Local Structure and Magnetic Characteristics of FINEMET Alloys Substituted by Vanadium

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Amorphous and nanocrystalline FINEMET-type alloys with vanadium addition up to 7 at% were investigated by the Mössbauer spectroscopy and magnetic methods. The outcomes evidence alterations in grain structure, although the main effect is related to the changes in intergranular phase. This induces diminution of mean hyperfine field, saturation induction and Curie temperature as well as the increase in coercivity.

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1. The subject and methods of the study

Nanocrystalline FINEMET® alloys obtained by controlled annealing of the amorphous precursor and composed of fine grains enclosed in an amorphous matrix are known as excellent soft magnetic materials [1, 2]. In order to improve the magnetic properties, various modifications of chemical composition have been proposed for the last decade [3–6]. In this paper, the substitution of iron atoms by vanadium ones is considered. Previous X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies indicate changes of local structure due to vanadium addition as well as preservation of the nanocrystalline structure with grains sizes of about 15 nm [7]. In this paper, the systematic Mössbauer study is presented, complemented with results of magnetic investigations.

The series of Fe$_{73.5-x}$V$_x$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ ribbons ($x = 1, 3, 5, 7$) was manufactured by rapid quenching from the melt. Subsequent annealing for 1 h at
540°C under vacuum caused partial crystallization resulted in arising of the fine-grain structure. The Mössbauer spectroscopy investigations were performed in the temperature range 300–570 K with the use of ⁵⁷Co(Rh) source of γ radiation, placed at a vibrator working in a constant acceleration mode, as well as a proportional detector and a vacuum furnace. Magnetic properties were determined with the use of a fluxmeter (for saturation induction and coercivity) and small angle magnetization rotation method (for magnetostriiction).

2. Results and discussion

The Mössbauer spectra of the as-quenched ribbons take on a smooth shape which verifies the amorphous structure of these alloys. A positive correlation factor \( a = 150 \text{ T s/mm} \) between magnetic hyperfine field (HF), \( B \), and isomer shift \( \delta \) was employed in the numerical analysis of spectra, which is (approximately) consistent with the derived relationship between mean values of these parameters (Fig. 1a). The magnetic HF distributions show a bimodal character (Fig. 1b) with growing low-field component when increasing vanadium concentration (Fig. 1c).

In order to verify the real nature of the low-field component, the quadrupole splitting \( \Delta \) was evaluated on the basis of spectra collected at elevated temperature, above the Curie point. The value \( \Delta/2 = 0.25 \text{ mm/s} \), which is much less than magnetic splitting \( 4\div6.5 \text{ mm/s} \), makes us sure that both components correspond to different local environments of iron atoms in the amorphous structure. Mean
HF as well as positions of the maxima shift almost linearly with $x$ (Fig. 1d). This allows conclusion that the most crucial changes result from the diminution of iron. We have found that the Curie temperature $T_c$ is also strongly influenced by vanadium addition. For example, its value has been reduced from about 600 K for pure FINEMET to 370 K for the alloy comprising 7 at% of vanadium. Similar value of the Curie temperature $T_c = 378$ K was determined from magnetic measurements [7].

Concerning the nanocrystalline samples, the spectra comprise a component with continuous magnetic HF distribution — attributed to the amorphous remainder — and a discrete one, in form of a set of five Zeeman sextets, originating from crystalline grains (Fig. 2a–c). Besides, the existence of a paramagnetic component was stated, being characterized by a distribution of quadrupole splitting and, for this reason, attributed to iron-pure regions inside the amorphous matrix. The relative contribution of these areas grows with vanadium concentration and reaches 24$\%$ for $x = 7$. Only slight but distinct changes in magnetic HF of individual sextets were found (Fig. 3a), which testifies alteration of grain structure, in accordance with previous XRD results indicating formation of Fe(V)$_3$Si phase [7]. Significant decrease in mean magnetic HF is observed, in correlation with saturation induction (Fig. 3b).

![Fig. 2. Mössbauer spectra of Fe$_{73.5-x}$V$_x$Cu$_1$Nb$_3$Si$_{13.5}$B alloys annealed for 1 h at 540$^\circ$C.](image)

![Fig. 3. Evolution of magnetic hyperfine field derived for individual sextets representing the crystalline phase (a), and mean magnetic hyperfine field as well as saturation induction $B_s$ derived for Fe$_{73.5-x}$V$_x$Cu$_1$Nb$_3$Si$_{13.5}$B alloys annealed for 1 h at 540$^\circ$C (b).](image)
Similarly as in amorphous samples (Fig. 4a), the considerable lowering of Curie temperature $T_{am}^{c}$ of the amorphous remainder in nanocrystalline alloys was found on the basis of the Mössbauer investigations, which evidences changes in chemical composition of the intergranular phase. Non-vanishing magnetic HF of some part of amorphous matrix (presumably close to grains surface) is observed even above $T_{am}^{c}$ (Fig. 4b). Saturation magnetostriction of as-quenched samples is a decreasing function of vanadium concentration and is reduced by 90% compared to pure FINEMET. A slight decrease in coercivity, compared with pure FINEMET, was also stated. For nanocrystalline alloys, the rapid increase in coercivity (by 40%) is found.

3. Conclusions

Both Mössbauer and magnetic outcomes show the weakening of magnetic properties of FINEMET owing to vanadium addition. The evolution of hyperfine parameters of individual phases evidences that the main reason of the magnetic properties decay are strong changes in the structure of intergranular phase, which make exchange interactions between crystallites less efficient.

References