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STRUCTURE AND MAGNETIC PROPERTIES OF $Fe_{73.5-x}V_xCu_1Nb_3Si_{13.5}B_9$ ALLOYS

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Abstract. The aim of this work was to study the influence of iron substitution by vanadium in amorphous and nanocrystalline $Fe_{73.5-x}V_xCu_1Nb_3Si_{13.5}B_9$ (x=1, 3, 5, 7) alloys on their structure and magnetic properties. We present our structural study of amorphous alloys prepared by melt spinning method. The structure of the samples was characterized by X-ray powder diffraction (XRD) and TEM. The structure stabilities and the structure evolution at a high temperature were addressed by the in-situ XRD experiment in DESY Hamburg. Experimental results reveal the influence of vanadium content on both magnetic and structural properties. Nanocrystalline state of the samples was confirmed by the presence of ultra-fine $Fe(V)_3Si$ phase with Fm3m space group. It was observed that the higher vanadium content, the higher crystallization temperature of $Fe(V)_3Si$ phase has been observed. Vanadium also influenced the crystallization temperature of the V_3B_2 and Fe_2B phase. Magnetic properties reflect the observed structural changes.

1. INTRODUCTION

It is generally known that nanocrystalline alloys called “Finemet” exhibits excellent soft magnetic properties. Its structure after nanocrystallization process contains Fe-Si nanocrystals randomly dispersed in an amorphous matrix. The substitution of iron by some other metals modifies the magnetic properties [1-3]. The aim of this work was to study the influence of iron substitution by vanadium in amorphous and nanocrystalline ($Fe_{73.5-x}V_xCu_1Nb_3Si_{13.5}B_9$ (x=1, 3, 5, 7) alloys on their structure, magnetostriction and magnetic properties.

2. EXPERIMENTAL PROCEDURE

In-situ high temperature X-ray powder diffraction measurements were performed in HASYLAB at DESY (Hamburg, Germany) at Petra2 experimental station located at Petra electron storage ring operating at the electron energy 11.28 GeV. The XRD patterns of Fe-based alloys were collected in a temperature range from 30 to 925 °C. The gradually annealed sample was illuminated for 30 seconds for each pattern by X-rays of wavelength λ=0.115 Å. Two-dimensional XRD patterns were recorded by a 2D (mar345) image plate detector. Precise radiation energy was determined by fitting a standard reference LaB_6 sample. The images taken from different stages of annealing were integrated into 2 Theta space by using Fit2D program. More details about the experiment can be found in [4-6]. Nanocrystalline character of the samples was confirmed by a TEM operating at 200 kV. The saturation magnetization and coercivity were determined from the hysteresis loops traced with fluxmeter in quasi DC magnetic field. Saturation magnetostriction was measured by the so-called small-angle magnetization rotation method [7].

3. RESULTS AND DISCUSSION

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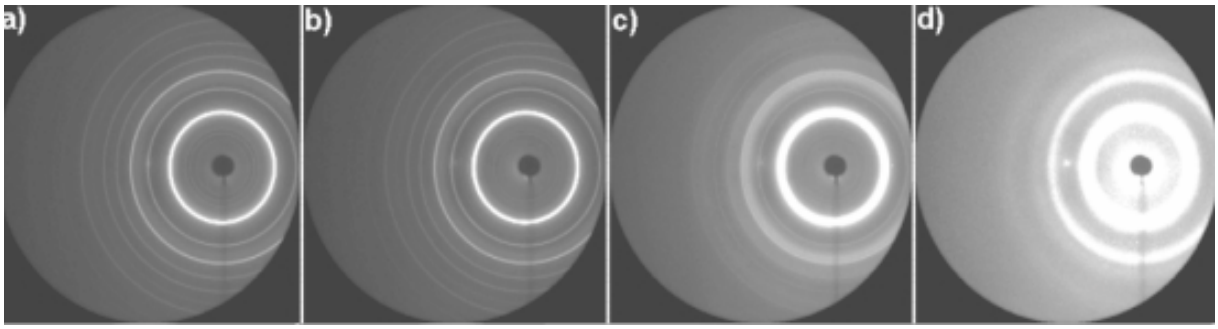

Fig. 1. D-S diffraction rings of the samples annealed at 524 °C, (a) *x*=1, (b) *x*=3, (c) *x*=5, (d) *x*=7.

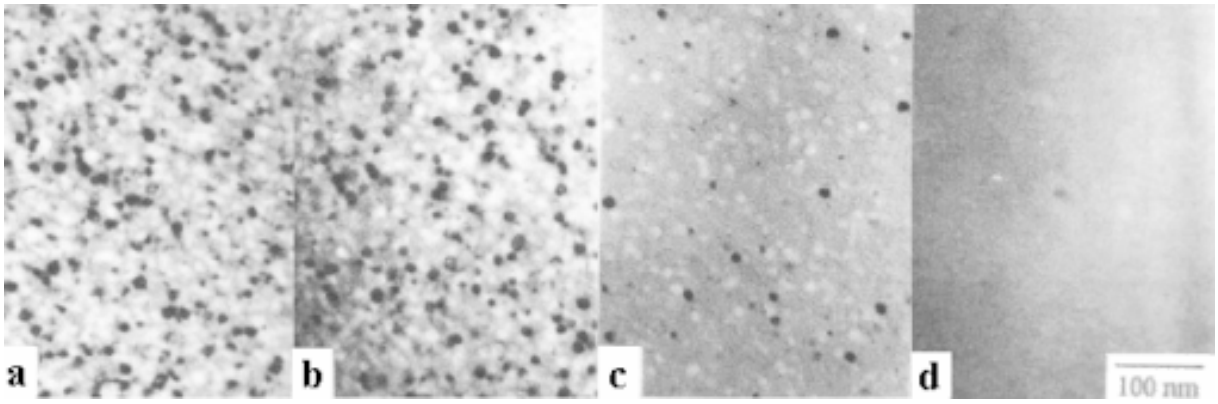

Fig. 2. TEM microphotographs of the samples annealed at 524 °C, (a) *x*=1, (b) *x*=3, (c) *x*=5, (d) *x*=7.

XRD observations on the samples with different V content at the same temperature of 524 °C indicate remarkable influence of V on the formation of nanostructure. Crystallization temperature of nanocrystalline phase increases with the V content. On the other hand, the volume fraction of nanocrystals decreases with increasing V content as it is at first sight visible from the sequence of Debye-Scherrer rings in Fig. 1. The diffuse haloes indicating the amorphous rest were apparently broadening with increasing V content. Also TEM images of the samples annealed at 524 °C confirm these results as it can be seen in Fig. 2. TEM images of the samples with $x \leq 3$ are typical for nanocrystalline alloys and as for sample with *x*=5 a very low amount of nanocrystals is revealed, while sample with *x*=7 is still amorphous.

In-situ X-ray powder diffraction is one of the most useful techniques giving a direct evidence of the structure evolution at elevated temperatures. Fig. 3 shows 3D plot of XRD patterns of (originally amorphous) $Fe_{66.5}V_7Cu_1Nb_3Si_{13.5}B_9$ alloy taken at different stages of annealing. The sample in as-quenched state shows diffuse pattern with long range modulation, what is typical for metallic glasses. A progressive decrease of diffracted signal, observable at high temperatures (up to 572 °C) is due to the continuous increase of Debye-Waller factor related to atomic motion about the equilibrium positions. At 572 °C the XRD profile changes, a small Bragg's peak appears at the top of amorphous background, demonstrating that the alloy starts to crystallize. By further annealing the peak becomes more pronounced which is a direct consequence of the progressive alloy crystallization. At about 750 °C the shape of the XRD pattern changes again, with new peaks appearing as a result of secondary crystallization. The individual XRD patterns from the $Fe_{66.5}V_7Cu_1Nb_3Si_{13.5}B_9$ alloy has been also made to show phase development. At 573 °C the fcc- $Fe(V)_3Si$ starts to crystallize. Its volume fraction increases upon a whole scanned temperature interval. At 725 °C two new phases crystallize: a tetragonal V_3B_2 one (S.G: P4/mbm, ICSD #88321) and a Nb-rich one. Phase analysis was performed on the XRD patterns from samples pre-annealed at 925 °C and cooled down to room temperature. The dominant reflections belongs to fcc $Fe(V)_3Si$ phase which is similar to Fe_3Si (S.G: Fm3m, PDF # 45 1207) but its lattice parameter is

Table 1. Magnetic properties of the samples.

V content [at.%]	B_S [T] a. q.	B_S [T] T_A=550 °C	λ_S [ppm] a. q.	T_C [°C]	H_C [A/m] a. q.	H_C [A/m] T_A=550 °C	H_C [A/m] T_A=650 °C
1	1,16	1,12	22	295	30	27	1201
3	0,93	1	17	225	22	28	167
5	0,55	0,62	11	146	25	30	52
7	0,3	0,28	2	105	27	38	57

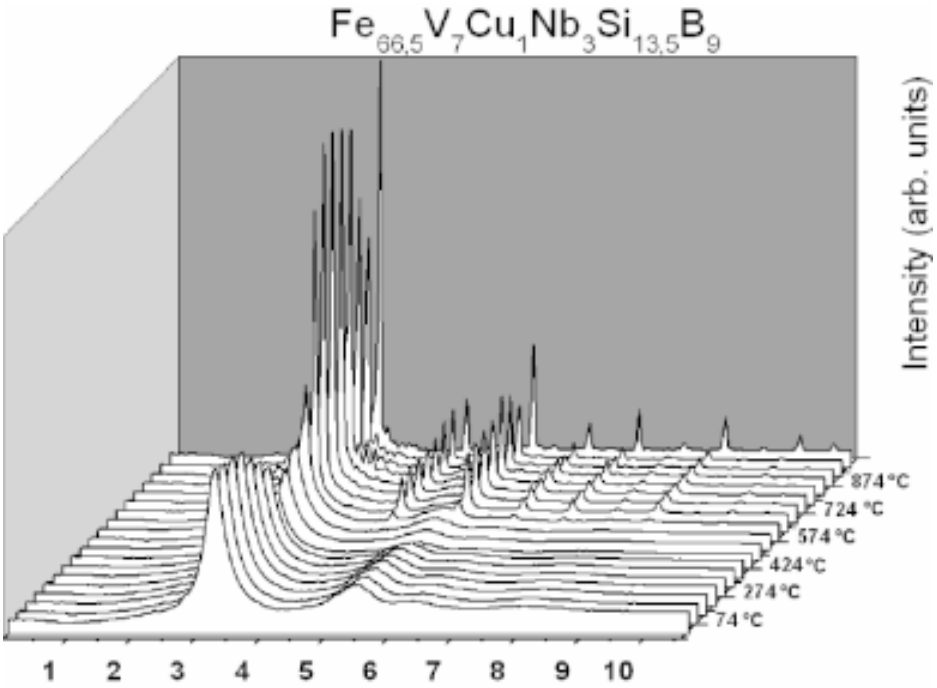

Fig. 3. 3D plot of XRD patterns of amorphous $Fe_{66.5}V_7Cu_1Nb_3Si_{13.5}B_9$ alloy taken at different stages of annealing.

larger (some amount of larger V atoms substitutes smaller Fe atoms in the Fe_3Si cell). The minor phase was indexed as V_3B_2 for high V content sample and Fe_2B tetragonal (S.G: I4/mcm, PDF # 361332) phase for samples with low content of V ($x \leq 3$).

Microstructural characteristics rule the magnetic behaviour in general, the more in the case of nanocrystalline materials. The values of magnetic anisotropy, effective magnetostriction, coercivity, Curie temperature of amorphous matric and saturation magnetization are strongly dependent on the grain size of crystallites, their volume fraction and the character of intergranular region [8-11]. V in $Fe_{73.5-x}V_xCu_1Nb_3Si_{13.5}B_9$ alloys could be included in FeSi nanocrystals, and this is reason why the coercivity for as-quenched alloys and for nanocrystalline alloys after annealing is higher that that for pure FINEMET. V also remains in the amorphous matrix or in the intergranular space and lowers its Curie temperature (Table 1). The results of magnetic measurements indicate that for higher V content ($x \geq 5$) the ferromagnetic exchange interactions between the grains becomes less efficient and, as a consequence, the coercivity increases and magnetization decreases (Table 1). Rapid in-

crease of the coercivity for samples annealed over 650 °C is caused by the crystallization of borides [9].

4. CONCLUSIONS

Taking into account all results of our experimental study on the V addition to FINEMET type alloys in the concentration range $1 \leq x \leq 7$, we can conclude:

1. Nanocrystalline state of the samples is represented by $Fe(V)_3Si$ nanocrystals with cubic lattice and space group Fm3m. Mean grain size of the crystals is about 15 nm. Vanadium increases the crystallization temperature of the $Fe(V)_3Si$ phase. The crystallized volume fraction of the $Fe(V)_3Si$ phase for all the samples annealed at the same temperature decreases with increasing V content.
2. Higher content of V prevents formation of borides.
3. Vanadium enters into the FeSi lattice forming $Fe(V)_3Si$ phase and also remains in the intergranular space and lowers its Curie temperature. For higher V content ($x \geq 5$) the ferromagnetic exchange interactions between the grains are less efficient and the coercivity increases and magnetization decreases.

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