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Thermal stability, dynamic mechanical analysis and nanoindentation behavior of FeSiB(Cu) amorphous alloys

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ABSTRACT

The aim of the present study is to investigate the crystallization behavior, microstructural evolution and mechanical behavior of the Fe-based amorphous alloy with three various compositions (at%): $Fe_{80.75}Si_8B_{11.25}$ (Cu-free and Silicon-rich alloys), $Fe_{85.2}Si_{0.9}B_{12.62}Cu_{1.28}$ and $Fe_{78.6}Si_{1.8}B_{17.75}Cu_{1.85}$ (Cu-containing and Si-poor alloys). The presence of Cu decreased the activation energy of the first crystallization peak and glass transition temperature. Furthermore, anomalous behavior was observed in Avrami exponent at the final stage of the crystallization of the Cu-containing alloys. Absence of Cu resulted in a coarse dendritic structure while finer and equiaxed grains were achieved by Cu addition. Nanoindentation size effect (the decrease of hardness with the increase of indentation depth) was observed in amorphous ribbons (regardless of composition) from 10 to 70 mN load and further increase of load did not change the hardness and Young's modulus noticeably. Isothermal annealing effectively increased the hardness (H) and Young's modulus (E_r) of the alloys. In addition, it was found that the plastic work of nanoindentation decreased after annealing in Cu-free alloy whereas it increased in Cu-containing one which could be due to the refined microstructure. Besides, shear bands around the indents in amorphous ribbons were disappeared after 1 h annealing which could be due to the change in plastic deformation mechanism from shear banding to strain-hardening.

1. Introduction

The state-of-the-art Fe-based amorphous alloys produced by the melt-spinning method and vastly used in motors, high frequency inductors, transformers and generators have become available since 1970 and since then, the effect of a variety of elements on the glass forming ability (GFA) and soft magnetic behavior has been taken into consideration. In 1988, Yoshizawa et al. [1] developed FeSiB(Cu, Nb) alloy known as Finement, showing superior soft magnetic behavior which means excellent permeability (10^4–10^5 at 1 kHz), low magnetic anisotropy, low core loss ($\approx$0.1 to 0.2 W kg^{-1} at 60 Hz and 1–2T) and low coercivity ($<$2 A/m).

In 1990, Suzuki et al. [2] introduced a new class of Fe-based amorphous alloy with composition of FeZrB known as Nanoperm. It seems that the stability of the amorphous phase in Zr-containing alloys (Nanoperm) is better than Nb-containing alloys (Finement); however, the new system has never been commercialized which is due to the strong tendency of oxidation in the presence of oxygen and as a result good casting skills and protective atmosphere are required [3–5].

In 1999, Willard et al. [6] developed a new class of nanocrystalline alloys with composition of FeCoZrB known as Hitperm that exhibited excellent soft magnetic properties at elevated temperature. Most recently, Makino et al. [7,8] produced a new class of Fe-rich FeSiBPCu alloy and named it as Nanomet. The new system showed high B_s value of 1.8–1.9 (T) nearly comparable to commercial silicon-oriented steels accompanied by extremely low core loss.

Among all those nanocrystalline systems, Finement alloys have been a low cost candidate and widely used in industries due to the desirable magnetic properties such as high saturation induction (1.2–1.5T), low coercivity ($<$15 A/m) and high permeability ($\approx 10^5$ at 1 kHz). The soft magnetic properties of the Finement alloys highly depend on the primary composition and microstructural features particularly grain size. For instance, B improves the GFA and refines the grain size through stabilizing the remaining amorphous matrix; however, higher percentage of B can also lead to the formation of high anisotropy phases such Fe_2B and/or Fe_3B being detrimental for soft magnetic behavior [3,9,10]. Cu is immiscible in Fe-based system and can provide heterogeneous nucleation sites for α-Fe(Si) nanoparticles which can lead to a fine and uniform dispersion of the α-Fe(Si) particles being essential for

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desirable soft magnetic behavior. Also, Nb impedes the further growth of nanoparticles and precipitation of the Fe_2B phase; however, this element is very expensive and is a major drawback to further commercialization of these boron-stabilized amorphous/nanocrystalline alloys.

Most studies on the ribbon-type Finement alloys have been focused on the enhancement of the soft magnetic properties owing to their main potential applications as magnetic materials. The improvement in magnetic properties requires heat treatment process such as stress relaxation annealing (to relieve residual stress and decrease magnetic anisotropy) and/or the nanocrystallization process (to form nanocomposite structure and increase the saturation magnetization). However, this partial crystallization can result in brittleness and fragility of the amorphous ribbons and make their handling very difficult especially in manufacturing of the large core for distribution transformer. Therefore, the study of the annealing process effect on the strength and mechanical integrity of the amorphous ribbon as a core material are quite important since winding amorphous ribbon around the core requires good bending ductility.

The absence of grains and grain boundaries in amorphous alloys (because of structural homogeneity) does not let the plastic deformation via dislocation slip; however, lack of defects and imperfections in crystal structure allows us to achieve higher strength and elastic modulus [11]. At temperature $T < 0.5T_g$, the plastic deformation is mainly concentrated on shear bands (strain localization), showing strain softening behavior (rather than hardening). This matter can be attributed to the local decrease in the viscosity of the glass [11]. Basically, the plastic deformation mechanism in amorphous materials is explained by two models: (i) shear transformation zone (STZ-model, a slight redistribution of local clusters of atoms over a diffuse volume) and, (ii) local atomic jump. In latter, the local dispersion of free volume controls the deformation mode in amorphous material and these sites would accommodate local shear (localized atomic jump into a vacancy). The presence of vein pattern (or river pattern) on fracture surfaces of amorphous materials represents highly localized zones of shear (brittle fracture with little yielding before failure).

Most of the investigations on the mechanical behavior of the amorphous alloys have been allocated to bulk metallic glasses (particularly Zr- and/or Pd-based alloys) and limited works have been conducted on the mechanical properties of the ribbon-type Fe-based amorphous alloys. Sun et al. [12] showed that the strength, elastic modulus and hardness of the FeSiBCu bulk metallic glass with thickness of 3 mm increased upon partial crystallization, reminding the relatively poorer packing efficiency of the amorphous material. Admittedly, amorphous alloys undergo a shear localization and macroscopically brittle failure at room temperature; however, they are still capable of reasonable plastic shear flow in microscale. In terms of determining the mechanical properties of amorphous ribbon, the nanoindentation method seems to be a useful technique since the thin cross-section of ribbon makes the conventional bulk metallic testing very challenging to employ despite its intrinsic downside such as the difficulty of determining the yielding point.

In the present work, a systematic and comprehensive investigation of the ribbon-type Finement alloys with different compositions was conducted to explore the crystallization kinetics and isothermal annealing effect around the crystallization temperature on the microstructure and mechanical behavior. The crystallization kinetics, microstructural features and mechanical behavior of the produced amorphous ribbons were considered by means of differential scanning calorimetry (DSC), transmission Kikuchi diffraction (TKD), transmission electron microscopy (TEM), dynamic mechanical analysis (DMA), atomic force microscopy (AFM) and the nanoindentation technique which is an effective method to measure the hardness and elastic modulus of the thin ribbons.

Table 1
Actual chemical composition of the produced ribbons (at%).

	Element				Thickness (μm)
	Fe	Si	B	Cu	
Sample 1	80.75	8	11.25	–	20 ± 5
Sample 2	85.2	0.9	12.62	1.28	26.76 ± 2.4
Sample 3	78.6	1.8	17.75	1.85	35.27 ± 4.03

2. Experimental procedure

Fe – B, Fe – Cu and Fe – Si masteralloys were prepared in a high frequency induction furnace and used to produce amorphous alloy via the melt-spinning method. ICP–OES instrument (model Perkin Elmer OPTIMA7300) was used to quantify the exact composition through digestion of samples in a mixture of $HCl + HNO_3$ (3 + 1), as results tabulated in Table 1.

The amorphous nature of the as-spun specimens was examined using XRD (PANalytical Empyrean Thin-Film XRD) with Cu-K_α radiation ($\lambda = 1.54056$ Å) from $2\theta = 20 - 120^\circ$ with step size of 0.026 and step time of 210 (s). In addition, High score plus software was used for phase identification and peak analysis.

The PIPs method was used to prepare samples for TEM analysis, including cutting ribbons into 2.5×1.5 mm in size and attaching them on a Cu grid using epoxy and then argon ion milling until a central perforation was observed. High resolution TEM was conducted using the Philips CM-200 field emission equipped with EDAX energy dispersive x-ray spectroscopy system. For transmission Kikuchi diffraction (TKD), the sample was mounted in a custom built Al TEM sample holder that clamped individual TEM foil at a tilt of 20° from horizontal. The sample was positioned at a short working distance (5–7 mm), so that it was just above the level of the top of the EBSD detector phosphor screen. The electron beam energy was set to 30 kV for all the analysis and the beam current was set to 1–10 nA with maximized depth of field. This last setting was imperative to achieve high-quality Kikuchi diffraction patterns from the samples. Transmitted Kikuchi diffraction patterns were imaged using a standard EBSD detector (Oxford Instruments Nordlys Nano) and processed using the Oxford Instruments Aztec 2.0 EBSD software. The spacing between measurements ranged from 4 to 10 nm and indexing rates were normally in the 70–80% range. Careful processing was required to eliminate some of the unindexed points. For obtaining high resolution images, sample was left for at least 1–2 h to minimize thermal and mechanical drifts and to improve the vacuum condition in the chamber.

The differential scanning calorimetry (DSC) was conducted using DSC-204F1 Phoenix (Netzsch Selb, Germany) to measure the crystallization peaks at different heating rates (5, 10, 20, 30 and 40 K/min).

Dynamic mechanical thermal analysis (DMTA) was utilized to pinpoint the glass transition temperature (T_g) and storage modules variation versus temperature using DMA 242 E Artemis equipment produced by Netzsch. Deformation mode, frequency and heating rate were tensile, 1 Hz and 5 K/min, respectively.

Nanoindentation experiments were carried out using UMIS instrument at room temperature employing a three-sided pyramid Berkovich tip at different loads: 10, 30, 50, 70 and 90 mN. The displacement (penetration depth) of the indenter was continuously monitored and load–displacement history of the indentation was recorded. The indenter was held at peak load for three seconds to remove any creep effect. Nanoindenter and sample were protected from possible air current in order to minimize thermal drift. ASTM E2546 was used as a guideline for indentation testing and all measurements were performed in the middle of the