Hyperfine magnetic fields in substituted Finemet alloys

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Abstract Transmission Mössbauer spectroscopy was used to determine the hyperfine fields of Finemet-type alloys in form of ribbons, substituted alternatively by Mn, Ni, Co, Al, Zn, V or Ge of various concentration. The comparative analysis of magnetic hyperfine fields was carried out which enabled to understand the role of added elements in as-quenched as well as annealed samples. Moreover, the influence of the substitution on the mean direction of the local hyperfine magnetic field was examined.

Keywords Mössbauer spectroscopy · Nanocrystalline alloys · Finemet · Hyperfine magnetic field

1 Introduction

Nanocrystalline Finemet (Fe-Cu-Nb-Si-B) alloys were discovered in 1988 [1] and for the last three decades have been intensively investigated because of their excellent soft magnetic properties. The material was prepared by two-step procedure. In the first step, rapid quenching of the melt caused formation of an amorphous ribbon, in the second one – the ribbon was submitted to annealing in well-matched conditions what enabled controlled crystallization of the initial amorphous material. As a result, a specific structure arised with Fe-Si nanocrystals dispersed in an amorphous, ferromagnetic surrounding. This caused the
exchange coupling between nanogranules occurred due to interactions through the amorphous matrix, giving rise to enhanced soft magnetic properties [2–4].

Many attempts have been made to improve magnetic, electric as well as mechanical properties of Finemet in order to extend their wide technological applications, including modifications of the original material and the preparing procedure. Among others, changes of the chemical composition have been widely studied [5–10]. Depending on the type and concentration of the addition (and some other parameters), the substituting atoms can be situated at different positions both inside the crystallites and in the amorphous matrix, modifying structure and properties of the material as well as the hyperfine parameters.

In this work, the comparative analysis of compositional evolution of hyperfine magnetic fields has been performed to get information about the role of added elements. Finemet-type alloys, substituted alternatively by Mn, Ni, Co, Al, Zn, V or Ge of various concentration were the subject of investigations. Since the nanocrystalline alloys were strongly inhomogeneous, both nanocrystallites and amorphous matrix were taken into consideration. It is known that grain boundaries and interfacial regions also affect the alloys properties [11], however, in Finemet family—due to complexity of Mössbauer spectra—it is very difficult to distinguish the corresponding component. The influence of the substitution on the mean direction of the local hyperfine magnetic field has been examined for selected alloys as well.

## 2 Experimental

Eight series of Finemet-type alloys with various kind of admixture atoms were investigated. Samples of amorphous ribbons were prepared by the melt-spinning technique. As a result, (0.5-1) mm wide and (40–50) μm thick ribbons originated. In order to induce partial crystallization of the alloys, annealing of the amorphous precursor was performed in a vacuum furnace at well-matched temperature. The detailed chemical composition and values of parameters of the annealing procedure are listed in Table 1. Room temperature $^{57}$Fe Mössbauer measurements were carried out with a $^{57}$Co(Rh) source of gamma radiation and a drive system working in a constant acceleration mode. Mössbauer spectra were numerically analyzed by the use of MOSFIT program based on the Varret method and the commercial NORMOS program.

## Table 1 Specification of the investigated Finemet-type alloys and the values of the coefficient $K$, determined on the basis of (1) for as-quenched alloys, in the range $x < 25$

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>$T_{\text{ann}}$ [°C]</th>
<th>$t_{\text{ann}}$ [h]</th>
<th>$K$ [T/at%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1) \text{Fe}_{73.5-x}\text{Mn}_x\text{Nb}_3\text{Cu}<em>1\text{Si}</em>{13.5}\text{B}_9$ ($x = 1, 3, 5, 7, 9, 11, 13, 15$)</td>
<td>a.q., 550, 575, 690</td>
<td>1</td>
<td>1.1</td>
</tr>
<tr>
<td>$(2) \text{Fe}_{73.5-x}\text{Ni}_x\text{Nb}_3\text{Cu}<em>1\text{Si}</em>{13.5}\text{B}_9$ ($x = 10, 20, 30, 40, 50, 60$)</td>
<td>a.q., 460, 530</td>
<td>1</td>
<td>0.03</td>
</tr>
<tr>
<td>$(3) \text{Fe}_{73.5-x}\text{Co}_x\text{Cu}_1\text{Nb}<em>3\text{Si}</em>{13.5}\text{B}_9$ ($x = 0, 7.35, 14.7, 22.05, 29.4, 570$)</td>
<td>a.q., 570</td>
<td>1</td>
<td>−0.04</td>
</tr>
<tr>
<td>$(4) \text{Fe}_{73.5-x}\text{Zn}_x\text{Nb}_3\text{Cu}<em>1\text{Si}</em>{13.5}\text{B}_9$ ($x = 1, 3, 5$)</td>
<td>a.q.</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>$(5) \text{Fe}_{73.5-x}\text{Al}_x\text{Nb}_3\text{Cu}<em>1\text{Si}</em>{13.5}\text{B}_9$, ($x = 0, 1, 2, 3, 5, 7$)</td>
<td>a.q., 490, 550, 650</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>$(6) \text{Fe}_{73.5-x}\text{V}_x\text{Cu}_1\text{Nb}<em>3\text{Si}</em>{13.5}\text{B}_9$ ($x = 1, 3, 5, 7$)</td>
<td>a.q., 550</td>
<td>1</td>
<td>1.2</td>
</tr>
<tr>
<td>$(7) \text{Fe}<em>{73.5}\text{Cu}<em>1\text{Nb}</em>{3-x}\text{Si}</em>{13.5}\text{V}_x\text{B}_9$ ($x = 1.5, 3$)</td>
<td>a.q., 550</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>$(8) \text{Fe}_{73.5}\text{Nb}_3\text{Cu}<em>1\text{Si}</em>{13.5-x}\text{Ge}_x\text{B}_9$ ($x = 1, 5, 10, 13.5$)</td>
<td>a.q., 550</td>
<td>1</td>
<td>−0.09</td>
</tr>
</tbody>
</table>
2.1 Hyperfine magnetic field

2.1.1 As-quenched alloys

On the whole, Mössbauer spectra of the investigated as-quenched alloys did not show any traces of crystallization—they take a shape of broad, smooth Zeeman sextets reflecting continuous distributions of the hyperfine parameters, characteristic of amorphous systems [12–17]. The used numerical procedures allowed to derive the hyperfine magnetic field (HMF) distribution from the experimental spectra. Selected spectra collected for the amorphous Finemet substituted by nickel and typical curves presenting HMF distributions are shown in Fig. 1a, b. The distributions take a shape of lines with one or two bumps The reason of such a shape is frequently discusses in the literature. According to a prevailing view, the maxima result from chemical inhomogeneity of the amorphous alloy and reflect different privileged surroundings of iron atoms. It must be noted that low-field maximum observed in the HMF distribution of amorphous alloys is sometimes interpreted as an artefact of the fitting procedure; particularly in the case when quadrupole interaction is strong, so first order perturbation theory (FOPT) approximation cannot be applied. In our case the position of low-field peak was not smaller than (4–5)T, which corresponds to considerably larger energy than the typical value of quadrupole interaction being found for amorphous Finemet alloys. Therefore, FOPT approximation constitutes a reasonable approach and the maxima in the distribution can be attributed to distinctly different, preferred local environments of iron atoms. One of them is analogous as in classical Finemet; the second (a low-field one) is clearly related to iron-poor surrounding.

In most cases, the high-field bump was predominant, its relative contribution was not smaller than 65 % and it gave the main share to the mean value of the HMF distribution. For particular series of Finemet alloys (listed in Table 1) the top values of hyperfine magnetic field of both parts of distribution and also the mean value over the whole distribution depended on atomic concentration of admixture elements, $x$. 

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**Fig. 1** Selected transmission Mössbauer spectra collected for Fe$_{73.5-x}$Ni$_x$Nb$_3$Cu$_1$Si$_{13.5}$B$_9$ amorphous alloys, (a) and derived hyperfine magnetic field distributions, (b)
Evolution of the mean hyperfine magnetic field $\langle B \rangle$ with atomic concentration $x$ is presented in Fig 2. In order to compare the role of admixture elements, first of all the results obtained for series (1)–(6) were analyzed in which the elements substituted iron in the chemical formula. Except for the series (3) with Co admixture, in all investigated alloys the mean hyperfine magnetic field decreases with rising concentration of admixture atoms and the dependence in general is not strictly linear. In the concentration range up to 25 at% a linear function was used to fit the relation, as the first approximation. The coefficient $K$ reflecting the reduction of $\langle B \rangle$ with unit growth of $x$ was evaluated, defined as follows:

$$\langle B \rangle = \langle B \rangle_{\text{max}} - Kx$$  \hspace{1cm} (1)

The values of $K$ are listed in the last column in the Table 1. The results are similar for admixture elements: V, Mn, Zn – the value of $K$ is about (1.1–1.2) T/at%. It can be believed that the influence of the substituted elements on mean HMF consists mainly in dilution of iron atoms in the amorphous alloy. This assumption is confirmed by the outcomes obtained for Fe$_{73.5}$Cu$_1$Nb$_{3-x}$Si$_{13.5}$V$_x$B$_9$ ($x = 1.5$, 3) alloys [15] in which iron concentration is independent of vanadium content; in this case hyperfine magnetic field is nearly constant.

In the case of Al addition the value of $K$ is much smaller (0.6 T/at%), the reason of which is not quite clear. It can be supposed, that the behavior is related to distinctly smaller atomic radius of Al than those characteristic of the elements stated before. This causes slightly stronger interaction between iron atoms and then the reduction of HMF is not so large as it might result from simple dilution.

The value of $K$ obtained for Ni admixture is still smaller and quite close to zero (0.03 T/at%) This means that in the concentration range $x < 25$ the contribution to the mean hyperfine magnetic field (measured at Fe) arising from Ni atom situated in the neighborhood is similar to that brought by Fe atoms and therefore mean HMF is nearly constant. Regarding larger atomic concentration of Ni, mean HMF is reduced much stronger with growing $x$, dropping to zero at $x = 60$. Such a behavior is quite different compared with binary Fe–Ni alloys which show non-zero magnetic splitting almost in the whole compositional range. This discrepancy arises from the presence of metalloids and is explained as a result of some inhomogeneity of iron atoms arrangement, observed in (Fe, Ni)–M (M—metalloid) crystalline and amorphous alloys. It is manifested by a shift of Fe atoms to the positions with higher number of metalloids in the immediate neighborhood [12]. The modification
of short-range order is evidenced by the evolution of HMF distribution, shown in Fig. 1b. With growing nickel concentration, a low-field shoulder of HMF distribution increases and becomes dominating at $x = 50$, reducing the value of mean HMF.

In the case of Co admixture the value of $K$ is negative, i.e. mean HMF increases with growing $x$. Such a behavior is observed up to $x = 36.5$, where the function reaches maximum and then slowly falls [13, 14]. Very similar results were reported also by other authors [5]. The non-monotonic evolution of mean HMF is not well correlated with decreasing trend of macroscopic magnetization reported by Mazaleyrat et al. [18] and Muller et al. [19]. A strong modification of electronic structure by Co addition or existence of regions which do not comprise iron and, consequently, are not detected with Mössbauer spectroscopy can be a possible explanation of the behavior.

In series (8) Ge substitutes silicon and concentration of iron becomes constant. Nevertheless it causes some reinforcement of exchange interaction resulting in the small negative value of $K = -0.09$ T/at%. Despite the results of XAFS investigations [17] suggest prolongation of the average interatomic distance between Fe atoms and their closest surrounding in these alloys, the small negative value of $K = -0.09$ T/at% is observed which presumably results from the slight rise of exchange interactions.

### 2.1.2 Annealed alloys

Selected Mössbauer spectra of the annealed alloys are presented in Fig. 3. They confirmed that thermal treatment resulted in formation of strongly inhomogeneous systems comprising both crystalline and amorphous areas as well as interfacial regions [12–17]. The results of microscopic investigations showed that crystallites take shape of grains of nanometric sizes and they are surrounded by amorphous matrix. This nanocrystalline structure is of great importance to excellent soft magnetic properties observed for those materials.

The spectra comprise overlapping discrete components (sextets), representing crystallites and a smeared sextet related to a continuous distribution of HMF which is attributed to the amorphous phase. In the case of classical Finemet, the crystalline grains have usually the structure of Fe(Si) or DO$_3$-type Fe-Si, depending on the annealing temperature. Similar (qualitatively) results were also obtained in the spectra collected for series (1)–(6) of substituted Finemet, however the values of hyperfine parameters evolved with the change of concentration of admixture atoms.
Spectra have been analysed using 4-8 sharp sextets composing a discrete subspectrum and one block of histogram-like HMF distribution for the continuous one. Depending on composition as well as the annealing temperature, different fraction of the discrete component is found and it represents various crystalline phases (analysed below).

Compositional evolution of the mean HMF of the amorphous matrix demonstrated considerable diversity of the shape. The reason is that the mean hyperfine magnetic field of the amorphous remainder depends not only directly on the concentration of the admixture elements but also on the degree of crystallization. As the added elements influence also the course of crystallization (among others the crystallization temperature) the considered dependence can be quite complicated and it is difficult to forecast its shape.

In comparison to the previous question, the compositional dependences of the crystalline grains structure are not so diverse, what is illustrated by the evolution of the HMF of individual sextets representing the crystalline phase (Fig. 4). As it is shown, only gradual changes of HMF values are observed. The analysis of the intensity of sextets as well as the results of structural investigations (not presented in this paper) enabled distinction between Fe(Si) solid solution and Fe₃Si – type DO₃ structure. In the first case sextets marked by symbols A8, A7, ...A4 are attributed to the iron atoms having 8, 7, ....4 iron atoms (respectively) in the first coordination shell. In the second one, besides the above-mentioned components attributed to iron atoms situated in site A, also sextet called D occurs attributed to iron atoms situated in that site. Each of them has 8 iron atoms in the first coordination shell and therefore its hyperfine parameters are very similar to those characterized iron atoms in position A8, even though they differ in respect of the second and further coordination shells. In many nanocrystalline alloys, because of the strongly overlapped subspectra, the sextets D, A8 and A7 are completely or partly inseparable. A significant contribution of sextets with smaller HMF, especially the sextet A4 (about 19.5 T) is indicative of bcc DO₃ - type phase.
It has been found that the influence of addition of vanadium, manganese and aluminum (instead of iron) on HMF values characterized individual sextets belonging to Fe-Si phase is not considerable and manifests itself in various ways. A slight but systematic decrease of HMF with V and Al concentration is observed. In both cases the changes refer mainly to the components with the highest values of HMF (D, A8, A7, A6). This means that both elements contribute to the crystalline phase. Relative intensities of sextets within the subspectrum representing crystalline grains remain nearly independent on \( x \) in the case of Finemet substituted by vanadium \([14, 15]\). Taking into account that with growing \( x \) the percentage of iron is reduced, it can be supposed that vanadium takes randomly both A and D positions in the crystal lattice, therefore the proportions of related sextets intensities do not change significantly. On the contrary, aluminum shares the grains being located in crystallographic position D which is occupied alternatively by iron and silicon atoms. This causes the strong increase of the relative intensity of sextet A4, which is evidenced experimentally \([12]\): at \( x = 5 \) and \( x = 7 \) only two main sextets D+A8+A7 and A4 dominate in the spectrum (with the ratio of intensities close to 1:3). This testifies formation of the ordered DO\(_3\) structure which is connected with the appropriate relation between number of Fe and Al+Si atoms within the crystalline phase. The increase of the width of individual lines with growing \( x \) gives an additional argument for incorporation of added elements into the grains: because of the chemical disorder the number of in-equivalent positions of the probe atoms \((^{57}\text{Fe})\) with different surroundings becomes larger, so many sextets with very close values of hyperfine parameters overlap making the lines of spectra wider.

Addition of manganese gives similar effects on HMF values as vanadium, although curves representing the HMF evolution are more rugged. We supposed, that the reason is that this element contributes to the crystallites, similarly as vanadium, but because of the wider range of composition this causes slightly larger changes of the HMF. Admixture of germanium (instead of silicon) leaves the HMF nearly constant, except for \( x = 15 \) for which slight increase of the values of the high-field sextets is observed.

Substitution by nickel and cobalt influences the HMF to the largest extent. Sextets denoted as D+A8, A7..., A4, that constitute the spectra of cobalt-poor samples, are similar as of Fe-Si grains of disordered DO\(_3\) structure in pure Finemet, although they are characterized by somewhat modified HMF values. The numbers (8, 7, ..4) should probably in this case be related to the total Fe+Co number of atoms in the first coordination shell. The hyperfine field of sextets A8 and A7 rises slowly up to about \( x = 37 \) and drops for higher Co concentration. The reason is that cobalt alters chemical order in both the first and the second coordination zone as well as causes changes in the spin density and interatomic distances.

For \( x > 7.4 \), an additional sextet of value over 33 T arises attributed to iron atoms with 8 magnetic near neighbors among which several atoms of cobalt are present. The existence of such a component in Mössbauer spectra evidences infiltration of cobalt atoms into crystalline phase. At the same time the considerable increase of contribution of the Zeeman sextets characterized themselves by the highest HMF values is observed which indicates modification of grain constitution: disordered (chemically) DO\(_3\) structure of Fe-Co-Si is replaced by bcc \((\text{Fe,Co})\text{Si}\) solid solution comprising about 5 at.% silicon. The enrichment of grains in magnetic elements is accompanied by diminution of the amorphous matrix in Fe and Co which is demonstrated as the strong drop of the mean value of HMF related to the amorphous remainder, observed for nanocrystalline samples rich in cobalt \([14]\).

In the case of Finemet substituted by nickel, it was found that the discrete subspectrum is multicomponent. In the compositional range \( x = 10 – 30 \) a set of sextets with hyperfine parameters and relative intensities characteristic of bcc-Fe(Ni, Si) solid solution dominates,
Table 2  The values of relative intensities of lines 2, 5 in a Zeeman sextet in respect of those of lines 3, 4 derived for selected as-quenched alloys

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>x</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{73.5-x}$Zn$_x$Nb$_3$Cu$<em>1$Si$</em>{13.5}$B$_9$</td>
<td>1</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.8</td>
</tr>
<tr>
<td>Fe$_{73.5}$Nb$_3$Cu$<em>1$Si$</em>{13.5-x}$Ge$_x$B$_9$</td>
<td>1</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>13.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

with low percentage of nickel and silicon. The components diminish with further increase of nickel concentration. Instead, components of medium HMF values appear interpreted as traces of tetragonal Fe(Ni, Si) and iron–boron phases. Moreover, a low-field sextet (B $\approx$ 4–8 T) as well as a paramagnetic doublet arise above x = 30; they are attributed to small amount of Fe-Ni invar phase. Presented conclusions are qualitatively consistent with X-ray results reported in [8]. The relatively weak changes of mean HMF of the amorphous matrix in the range 10 $\leq$ x $\leq$ 50 are observed, despite the quite different extent of crystalline phase. This seems to result from the similar proportions between transition metals and metalloids both in amorphous and crystalline phase.

2.2 Magnetic moments orientation

In the case of unpolarized dipole radiation, relative intensities of lines 2, 5 in a Zeeman sextet in respect of those of lines 3, 4 are connected with $< \cos^2 \psi_R >$—average value of $\cos^2 \psi_R$, where $\psi_R$ means the angle between the incident gamma beam and the local hyperfine magnetic field (which in the case of iron is opposite to the magnetic moment), through the following relations [20]:

$$p = I_{2.5}/I_{3.4}, \quad p = 4 \cdot (1 - < \cos^2 \psi_R >)/(1 + < \cos^2 \psi_R >)$$

$$< \cos^2 \psi_R > = (4 - p)/(4 + p)$$

Therefore, some information about alignment of atomic magnetic moments can be derived from Mössbauer spectra by determining p. In the case of Finemet-like amorphous ribbons p $\approx$ 3 is the common value and often it is reduced in the course of annealing procedure.

It has been found that in most series of investigated as-quenched alloys the values of the parameter p ranges from 2.5 to 3.4 (±0.3). The most interesting, untypical results of the analysis are collected in Table 2. In the alloys substituted with zinc and germanium p changes with increasing x from typical values about 3, which means that alignment of magnetic moments in-plane of ribbon is preferred, to about 1.8, which points to some slight preference of out-of-plane orientation of magnetic moments. That behavior is likely related to magnetoelastic effects and depends on strain distribution as well as inhomogeneity of the samples.
3 Conclusions

The presented studies of as-quenched Finemet-type alloys showed different influence of added elements on the hyperfine magnetic field distribution. Substitution of iron by V, Zn, Mn resulted mainly in reduction of mean HMF related to dilution of magnetic iron atoms. Substitution of iron by nickel and cobalt influenced the HMF to the largest extent, which evidenced alterations in the chemical order as well as changes in spin density and interatomic distances. The compositional evolution of HMF values characterized particular sextets, belonging to the component representing nanocrystalline phase, proved that the added elements infiltrated the grains. However, they were situated in different positions in crystal lattice – Ni, Co, V, Mn took randomly the positions of iron in sites A and D, while Al, Ge occupied mainly site D what strongly changed atomic order, particularly for (5–7) at% of Al. In some cases substitution caused alteration of crystalline structure (from Fe(Si) solid solution towards DO$_3$ – type structure or vice-versa), induced formation of other crystalline phases, changed short-range order and magnetic properties of the amorphous remainder or direction of the local hyperfine magnetic field in the as-quenched alloys. The presented results give a novel view to the question of the complex magnetic interactions in substituted Finemet alloys and can be helpful in the technological optimization of the soft magnetic materials dedicated for electrotechnical applications, especially in order to improve energy efficiency and energy saving.

References


