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Role of Niobium in the nanocrystallization of a $Fe_{73.5}Si_{13.5}B_9Nb_3Cu$ alloy

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Abstract

The nanostructure of a nanocrystalline $Fe_{73.5}Si_{13.5}B_9Nb_3Cu$ alloy has been studied by means of Mössbauer spectroscopy, 1D and 3D atom probes. After 6 h at 520 °C, the crystallized fraction of the alloy is about 53%. α-Fe(Si) nanocrystals, 10–20 nm in diameter, are embedded in a retained amorphous matrix. They have a near $Fe_{80}Si_{20}$ composition and exhibit a DO_3 structure. The very low number density of Cu-rich particles does not match with the hypothesis of a systematic heterogeneous precipitation of α-Fe close to Cu-rich particles. A detailed analysis of the distribution of alloying elements in the retained amorphous matrix reveals the formation of a Nb-rich shell around α-Fe(Si) nanocrystals. It is proposed that this shell is formed during the growth of nanocrystals and the decomposition of the matrix, which tends toward a Fe_3B composition. The Nb-rich shell behaves as a diffusion barrier which inhibits the growth of nanocrystals. However, despite the presence of a Nb-rich shell, the junction between adjacent nanocrystals may occur, even if this phenomenon is rare.

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1. Introduction

The nanostructured $Fe_{73.5}Si_{13.5}B_9Nb_3Cu$ alloy, designated as FINEMET [1], is a soft magnetic material which combines a high saturation magnetization with a good magnetic permeability. These properties are strongly related to the

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nanocrystalline structure of this material [2]. Such a nanostructure is achieved by annealing melt-spun $Fe_{73.5}Si_{13.5}B_9Nb_3Cu$ amorphous ribbons in a temperature range wherein the primary crystallization of α-Fe(Si) grains is involved. After the crystallization heat treatment, 10–20 nm large α-Fe(Si) grains are embedded in a remaining amorphous matrix [1,3,4].

Previous works have shown that Cu may act as a nucleation element [1,3,5], whereas Nb is thought to inhibit the growth of α-Fe(Si) grains [3]. Though experimental evidence has been given for the role of Cu [6], Nb distribution in the nanocrystalline state still needs to be established at a near atomic scale for giving the evidence that this element behaves as a growth inhibitor.

The aim of this study is to correlate the distributions of alloying element with both the structural evolution of the alloy and its magnetic properties. This correlation requires the determination of several parameters, such as the composition in the amorphous matrix and in the nanocrystals, the relative distribution of each element in the matrix and the crystallized volume fraction. For this purpose, both the amorphous and nanocrystalline states of the material have been investigated by means of Mössbauer spectrometry (MS), hysteresimetry, 1D and 3D atom probes.

2. Experimental

Amorphous ribbons with nominal atomic composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ were prepared using the single roller melt-spinning technique under Ar atmosphere with a speed of 35 m/s. The as-quenched ribbons, 2 mm wide and 30 μm thick, were submitted to a thermal treatment under secondary vacuum at 520 °C for 6 h. ^{57}Fe MS analyses were performed at room temperature with a conventional spectrometer using a ^{57}Co source in a rhodium matrix. Ribbons were analysed by transmission, over their whole thickness. Coercive field and saturation magnetization are deduced from the hysteresis loop using the hysteresimeter M2100 (S2iS).

Specimens for the energy compensated one-dimensional atom probe (1DAP) and the tomographic atom probe (TAP) were prepared in the form of a very sharp tip (radius of curvature ~50 nm). The tip preparation was achieved by electropolishing specimen, first prepared as 50 μm × 50 μm rods, in a 95% 2-butoxyethanol, 5% perchloric acid solution at room temperature. The 1DAP was used for determining compositions with a maximum of accuracy, due to its excellent mass resolution and low detection limit [7]. The TAP [8] was used in order to determine the 3D distribution of all five elements present in the alloy at the near atomic scale. Atom probe analyses were performed at 10^{-8} Pa, with a tip temperature of 60 K, a pulse fraction of 19% and a pulse repetition rate of 1.7 kHz.

3. Results

3.1. Magnetic study

Local structure of as-quenched and treated samples was studied by transmission MS. This technique allows the crystalline fraction in the treated sample to be measured [9,10]. The Mössbauer spectrum for the as-quenched sample is shown in Fig. 1. It was fitted with an hyperfine distribution typical for amorphous alloys, confirming the amorphous state. The calculated mean hyperfine field is 21.5 T and is typical for Fe–Si–B-based amorphous alloys [11].

The Mössbauer spectrum of the treated sample (Fig. 2) contains a crystalline and an amorphous components, showing that the sample is not fully crystallized and contains a remaining amorphous phase. This result shows that a nanocrystalline structure is obtained in this sample after heating for 6 h at 520 °C.

The crystalline fraction is fitted with seven sextets according to Zemcik et al. [12], corresponding to the different environments around Fe atoms in the BCC α-Fe(Si) unit cell. The hyperfine parameters (isomer shift δ, the quadrupole shift ε, the hyperfine field B, the relative Mössbauer intensity RA%) are reported in Table 1. In the treated sample, the remaining amorphous phase