the milling speed and time, as well as the composition of the milling balls. The materials were thoroughly characterized at every step of the processing, and the structure, properties, processing, and performance relationships established.

II. EXPERIMENTAL PROCEDURE

A. Flakes preparation

The initial gas atomized FeSi-P amorphous alloy powder mostly consist of ~25um spherical particles, Fig. 2(a) shows an SEM micrograph. As supplied containers were first placed in an argon filled glove box and subsequently opened. Desired amounts of the powder were transferred to stainless still jars, along with stainless steel milling balls. Finally, toluene (≥99.5% purity) was introduced to the jars as the milling medium, and the jars were sealed airtightly. Eventually, the sealed jars were removed from the glove box and placed in a planetary ball mill for the subsequent milling.
The milling time varied between 1 and 25 hours, but the rotation speed was kept constant at 500 rpm in all experiments. The milling was executed using stainless steel balls with diameters ranging from 3 to 10 mm, as well as using a few combinations of different ball diameters. The ball-to-powder weight ratio varied between 2.6 and 10. A complete list of ball combinations is shown in Table I, and a complete sample list is shown in Table II. After the milling, the jars were transferred back to the argon filled glove box and opened. The powders were separated from the balls, and washed three times in reagent-grade alcohol. Later, the powders were dried in vacuum for 1 hour - using the exchange chamber of the glove box - and eventually stored in the glove box for subsequent experiments. In order to reduce the coercivity, some samples were transferred to a tube furnace and annealed for 1 hour in flowing argon at temperatures between 300–450 °C.

### Table I

**BALL MILLING CONDITIONS FOR FE-P-SI FLAKES**

| Level | A: Stainless steel ball compositions | B: Ball-to-powder ratio |
|-------|-------------------------------------|-------------------------|
| 1     | φ3 mm                               | 2.6:1                   |
| 2     | φ6 mm                               | 5:1                     |
| 3     | φ3 and φ6 mm                        | 10:1                    |
| 4     | φ6 and φ10 mm                       | -                       |

φ represents the diameter.

### Table II

**FLAKE THICKNESS AND LENGTH, SATURATION MAGNETIZATION AND COERCIVITY OF THE AS-MILLED AND ANNEALED FE-P-SI SAMPLES**

| Sample   | Milling time (h), anneal temp. (°C) | Flakes thickness (μm) | Flakes length (μm) | Saturation magnetization (emu/g) | Coercivity (Oe) |
|----------|-------------------------------------|-----------------------|--------------------|----------------------------------|-----------------|
| raw      | 0                                   | -                     | 1.9-58.6           | 164.0                            | < 0.5           |
| S (A1B1) | 4                                   | 1.9-20.3              | 17.2-35.4          | 162.0                            | 30              |
| S (A1B1) | 8                                   | 0.6-26.4              | 4.1-52.3           | 158.8                            | 32              |
| S (A2B1) | 4                                   | 0.6-21.4              | 3.6-49.9           | 159.2                            | 32              |
| S (A2B1) | 8                                   | 0.5-28.1              | 2.6-31.1           | -                                | -               |
| S (A2B2) | 8                                   | 1.2-26.8              | 8.7-46.3           | -                                | -               |
| S (A1B1) | 4                                   | 0.8-27.1              | 5.3-53.3           | -                                | -               |
| S (A3B3) | 10                                  | 0.2-22.7              | 3.4-36.2           | -                                | -               |
| S (A3B3) | 16                                  | 0.2-21.1              | 3.2-58.6           | -                                | -               |
| S (A3B3) | 25                                  | 0.1-20.5              | 2.1-33.9           | -                                | -               |
| S (A2B3) | 8                                   | 0.8-15.2              | 4.5-38.6           | -                                | -               |
| S (A2B3) | 16                                  | 0.3-14.6              | 3.0-44.5           | -                                | -               |
| S (A2B3) | 20                                  | 0.1-2.8               | 2.3-16.2           | 136.5                            | 39.0            |
| S (A2B3) | 20                                   | 0.1-2.8               | 2.3-16.2           | 134.6                            | 18.8            |
| S (A2B3) | 20                                  | 0.1-2.8               | 2.3-16.2           | 133.7                            | 18.8            |
| S (A2B3) | 20                                  | 0.1-2.8               | 2.3-16.2           | 131.7                            | 103.1           |
| S (A4B1) | 8                                  | 1.9-20.3              | 17.2-35.4          | 150.7                            | 0.7             |

S (AxBy) means that the sample was milled using stainless steel ball composition as level x and ball-to-powder ratio as level y. For example, S (A1B1) represents the following milling condition: 3 mm diameter stainless steel ball and the ball-to-powder ratio of 2.6:1.

The annealed flakes were the flakes prior milled in Toluene using A2B3 milling condition at 500 rpm for 20 h.

### B. Characterization and measurements

The powders were thoroughly characterized at every processing step. The structure and morphology [10, 11, and 12] were examined by a Rigaku Ultima IV X-ray diffractometer (XRD) (Cu Ka radiation element) and a Hitachi S-4800 scanning electron microscope (SEM), equipped with an energy-dispersive X-ray spectrometer (EDS). The average sizes of the poly-nanocrystalline flakes were calculated by the Nano Measurer plots. The magnetic properties at room temperature were measured by a vibrating sample magnetometer (VSM) with a maximum applied magnetic field of 20 kOe.

![XRD patterns](image)

**Fig. 1.** (a) XRD patterns of FeSi-P powders milled using 6 mm diameter stainless steel balls in Toluene for 4 h with ball–to–powder weight ratio of 2.6, and for 20 h with ball–to–powder weight ratio of 10 and subsequently annealed at 450°C for 1 h.

(b) Energy dispersive X-ray (EDX) analysis of FeSi-P powder before and after ball milling for 20 h, using the milling condition A2B3 respectively.

### III. RESULTS AND DISCUSSIONS

It is clear from the scanning electron microscope analysis (Fig. 2) and Table II, that the amorphous FeSi-P alloy powder can be crushed into flakes. Apparently, the milling combination of A2B3 (6mm balls, 20 hours milling time) was the most efficient. The resulting flakes had the thickness of only 0.1 μm, and the aspect ratio exceeded 70:1. Other milling balls combinations were less efficient. Smaller balls, like the...
3mm ones, showed little impact on the shape of the raw material. A2B2 combination typically produced spherical particles. The flakes embedded in magnetodielectric composite [13] inductor cores should be aligned, so that the applied magnetic field is in plane of the flakes, and Eddy currents are normal to the flakes. If the flakes are much thinner than the skin depth at a given frequency, then the conduction losses can be reduced dramatically. This specific material is intended to be used at around 200MHz, where the skin depth is about \(1\ \mu\)m. Therefore the thickness of the best flakes is only about one tenth of the skin depth.

Eddy current losses are the primary loss challenge in magnetodielectric composites at high frequencies. The other major source is the magnetic coercivity. The starting powder had an ultra-low coercivity of less than 0.5 Oe. The coercivity gradually increased with the milling time and eventually reached 39 Oe, as the milling inevitably increased the density of defects and resulted in residual stress (Fig. 3, Table II). XRD analysis (Fig. 1 (a)) revealed that the flakes remained amorphous after the ball milling. The saturation magnetization of the material decreased by about 15% after milling for 20 hours.

In order to reduce the stress and reduce the coercivity, the flakes were subsequently annealed in flowing argon for 1 hour between 300–450 °C. The coercivity and saturation magnetization initially improved with temperature, and respectively reached 18.8 Oe and 146.88 emu/g at 375 °C. The lowest coercivity reported in the literature for comparable flakes is about two times higher [14]. Magnetic properties gradually declined after annealing at higher temperatures. For example, the coercivity increased dramatically after annealing at 450 °C because the amorphous flakes started to crystallize. XRD analysis (Fig. 1(a)) revealed the presence of Fe5SiP phase. According to the Scherrer’s equation, the average grain size was 294 nm.

Despite all of the precautions, we anticipated that the flakes [15] processing would result in some oxidation of the initial material. The oxidation is partially responsible for slightly decreased saturation magnetization measured after the milling [16]. EDX analysis (Fig. 1(b)) revealed that the oxygen content increased from 2 wt. % to 6 wt. % after milling the amorphous spherical powder for 20 hours. At the same time, we could not detect any contamination caused by the stainless steel jar and balls during the milling.

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FeSi-P alloy amorphous spherical powders exhibit a relatively high saturation magnetic flux density $B_s$ of 1.5 T, as well as ultra-low coercivity below 0.5 Oe. Such powders can be used in magnetodielectric composite inductor cores. In order to achieve the desired balance between high $B_s$ and low core loss properties, the spherical particles were turned into amorphous flakes by ball milling. The resulting flakes boasted high aspect ratios in excess of 70:1, and superior magnetic properties. The best results were achieved by milling for 20 hours with 6 mm balls at 500rpm. The final thickness of the flakes equals 0.1 μm and is sufficiently small to effectively inhibit eddy current. The flakes were post-annealed at 375 °C for 1 hour in argon to achieve a high $B_s$ of 1.4 T and low coercivity of 18.8 Oe. In summary, an experimental protocol that allows to reliably synthesize amorphous flakes with a high shape anisotropy and excellent magnetic properties have been successfully developed in this study.

References

[1] C. Zhang, J. Jiang, S. Bie, L. Zhang, L. Miao, and X. Xu, “Electromagnetic and microwave absorption properties of surface modified Fe–Si–Al flakes with nylon,” J. Alloys Compd., vol. 527, pp. 71-75, Jun. 2012.
[2] A. Makino, T. Hatanai, Y. Naitoh, and T. Bitoh, “Applications of nanocrystalline soft magnetic Fe-M-B (M = Zr, Nb) alloys “NANOPERM®,” IEEE Trans. Magn., vol. 33, no. 5, pp. 3793-3798, Sep. 1997.
[3] Sokolov, A. S., Andalib, P., Chen, Y., & Harris, V. G. (2016). Single-point FMR linewidth measurement by TE 10 rectangular transmission cavity perturbation. IEEE Transactions on Microwave Theory and Techniques, 64(11), 3772-3780. DOI: 10.1109/TMTT.2016.2591924
[4] D. Nuetzel, G. Rieger, J. Wecker, J. Petzold, and M. Müller, “Nanocrystalline soft magnetic composite cores with ideal orientation of the powder flakes,” J. Magn. Magn. Mater., vol. 196-197, pp. 327-329, May 1999.
[5] X. Zhong, J. Chen, L. Wang, B. Li, and L. Li, “Properties of FeSiAl-based soft magnetic composites with AlN/Al2O3 and hybrid phosphate-silane insulation coatings,” J. Alloys Compd., vol. 735, pp. 1603-1610, Feb. 2018.
[6] L. Liu, Y. Yan, K. D. T. Ngo, and G. Q. Lu, “NiCuZn Ferrite Cores by Gelcasting: Processing and Properties,” IEEE Trans. Ind. Appl., vol. 53, no. 6, pp. 5728-5733, Nov.-Dec. 2017.
[7] Q. Li, Y. Chen, and V. G. Harris, “Particle-size distribution modified effective medium theory and validation by magnetodielectric Co-Ti substituted BaM ferrite composites.” J. Magn. Magn. Mater., vol. 453, pp. 44-47, May 2018. https://doi.org/10.1016/j.jmmm.2018.01.013
[8] L. Cao, J. T. Jiang, Z. Q. Wang, Y. X. Gong, C. Liu, and L. Zhen, “Electromagnetic properties of flavor-shaped Fe-Si alloy particles prepared by ball milling,” J. Magn. Magn. Mater., vol. 368, pp. 295-299, Nov. 2014.
[9] R. M. Walser, W. Win, and P. M. Valanju, “Shape-optimized ferromagnetic particles with maximum theoretical microwave susceptibility,” IEEE Trans. Magn., vol. 34, no. 4, pp. 1390-1392, Jul. 1998.
[10] R. M. Walser and W. Kang, “Fabrication and properties of microforged ferromagnetic nanoflakes,” IEEE Trans. Magn., vol. 34, no. 4, pp. 1144-1146, Jul. 1998.
[11] X. Wang, R. Gong, H. Luo, and Z. Feng, “Microwave properties of surface modified Fe-Co-Zr alloy flakes with mechanochemically synthesized polystyrene,” J. Alloys Compd., vol. 480, no. 2, pp. 761-764, Jul. 2009.
[12] W. Kang, “Microforging Effect on the Microstructure and Magnetic Properties of FeSiB-based Nano flakes,” J. Mater. Sci. Technol., vol. 28, no. 4, pp. 303-307, Apr. 2012.
[13] J. Neige, T. Lepeit, A.-L. Adenot-Engelvin, N. Malléjac, A. Thiaville, and N. Vukadinovic, “Microwave permeability of FeNiMo flakes-polymer composites with and without an applied static magnetic field,” IEEE Trans. Magn., vol. 49, no. 3, pp. 1005-1008, Mar. 2013.
[14] X. Wang, R. Gong, P. Li, L. Liu, and W. Cheng, “Effects of aspect ratio and particle size on the microwave properties of Fe–Cr–Si–Al alloy flakes,” Mater. Sci. Eng., A, vol. 466, nos. 1–2, pp. 178–182, Sep. 2007.
[15] B. Z. Cui, M. Marinescu, and J. F. Liu, “Anisotropic NdFe14B submicron flakes by non-surfactant-assisted high energy ball milling,” IEEE Trans. Magn., vol. 48, no. 11, pp. 2800-2803, Nov. 2012.
[16] Z. Raelison, C. Leteire, J. Neige, A. L. Adenot-Engelvin, G. Pourroy, and N. Vukadinovic, “Preparation and microwave properties of silica coated Ni–Fe–Mo flakes composites,” IEEE Trans. Magn., vol. 49, no. 3, pp. 986-989, Mar. 2013.