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Partitioning of Co upon the nanocrystallisation of soft magnetic FeCo(Zr, Nb)B alloys – a ^{59}Co NMR study

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^{59}Co NMR spectroscopy has been used to monitor structural modifications of $(Fe_{0.5}Co_{0.5})_{89}Zr_7B_4$ and $(Fe_{0.25}Co_{0.75})_{81}Nb_7B_{12}$ amorphous ribbons subject to different heat treatments. The characteristic features of ^{59}Co NMR spectra in the as-cast samples indicate a compositional modulation of $(Fe_{0.25}Co_{0.75})_{81}Nb_7B_{12}$, whereas $(Fe_{0.5}Co_{0.5})_{89}Zr_7B_4$ ribbon is more homogenous, indicating, however, a slight preference to form $Co_{78}Zr_{22}$-like environments. Upon heat treatment, a precipitation of an ordered (B2) CoFe crystalline phase is observed in both systems.

Key words: *nanocrystalline material; NMR; hyperfine field*

1. Introduction

Nanocrystalline FeCo(Zr, Nb)B(Cu) alloys (better known under their technical name HITPERM), prepared by devitrifying melt-spun amorphous precursors, have been the subject of intense research during the last few years [1–5]. This interest is driven by a technological demand for soft magnetic materials offering large magnetic induction, and at the same time being capable of operating at elevated temperatures.

The microstructure of these materials consists of nanocrystalline FeCo grains embedded in a surrounding amorphous matrix. Among the most significant structural parameters determining the magnetic behaviour of these two-phase systems are the size and volume fraction of crystalline grains as well as the structural and compositional nature of the remaining intergranular phase. In addition, it is well known that the magnetic properties of crystalline Fe-Co, such as magnetization and magnetocrystalline anisotropy, vary with composition and also depend on the degree of ordering

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[6]. Therefore, in order to optimise the properties of HITPERM materials, it is important to study in detail the development of the nanocrystalline structure during annealing, and especially the partitioning of different atomic species between the constituent phases, as well as the degree of ordering in FeCo nanocrystals.

This kind of structural information can be obtained by studying the distribution of hyperfine fields, which are extremely sensitive to local atomic configuration, and thus reflect the structural and chemical order in alloys. In this paper, we present the results of a ^{59}Co nuclear magnetic resonance (NMR) experiment that enables the partitioning of Co atoms in the FeCo(Zr,Nb)B system to be followed as it varies with increasing annealing temperature.

2. Experimental

Amorphous ribbons with a composition $(Fe_{0.5}Co_{0.5})_{89}Zr_7B_4$ (sample A) and $(Co_{0.75}Fe_{0.25})_{81}Nb_7B_{12}$ (sample B) have been obtained in vacuum by the planar flow casting technique. Pieces of amorphous ribbons were subsequently annealed under high vacuum for 1 hour, at 510 °C and 560 °C in the case of sample A and at 450 °C and 600 °C in the case of sample B, in order to prepare samples with different volume fractions of nanocrystalline particles.

The ^{59}Co NMR experiment was performed at 4.2 K in a zero magnetic field using a coherent, phase sensitive spin echo spectrometer. Several sets of NMR spectra were recorded, every 1 MHz in the frequency range 20–320 MHz, at varying excitations of the r.f. field amplitude. The ^{59}Co NMR frequency can be readily interpreted as finger prints of different structural components (nanocrystalline precipitates, amorphous remainder) – the structural information can thus be extracted in a straightforward way. On the other hand, the applied experimental procedure provides the value of the local restoring field acting on the magnetization in different structural components of the sample. In this way, microscopic magnetic information is added to structural information.

3. Results

We have previously reported a detailed NMR study of nanocrystallisation in $(Fe_{0.5}Co_{0.5})_{89}Zr_7B_4$ ribbon [7, 8]. It was shown that the ^{59}Co spectrum recorded for the as-quenched sample represents a broad distribution of different atomic environments, typical of a disordered amorphous material (Fig. 1). The lack of any peaks and spectral features confirms that the atoms are intermixed and there are no crystalline precipitates in the specimen. The maximum of spectrum intensity, located around 200 MHz, is mainly determined by the average proportion of transition metal (Co, Fe) and nonmagnetic elements (Zr, B), whereas a broad line width reflects a predominantly random distribution of magnetic and nonmagnetic elements [7]. This was also supported by an almost flat frequency dependence of the restoring field, reflecting an effective averaging of local anisotropies, which have a random character in the amorphous state [8].

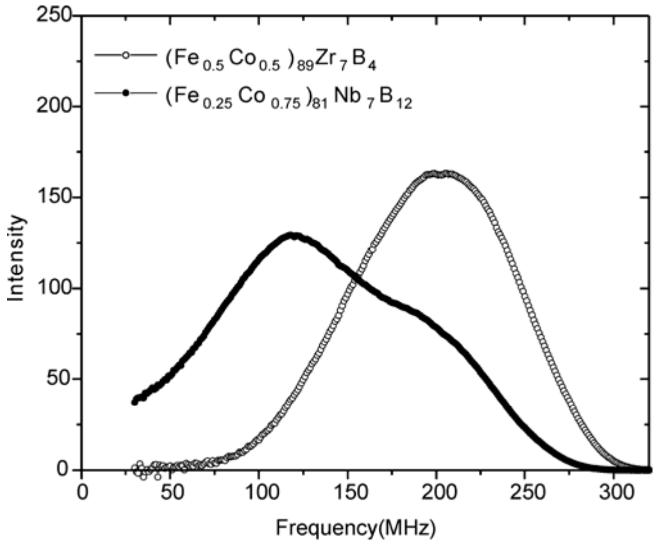

Fig. 1. ^{59}Co NMR spectra of as-cast $(Fe_{0.5}Co_{0.5})_{89}Zr_7B_4$ and $(Co_{0.75}Fe_{0.25})_{81}Nb_7B_{12}$ amorphous ribbons recorded at 4.2 K

In contrast to this, the ^{59}Co hyperfine field distribution for the as-cast amorphous ribbon of $(Fe_{0.25}Co_{0.75})_{81}Nb_7B_{12}$ (also shown in Fig. 1) exhibits a bimodal shape with two broad maxima. This kind of hyperfine field distribution reveals the presence of two types of Co local environments in the Nb-containing alloy. The two maxima of spectrum intensity at around 120 MHz and 200 MHz are assigned to Co atoms located in Nb-rich and Nb-poor regions, respectively.

After annealing, NMR spectra recorded from both types of ribbons display a characteristic split into two components (Fig. 2a). The spectrum component representing the amorphous matrix is downshifted in frequency with respect to the line from the as-quenched precursor, reflecting a higher proportion of nonmagnetic elements. The frequency shift is especially drastic in the case of $(Co_{0.75}Fe_{0.25})_{81}Nb_7B_{12}$ (about 30 MHz). In the case of $(Fe_{0.5}Co_{0.5})_{89}Zr_7B_4$, the line position was found to be only partly due to the depletion of Co and Fe. An additional, important factor is compositional modulation due to the tendency of Co and Zr to cluster. This tendency is driven by a negative heat of mixing of Co and Zr, resulting in the preferential formation of environments that have a composition close to $Co_{78}Zr_{22}$ [7]. This was clearly evidenced by the development of a two component structure after annealing at 560 °C, although such a tendency was already hinted at by certain features in the NMR spectrum of the as-quenched $Fe_{44.5}Co_{44.5}Zr_7B_4$ ribbon [8].

The high-frequency component of the NMR spectra in the annealed samples corresponds to the crystalline CoFe part (Fig. 2b). Short-range order present in the samples can be studied by comparing these spectral components with selected reference spectra from well-characterized samples of known composition. Such an analysis has been performed for $(Fe_{0.5}Co_{0.5})_{89}Zr_7B_4$ alloys and shows that the crystalline phase has the composition close to that of the highly ordered B2 phase ($Co_{50}Fe_{50}$ alloy) [7]. Two characteristic features of the NMR spectrum in $(Fe_{0.5}Co_{0.5})_{89}Zr_7B_4$ show that the nanocrystallites are enriched in Fe with respect to the nominal 50:50 composition. One of them is a slight frequency up-shift (to 291 MHz) with respect to 287 MHz, the latter being characteristic of a perfectly ordered B2 phase with a composition of $Co_{50}Fe_{50}$. Another is the presence of high frequency satellites spaced by +7 MHz, which are due to antisite Fe atoms on the Co sublattice.

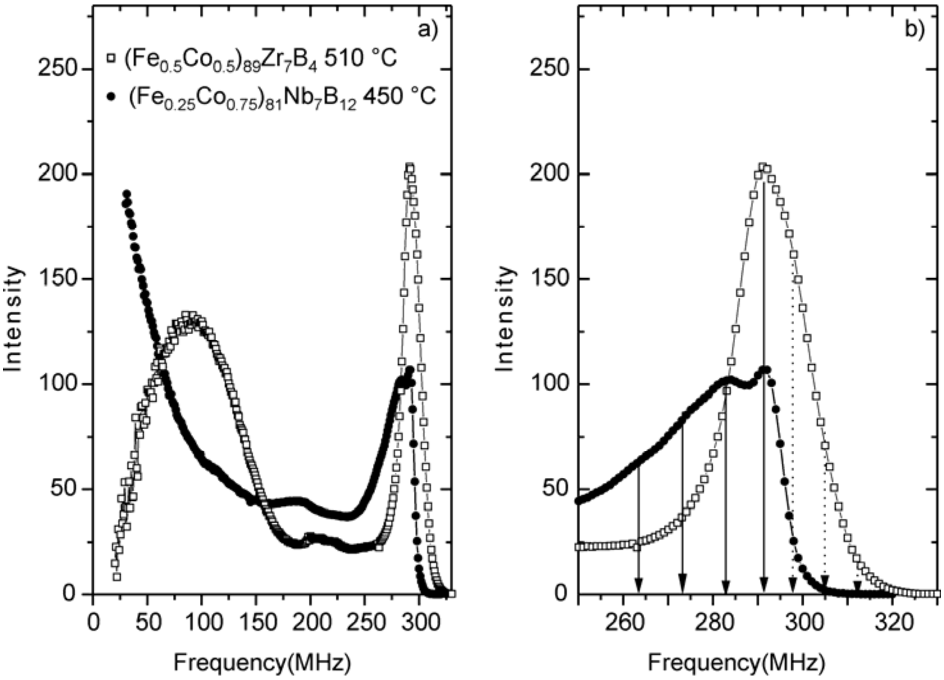

Fig. 2. ^{59}Co NMR spectra of $(Fe_{0.5}Co_{0.5})_{89}Zr_7B_4$ ribbon annealed at 510 °C and $(Co_{0.75}Fe_{0.25})_{81}Nb_7B_{12}$ annealed at 450 °C (a) and the high frequency part of the spectrum in greater detail (b); the arrows indicate the positions of satellite lines due to Co and Fe atoms located in antisite positions of the B2 structure of $Co_{50}Fe_{50}$

The analysis of the satellite intensity in terms of the hyperfine field model developed for B2 ordered CoFe alloys [9] allowed estimation of the crystal composition as $Co_{45}Fe_{55}$ [7]. A similar tendency to preferentially crystallize in the B2 phase is also displayed by $(Co_{0.75}Fe_{0.25})_{81}Nb_7B_{12}$ samples, as evidenced by the characteristic peak in the NMR spectrum in Fig. 2b. This is interesting, considering that the composition of the matrix of departure is considerably Co-enriched compared to $(Fe_{0.5}Co_{0.5})_{89}Zr_7B_4$. The presence of surplus Co in the highly ordered B2 sublattice manifests itself in the long tail of this spectral component, extending down to 150 MHz, with a characteristic satellite structure due to different nearest neighbour environments of Co.

These results clearly demonstrate that unique nanoscopic structural information can be obtained from studying ^{59}Co hyperfine field distribution using nuclear magnetic resonance. Further studies, including the correlation of observed spectral features with the variation of the restoring field, are currently underway.

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