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Composition dependence of microstructure, magnetic and microwave properties in ball-milled FeSiB nanocrystalline flakes

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ABSTRACT

The soft magnetic nanocrystalline/amorphous FeSiB flakes were fabricated by the ball-milling method and evaluations were made of the composition, microstructure, magnetic and microwave properties in the milling process. An investigation of the relationship between microstructure and magnetic/microwave properties showed that the electromagnetic characteristics were attributed to the changes of nanograin size, crystal and amorphous content corresponding to the composition variation. The replacing of Fe atoms by Si in α-Fe crystal caused the decrease of grain size, saturation magnetization and coercivity, while B content devoted to amorphous phase and decreased the permittivity. Consequently, it was observed that the optimum composition for microwave performance is $Fe_{82}Si_5B_{13}$.

1. Introduction

FeSiB-based nanocrystalline alloys have been widely investigated in last decades, not only due to its outstanding soft magnetic properties, which makes it adequate for industrial applications, but also for its two-phase nature which allows us to perform fundamental studies in magnetism regarding the coupling of nanocrystals [1–3]. In recent years, with a growing interest in particle shape and size dependence of dynamic magnetization in ferromagnetic powders [4,5], ultrafine nanocrystalline alloy flakes have attracted much scientific attention in the field of advanced electromagnetic absorbing material [6,7].

Mostly, nanocrystalline alloys are obtained by annealing or mechanical grinding of the amorphous precursor. Amorphous precursor is generally the metallic glass ribbon made by rapid quenching. In the case of annealing, an additional grinding process is needed for flake shaping and size controlling of the as-anneal alloys.

This paper aims at simplifying the process it takes to fabricate nanocrystalline flakes and investigating the composition dependence of key properties for potential absorption application. Therefore, FeSiB nanocrystalline alloy flakes were synthesized by a rapid and cost-effective method, ball milling of elemental powder mixtures, while no other additional processes were required for precursor preparation or post-modification. Influence of elemental contents on magnetic and microwave properties was studied through the change of material's microstructure and constitutive parameters.

2. Experimental procedure

Experiments were carried out using Fe, Si, B elemental powders of purity $\geqslant$99%. Ball milling of powder mixture was done by a QMC1 planetary mill firstly for 30 h without medium and then with anhydrous grain alcohol as medium for desired hours. Milling hours mentioned in this paper indicated the time spend on the secondary milling process (milling with medium).

Microstructure and composition of powders were characterized by Philips X' Pert Pro X-ray diffractometer (XRD) and JSM-2011F transmission electron microscopy with energy dispersive X-ray analysis (TEM/EDX). Mean grain size of crystallites was estimated by Scherrer's formula. A JSM-5900LV microscope was used for scanning electron microscopy (SEM) studies. Magnetic hysteresis loops were collected using LakeShor7300 vibrating sample magnetometer (VSM) at room temperature with an applied magnetic field up to $\pm 10^4$ G. For microwave test, as-milled powders were firstly mixed with paraffin solvent at weight ratio 3:1, then filled in a coaxial die after cooling, and finally compacted to a toroidal shape of thickness less than 3 mm. The microwave properties [$\varepsilon(\omega)$, $\mu(\omega)$] of flakes–paraffin composites were measured in the 0.5–18 GHz range with a APC7 coaxial line associated with an Agilent 8720 ET vector network analyzer.

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3. Results and discussion

For the purpose of identifying the crystallization phases, XRD analysis was conducted for as-milled FeSiB flakes. It is observed that all the samples contain only α-Fe phase and have grain size D drops with milling time (Fig. 1), in line with the reported microstructure evolution during milling process [8,9]. More noteworthy is the fluctuation of grain size with composition. Distribution of the elemental atoms in microstructure should be concerned.

Fig. 2 shows TEM micrographs of as-milled $Fe_{82}Si_5B_{13}$ flakes, and the contents of each element measured by EDX are listed in Table 1. The two-phase structure of nanocrystals embedded in amorphous matrix is clearly shown in Fig. 2(a) and (b). It is found that the crystallites of about 10 nm are mainly composed of iron and a small amount of additive silicon (boron) atoms, while the amorphous matrix is formed by boron and few silicon atoms. Comparing with the nominal composition of material, silicon and boron atoms show different dispersion trends: the main part of the former enters into α-Fe crystal lattice to replace iron atoms while the other forms amorphous phase. Therefore, at the same milling time, grain size decreases with increasing silicon content, due to the mismatching and defections in crystal structure caused by replacement. Additionally, the decrease of boron content could result in less amount of amorphous phase, then improve the brittleness of particles and enhance the milling effect, to make smaller and thinner flakes. This nanocrystalline/amorphous structure and flaky morphology (Fig. 3) are the goal of our synthesis method.

Magnetic properties of material are technically determined by synthesis method and composition, but in further analysis they are rooted in microstructure and compositional dispersion. As can be seen from Fig. 4, soft magnetic properties deteriorate gradually during ball-milling process, and both the values of saturation magnetization M_S and coercivity H_C drop with the replacing of boron content with silicon in nominal composition. Considering surface effect and random anisotropy model of nanomaterial [10,11], the impurity and disordered spin arrangement of surface area cause the decrease of M_S and the exchange coupling between nanograins averages out the anisotropy of particle as $H_C \propto D^6$, smaller the grain size stronger the effect. Therefore, the relationship between magnetic properties and composition can be understood by the change of grain size and silicon content, as M_S and H_C decrease with diminishing nanograin size and with increasing silicon concentration (Si at% < 15) [8]. Moreover, since material's particle size and flake thickness continuously reduce during milling process (Fig. 3), the decrease of M_S and the increase of H_C with milling time can be explained by the change of particles' morphology [12,13].

Microwave permeability and permittivity are the key parameters for EM absorber. Generally speaking, high permeability

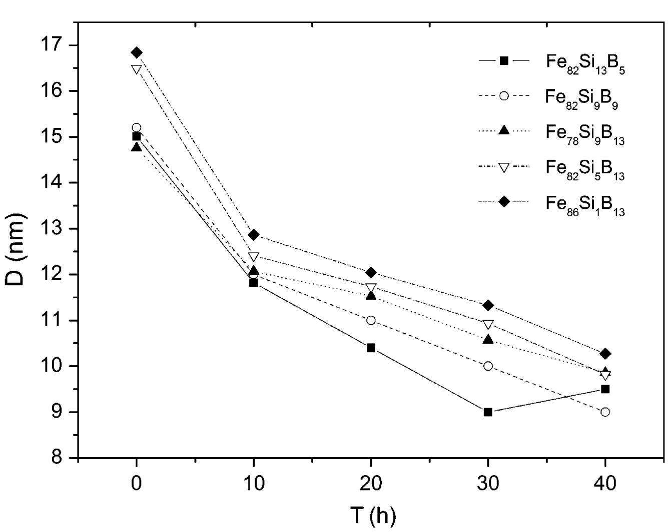

Fig. 1. Effect of milling time (T) and composition on nanocrystal grain size (D) of as-milled FeSiB flakes.

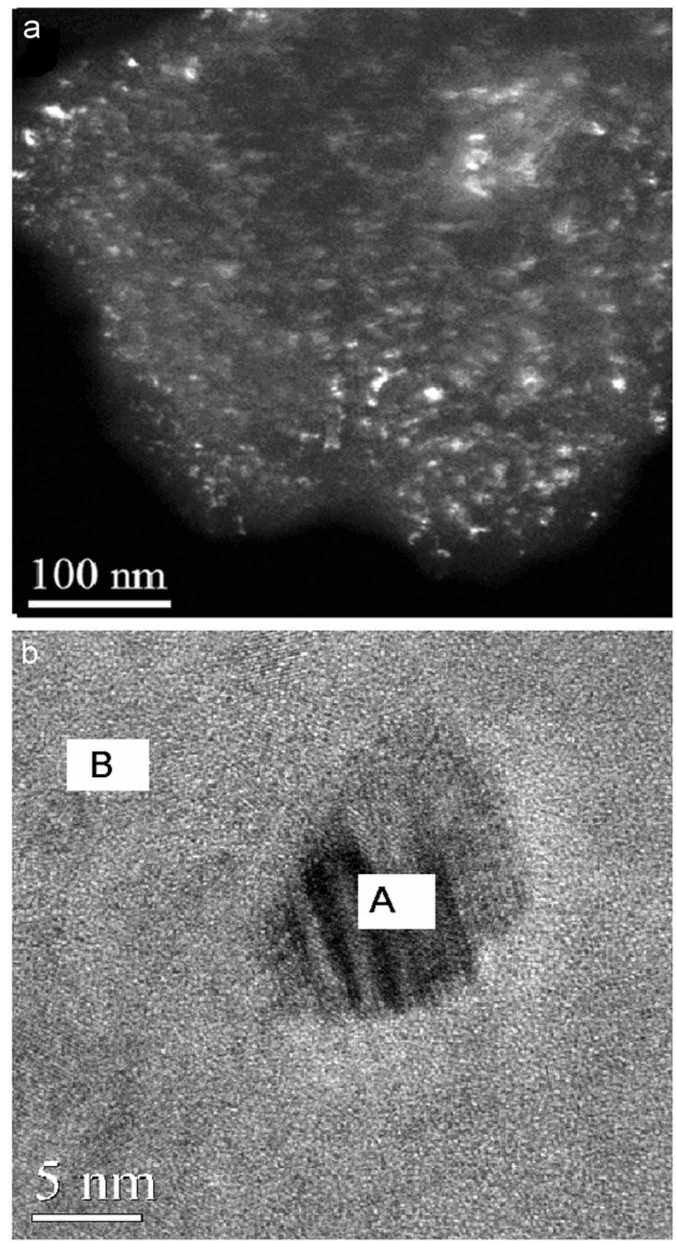

Fig. 2. TEM photographs of as-milled $Fe_{82}Si_5B_{13}$ flakes. *A* part corresponds to amorphous matrix and *B* part corresponds to α-Fe crystals listed in Table 1.

Table 1
EDX analysis of as-milled $Fe_{82}Si_5B_{13}$ flakes (unit: at%)

Parts	Fe	Si	B
Matrix	0.13	1.42	98.46
Crystal	88.25	4.59	7.16