



Microstructural characterization of gas atomized $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ and $\text{Fe}_{97}\text{Si}_3$ alloys

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ARTICLE INFO

Article history:

Received 1 July 2010

Received in revised form

16 November 2010

Accepted 5 December 2010

Available online 10 December 2010

Keywords:

Soft magnetic materials

Powder metallurgy

Atomization

Microstructure

ABSTRACT

Powder particles of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ and $\text{Fe}_{97}\text{Si}_3$ soft magnetic alloys have been prepared by gas atomization. The gas atomized powder was microstructurally characterized and the dependence of coercivity with the composition and powder particle size investigated. As-atomized powder particles of both compositions were constituted by a bcc α -Fe (Si) solid solution. The $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ powder particles presented a grain microstructure with dendrite structure, which dendrite arms were enriched in Nb. The coercivity increased as the particle size decreased, with a minimum coercivity, of 5 Oe, measured in the $\text{Fe}_{97}\text{Si}_3$ alloy in the range of 50–100 μm powder particle size. The coercive fields were quite higher in the $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ than in the $\text{Fe}_{97}\text{Si}_3$ powder, due to the Nb addition, which produced a phase segregation that leads to a noticeable magnetic hardening.

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1. Introduction

The microstructure of the amorphous alloys obtained by rapid solidification from the melt is characterized by the lack of long range order. Therefore, rapid quenched amorphous magnetic alloys behave as very soft, as a consequence of the absence of magnetocrystalline anisotropy. However, usually these excellent soft magnetic properties drastically deteriorate upon crystallization. Nevertheless, Fe-rich amorphous alloys containing small additions of Cu and Nb, $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$, exhibit softer magnetic behavior, with coercivities in the range of mOe, after partial crystallization [1,2]. This effect is related to the primary crystallization of bcc α -Fe (Si) fine grains, with typical grain size of nm, embedded in a residual amorphous matrix. Such microstructure is due to the alloying with insoluble elements, and where Cu atoms would promote nucleation of grains and the big Nb atoms would hinder their growth.

In addition, the Fe–Si alloys, $\text{Fe}_{97}\text{Si}_3$, are the soft magnetic alloys most widely used, due to their combination of low magnetostriction and high saturation magnetization that make these materials especially suitable for transformer cores and magnetic shielding.

To obtain soft magnetic materials of small dimensions is still a challenge. Therefore, a big research effort has been dedicated to obtain small particles of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ [3–5] and Fe–Si

[6,7] mainly by ball milling. An increase of the coercive field with decreasing particle size in ball milled $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ has been observed [3,4], and this increase was attributed to the large stress induced by ball milling and an intrinsic dependence of the coercivity with the particle size. Studies of magnetic properties of gas atomized AlMnSi powder particles had been also reported [8].

To avoid the stress induced by ball milling, gas atomization could be thought to obtain powder particles, and in a previous work, carried out on powders obtained from mechanical grinding of melt spun samples, some preliminary results on gas atomized particles were collected [4]. These previous results indicate a remarkable difference in coercivity for powder particles of similar size of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ and $\text{Fe}_{97}\text{Si}_3$ compositions. Gas atomization is a rapid solidification process, where the liquid melt solidifies at a cooling rate of the order of 10^4 – 10^5 K s^{-1} and produces powder particles of small size, below 100 μm .

In this work, the effect of the gas atomization on the solidification microstructure and the relationship with the differences in the corresponding coercive field has been analyzed in $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ and $\text{Fe}_{97}\text{Si}_3$ alloys. Both alloys present excellent soft magnetic properties and powder particles of these alloys could be used as materials with more adjustable shape than the ribbons, to be used as performing magnetic materials in the magnetic cores of inductive devices working at the high temperature range and microelectronic devices.

In this work it will be shown that the effect of Nb addition to gas atomized samples, far from producing grain refinement as it

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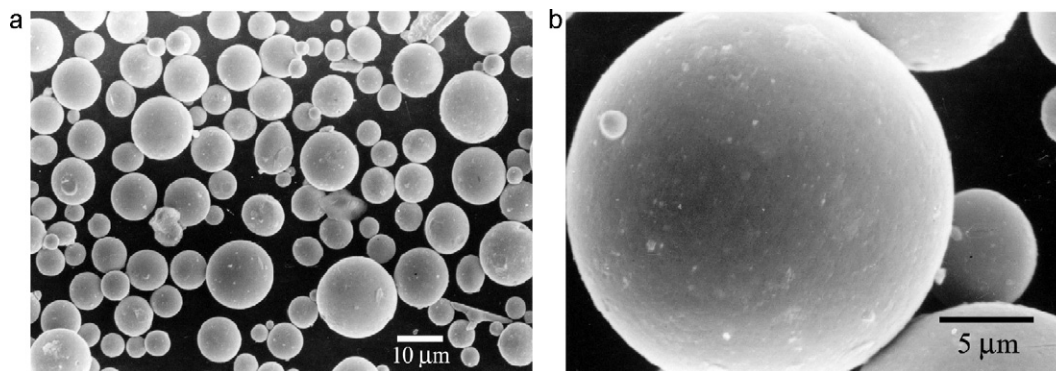


Fig. 1. SEM micrographs of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ powder particles, (a) at low and (b) at higher magnification.

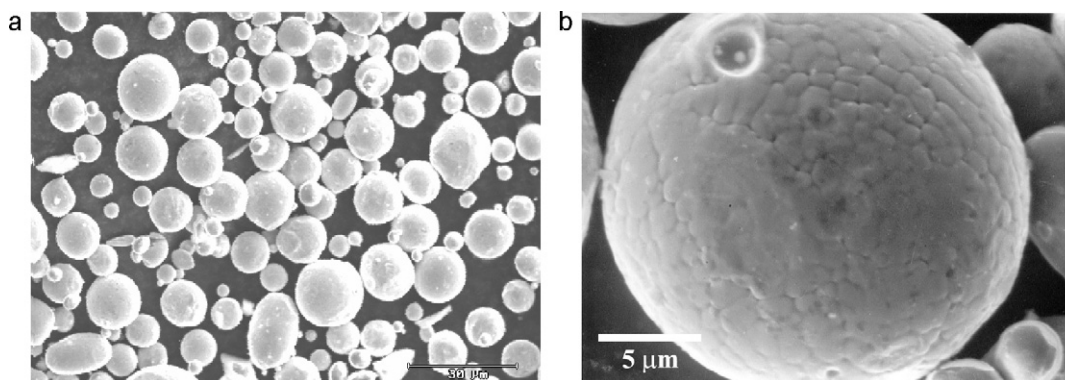


Fig. 2. SEM micrographs of $\text{Fe}_{97}\text{Si}_3$ powder particles, (a) at low and (b) at higher magnification.

happens for melt spun samples, gives rise to phase segregation that leads to a noticeable magnetic hardening.

2. Experimental techniques

$\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ and $\text{Fe}_{97}\text{Si}_3$ alloys, the composition is expressed in atomic percent, were gas atomized at CENIM. Gas atomization is a containerless process, where the liquid melt solidifies rapidly at high undercooling, with a cooling rate of the order of 10^4 – 10^5 K s^{-1} . These atomizations were carried out in a confined nozzle atomizer. The $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ at % alloy (83.4 Fe–7.7 Si–1.2 B–5.66 Nb–1.3 Cu % in weight) was prepared from FeSi_3 and Fe–Nb master alloys and Fe, B, and Cu elements. The $\text{Fe}_{97}\text{Si}_3$ alloy (96.5 Fe–7 Si % in weight) was prepared from a master alloy FeSi_3 and Fe element. Both compositions were melted in a magnesia crucible by induction heating under helium gas and were superheated to 210 and 140 K, respectively, above the liquid temperature prior to atomization. When the melt superheat was reached, the melt was teemed via a refractory tundish through a confined nozzle of 4 mm bore, made of zirconia. Atomization of the melt was achieved at the nozzle exit by an annular jet of helium of 2.2 MPa. The resulting powder was allowed to cool down in the inert gas atmosphere of the atomizer. Afterwards, it was collected in air and sieved to achieve separation into three size ranges: <25, 25–50 and 50–100 μm powder particles.

Compositions were tested by mass absorption spectroscopy. The morphology and microstructure of the as-atomized powder particles as a function of the size range were investigated by means of X-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation, optical microscopy and scanning electron microscopy (SEM) equipped with an X-ray energy dispersive analysis unit (EDX) on powder particles and cross sections, set up in resin and polished. Some samples were also etched, for 40 s, in a 2% Nital solution (2 ml HNO_3 + 98 mol ethanol). The coercive field, H_c , measurements of the powder were carried out in a vibrating sample magnetometer PPMS-VSM Quantum Design at 300 K and with a maximum field of 4 T, on encapsulated samples. To determine the coercive field it has not been necessary to apply the demagnetizing factor.

3. Results and discussion

Direct observations of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ powder particles in the scanning electron microscope, Fig. 1, showed that they were spherical in shape, with very smooth surface, and little agglomeration, for all the powder particle sizes.

Powder particles of $\text{Fe}_{97}\text{Si}_3$ were mainly spherical, but with some defective and ellipsoidal powder particles, and more agglomeration of particles. The surfaces were rough, with clear dendritic arms, as it is shown in Fig. 2. $\text{Fe}_{97}\text{Si}_3$ is a binary alloy in proportion Metal₉₇Metalloid₃, which corresponds a solid solution phase, therefore it crystallized very fast, even, sometimes, before the spheroidisation of the powder particles.

The X-ray diffraction patterns show a strong signal of bcc α -Fe (Si) solid solution for all the powder particles of both alloys, without evidence of formation of amorphous phase. Fig. 3 illustrates the X-ray diffraction pattern of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ of particle size 25–50 μm , as representative of all of them.

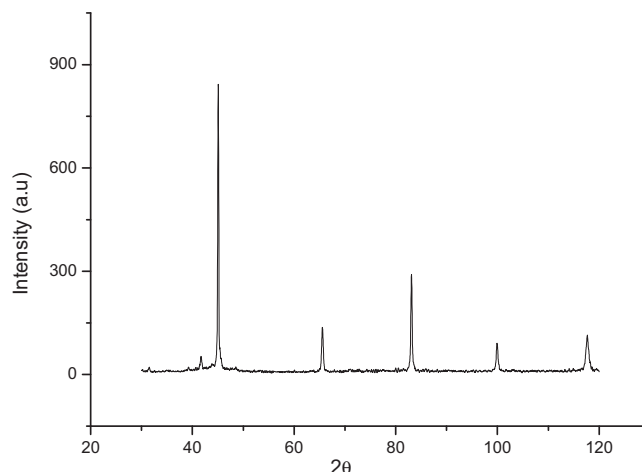


Fig. 3. The X-ray diffraction patterns of the as-atomized $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$.

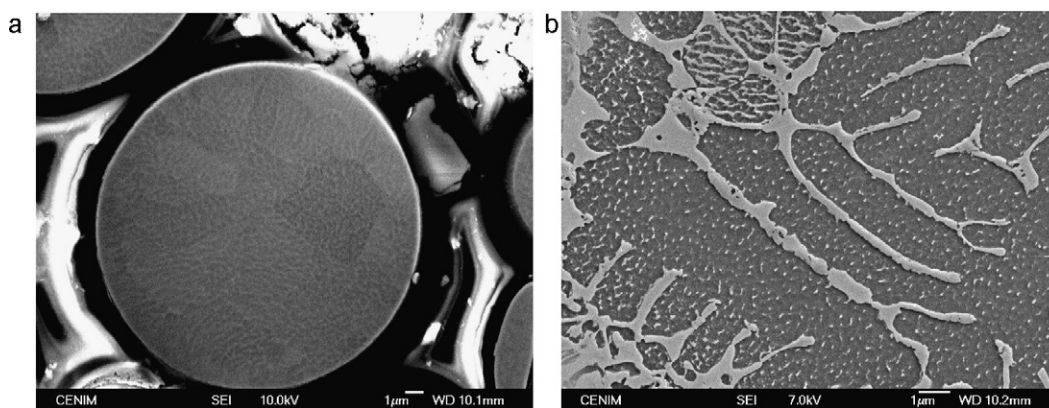


Fig. 4. SEM micrographs of cross sections of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ powder particles, (a) at low and (b) at higher magnification.

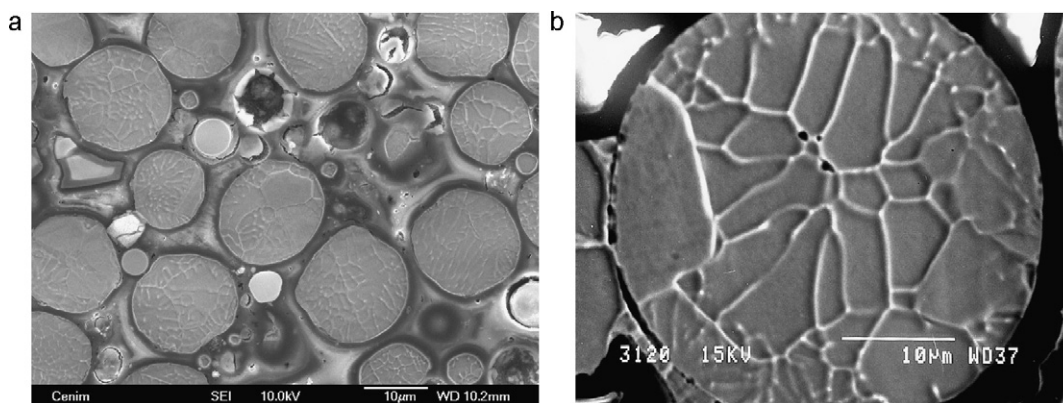


Fig. 5. SEM micrographs of cross sections of $\text{Fe}_{97}\text{Si}_3$ powder particles, (a) at low and (b) at higher magnification.

Fig. 4 shows the microstructure in SEM observations of as-atomized powder cross sections. $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ powder particles showed a fine microstructure, with large equiaxed grains, several microns in size, with a fine cellular-dendritic structure superimposed, Fig. 4a. Few grains were observed per section, and some nucleation rose from the surface and also there was internal nucleation, from scarce nuclei. The microstructures of all as-atomized powder particles below $100\ \mu\text{m}$ were very similar.

To investigate the composition of the fine cellular-dendritic microstructure, EDX microanalysis was carried out in an anomalous particle where the dendritic arms were especially coarse, Fig. 4b. EDX analysis indicated that the matrix was rich in Cu, without Nb, meanwhile the dendritic arms were Nb enriched, without Cu. Quantitative EDX analysis showed the composition in the dendrite arms corresponds to a fcc $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$ phase. The fact that this phase did not appear in the XRD diffraction pattern indicated that its volume fraction is below 3%. Therefore, during the atomization, the solidification front was not fast enough as to avoid the partitioning of the liquid and the Nb rich liquid was the first to solidify into the dendrite arms. The presence of this dendrite segregated phase, presumably not magnetic because is fcc, generates a gradient of physical properties inside the grain that exerts a magnetic hardening effect. This effect does not exist in $\text{Fe}_{97}\text{Si}_3$ compounds for which consequently the coercivity is smaller. The remaining liquid was impoverished in Nb, so the alloy lost the capacity to hinder the grain growth, and the grain nucleated on the Cu clusters grow up to several microns.

Therefore, although $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ had a complex composition, with five elements of different atomic radii, a suitable proportion Metal_{77.5}Metalloid_{22.5}, and partially amorphous $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ melt spun ribbons had been obtained at low

wheel speed [9], no evidence of amorphous phase was obtained in the as-atomized powder particles. And even the cooling rate achieved in the gas atomization process was not enough to avoid the partitioning of the liquid.

Fig. 5 shows cross sections of $\text{Fe}_{97}\text{Si}_3$, of samples etched with Nital, where grain borders were clearly revealed after etching. Larger grains, $10\ \mu\text{m}$ size, are observed, nucleated mainly in the interior of the particles. There were few grains per observed section and the microstructure was very similar in the three powder size ranges.

The coercive field, H_c , measurements are collected in Table 1 for the three powder particle sizes of both studied alloys, showing an increase of the coercivity as the particle size decreased, in both alloys. Thus, the H_c of the $\text{Fe}_{97}\text{Si}_3$ powder nearly became double and triple, when the particle size decreased from $50\text{--}100$ to $25\text{--}50$ and $<25\ \mu\text{m}$ particle size, with a minimum H_c of 5 Oe. On the other hand, also was remarkable the big difference between the high values of the H_c in the $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ and the low values in the $\text{Fe}_{97}\text{Si}_3$ alloys. The coercive field of the $\text{Fe}_{97}\text{Si}_3$ alloy is nearly one sixth than the H_c of the $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ alloy.

The magnetic hardening with the decrease of the particle dimension was already observed by Hernando et al. in ball milled

Table 1
Coercive field of both alloys as a function of the powder particle.

Powder particle size, μm	H_c , Oe $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$	H_c , Oe $\text{Fe}_{97}\text{Si}_3$
<25	72	14
$25\text{--}50$	65	10
$50\text{--}100$	29	5

materials and it was partially attributed to the high stress induced by the milling and to an increase of the effective magnetic anisotropy with decreasing the volume of the sample [3].

The stress in the gas atomized powder can be almost neglected and the microstructure of the three particle sizes was very similar for each alloy, therefore, the decrease of the volume should be the main responsible of the magnetic hardening observed on both materials.

According to the structural characterization reported here, the higher coercivity fields of the $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ alloy, than those of the $\text{Fe}_{97}\text{Si}_3$ one, is a consequence of the higher content of alloying elements that gives rise to the partitioning of the liquid, with dendrite arms Nb rich and a Cu rich matrix, with the presence of small precipitates fcc $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$ which would act as obstacles and hinder the domain walls motion. Therefore, the presence of the Nb rich phase induces an enhancement of the effective magnetic anisotropy constant of the grain that according to our previous theoretical model [4] induces the hardening observed for this composition.

4. Conclusions

Gas atomization produced $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ and $\text{Fe}_{97}\text{Si}_3$ spherical powder particles, below 100 μm diameter. The powder particles were fully crystalline formed by bcc $\alpha\text{-Fe (Si)}$ solid solution, with large grains nucleated mainly in the interior, without any evidence of formation of amorphous phase.

The microstructure of each alloy was very similar independently of the powder particle size. The microstructure of the $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ powder particles consisted of large grains

with a $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$ dendritic network superimposed. The $\text{Fe}_{97}\text{Si}_3$ powder particles were also constituted by larger grains.

The coercive field increased as the powder particle size decreased, achieving its minimum of 5 Oe for the $\text{Fe}_{97}\text{Si}_3$ powder particles in the range 50–100 μm .

For the same powder particle size and similar grain size the coercive fields for the $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ powders were almost one order of magnitude higher than those of the $\text{Fe}_{97}\text{Si}_3$ compound. Our structural characterization have shown that (i) the addition of Nb is not reflected in the grain size and (ii) in contrast, a Nb rich segregated phase acts as pinning center, so increasing the effective magnetic anisotropy constant [4] and producing an additional hardening. However, the coercivity of all the samples studied here increases with decreasing particle size due to the subsequent decrease of the number of grains or magnetic domains in each particle as predicted in our previous work [4].

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