Influence of annealing on the crystallographic structure and some magnetic properties of the $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ nanocrystalline alloys

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The influence of annealing on the structure and some magnetic properties of $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ ($x = 1, 2, 3$) alloys has been studied. The results confirmed the nanocrystalline character of these alloys in the temperature range 550–650 °C. The influence of the uranium content on the structural stability has been observed for annealing treatment at high temperature, i.e. at about 700 °C. The coercive field strongly depended both on the annealing temperature and on the uranium content. A minimum value of H_c was observed after annealing at 550 °C. Core losses of all alloys in the nanocrystalline state decreased with increasing uranium content.

1. Introduction

Recently, Yoshizawa *et al.* [1] developed a new soft magnetic material called "FINEMET" characterized by an ultrafine grain structure prepared by the crystallization of Fe–Cu–Nb–Si–B alloys. The soft magnetic properties of FINEMET alloys are attributed to the ultrafine structure of the Fe_3Si phase with DO_3 structure and with 10–20 nm grain size, appearing after annealing at about 550 °C and randomly dispersed in the amorphous matrix [2, 3]. The existence and thermal stability of this structure are explained by the presence of copper and niobium. The non-solubility of copper in iron greatly increases the nucleation rate of iron-rich crystallites and small atomic percentages of niobium hinder very effectively the growth of the original nuclei [4]. The soft magnetic properties disappear on annealing at 650 °C due to precipitation of borides and the appearance of inhomogeneous grains in the ultrafine bcc grain structure. A higher annealing temperature (700 °C) leads to the formation of a polycrystalline structure in the Fe–Cu–Nb–Si–B alloys [5–7].

There are a number of scientific papers dealing with improvement of soft magnetic properties of Fe–Cu–Nb–Si–B alloys by substituting niobium by other elements M (M = Mo, Ta, W, Cr, ...) [5, 6, 8]. In other papers, the influence of silicon and boron content on the magnetic and structural properties of nanocrystalline materials has been investigated [9].

The aim of this work was to study the influence of annealing treatment on the structure and some magnetic properties of the $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ nanocrystalline alloys. Considering the atomic diameter of uranium, we expected it to have a more significant influence on the retarding of grain growth during crystallization than has niobium.

2. Experimental procedure

$Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ amorphous ribbons were prepared by the melt-spinning technique. The alloys were melted by induction melting in a silica crucible in an inert argon atmosphere and, at a pressure of 0.05 MPa, were extruded through a 6 mm wide slit placed at the bottom of the crucible, on to a rapidly rotating copper disc with diameter of 160 mm. The circumferential speed of the disc was about 25 m s^{-1}. Heat treatments were performed at temperatures of 350, 450, 550, 600, 650, 700 °C for 1 h in a vacuum furnace. The structure of the samples was checked using a transmission electron microscope (TEM) operating at 200 kV, a cylindrical camera X-ray diffractometer, differential scanning calorimetry (DSC) analysis, and Mössbauer spectroscopy. To obtain the grain-size distribution from transmission electron micrographs, the scientific image analyser DIPS 4.0 was used. For each sample, more than 500 grains were analysed. The d.c. coercive field was determined from the hysteresis loop traced with fluxmeter (in quasi d.c. magnetic field) and core losses were determined from the hysteresis loop traced in an a.c. (50 Hz) magnetic field with the digital storage oscilloscope.

3. Results

3.1. Structure observations

Mössbauer spectroscopy, X-ray diffraction and TEM confirmed the amorphicity of the prepared ribbons. No influence of annealing at temperatures up to 450 °C on the crystallographic structure of the samples was observed. The annealing at 550 °C significantly changed the crystallographic structure of the samples. Transmission electron micrographs show their nanocrystalline character and no influence of the uranium content on the grain size of the Fe_3Si phase was observed (Fig. 1a). Neither annealing at 600 °C nor at 650 °C change the nanocrystalline character of all samples significantly. We did not observe the influence of these temperatures on the remarkable grain growth of the Fe_3Si phase. However, the precipitation of borides was predicted [6, 10] and the diffraction patterns showed the decrease in the amorphous remainder of all the samples (Fig. 1b). Figs 2 and 3 show the log-normal grain-size distribution of $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys annealed at the temperatures of 550 and 650 °C, respectively. The mean grain ze, d, values and the standard deviation are presented in Table I.

Transmission electron micrographs obtained from the samples annealed at 700 °C show that the grain size of the Fe_3Si phase increased up to 60 nm, but it did not increase so significantly as was observed in classic FINEMET and in the $x = 1$ sample annealed at this temperature (Fig. 4a and b).

X-ray observations complete the results obtained by TEM. For all the samples annealed at 550 °C, reflections from the Fe_3Si phase were observed. Annealing at 650 °C caused precipitation of borides and, in the $x = 3$ samples, the Fe–Si–B phase was also precipitated (Fig. 5). X-ray diffraction for $x = 2$ indicated the existence of the Fe–Si–B phase, but it did not confirm it unambiguously. Such a small volume fraction of the Fe–Si–B phase could not be detected by the electron diffraction method.

Mössbauer spectra of nanocrystalline samples annealed at 700 °C are presented in Fig. 6. These spectra

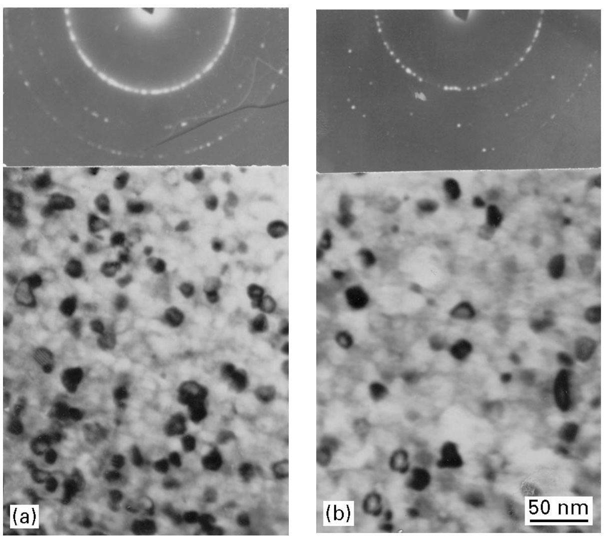

Figure 1 Nanocrystalline structure of $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys annealed at: (a) 550 °C; (b) 650 °C.

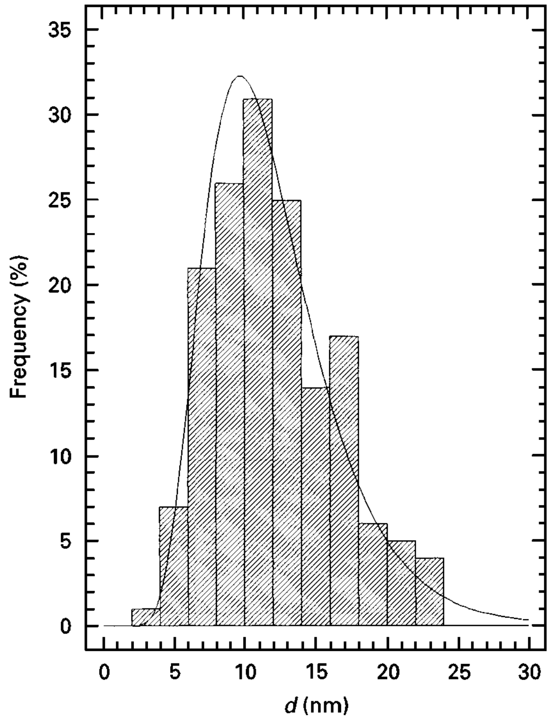

Figure 2 Log-normal grain-size distribution of $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys annealed at 550 °C.

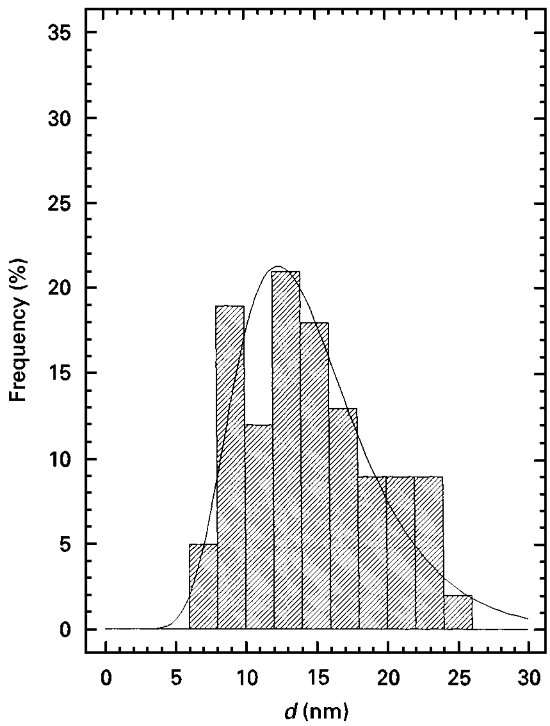

Figure 3 Log normal grain-size distribution of $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys annealed at 650 °C.

TABLE I Mean grain size, d, and standard deviation, S.D., of the $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys at annealing temperature, T_a

T_a (°C)	d (nm)	S.D. (nm)
550	12.0	4.6
650	14.7	5.0

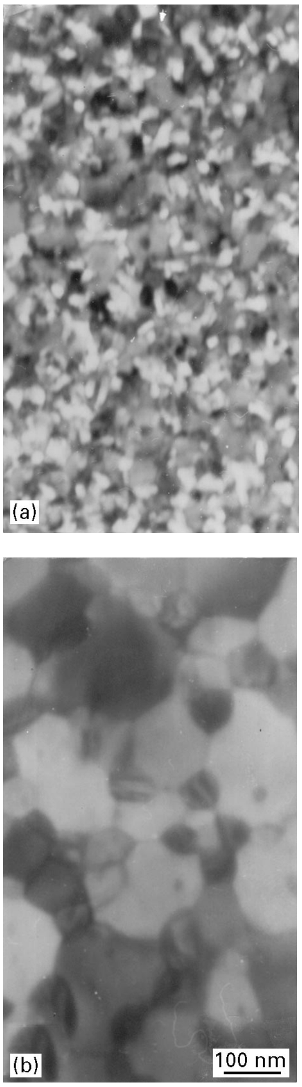

Figure 4 The structure of $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys annealed at 700 °C: (a) $x = 2$ and 3; (b) $x = 0$ and 1.

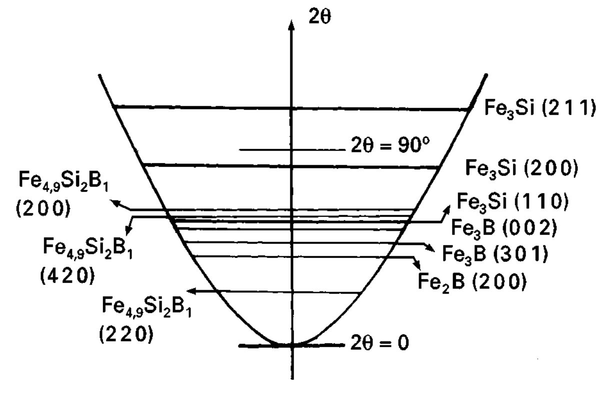

Figure 5 X-ray spectra of $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloy annealed at 650 °C (the parabola signifies the border of the reflection area of the camera's film).

show the formation of the Fe_3Si–DO_3 structure (at a temperature of about 550 °C) and borides (annealing temperature up to 650 °C). The content of the amorphous remainder decreases with uranium content (from 11.0% for $x = 1$ to 7.1% for $x = 3$). In the $x = 3$ sample we also observed a ferromagnetic phase with

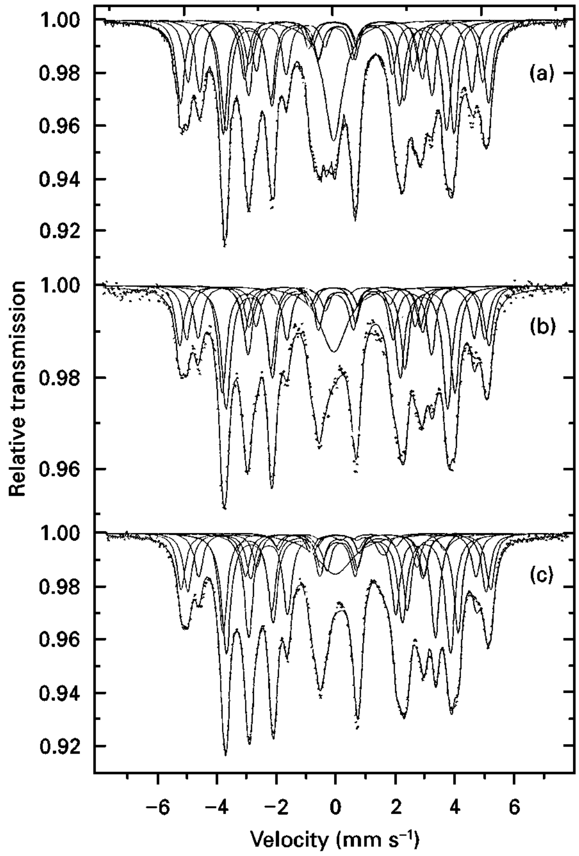

Figure 6 Mössbauer spectra of $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys annealed at 700 °C: (a) $x = 1$; (b) $x = 2$; (c) $x = 3$.

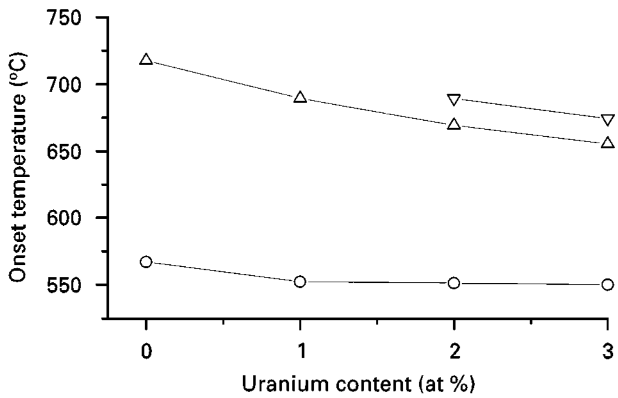

Figure 7 Dependence of the phase transition temperature on the uranium content obtained from DSC analysis (heating rate 20 K min^{-1} peak). (○) First peak, (△) second peak, (∇) third peak.

high quadrupole splitting, which could be assigned to the Fe–Si–B phase with DO_{11} structure [12]. While the precipitation of this phase is observable at 650 °C (indicated by XRD), growth of this phase is remarkable at a higher annealing temperature (700 °C).

DSC analysis showed that the uranium content has no remarkable influence on T_{cryst} of the Fe_3Si phase (first peak in Fig. 7), but decreases the crystallization temperature of the borides (second peak). We suppose that the third peak, observable only for $x = 2$ and 3 samples, is caused by the precipitation of the Fe–Si–B phase.

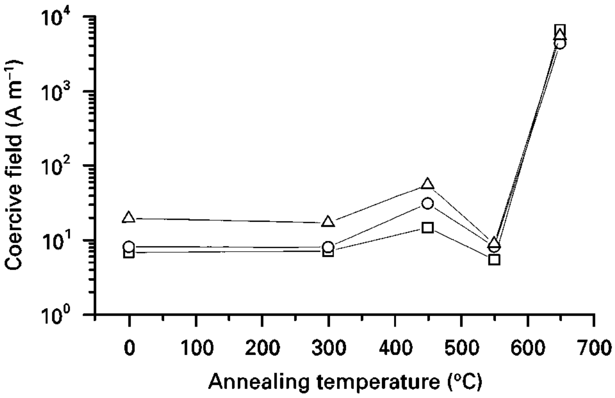

Figure 8 Dependence of the coercive field on the annealing temperature for various uranium contents in $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys: x = (□) 1, (○) 2, (△) 3.

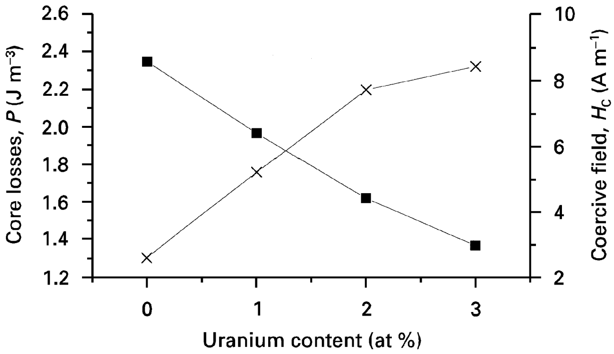

Figure 9 Dependence of (■) the core losses, P, and (X) the coercive field, H_c, in $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys annealed at 550 °C, on the uranium content.

3.2. Magnetic properties

Fig. 8 shows the dependence of the coercive field on the annealing temperature in the $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys. The decrease of the coercive field after annealing at 300 °C is caused by the relaxation of internal stresses introduced into the amorphous material during its preparation. After annealing at 450 °C, the coercive field in all the samples increased and then dropped to its minimum value at 550 °C. We suppose that, after annealing at 450 °C, clusters are formed which play the role of domain-wall pinning centres [13]. The presence of clusters was not confirmed by TEM, despite the fact that their size should be comparable with the domain wall thickness. The existence of a similar peak has been observed [14]. The results of core loss measurements and bulk coercive field as a function of uranium content after annealing at 550 °C, in comparison with that for FINEMET without uranium, are shown in Fig. 9. It is interesting that, while the coercive field increases for samples with higher uranium content, core losses decrease with increasing uranium content and, in all cases, are lower than that for classic FINEMET.

4. Conclusion

Structural observations showed that annealing at 550 °C led to the formation of nanocrystalline structure in the $Fe_{73.5}Cu_1Nb_{3-x}U_xSi_{13.5}B_9$ alloys. This structure is stable up to 650 °C, when the precipitation of the borides and Fe–Si–B phase, mainly for $x = 3$, was observed. The influence of the uranium content on the structural stability has been observed for annealing treatment at high temperature, i.e. at about 700 °C. The uranium content has no influence on T_{cryst} of the Fe_3Si phase but it decreases the crystallization temperature of the borides and Fe–Si–B phase. The coercive field strongly depends both on the annealing temperature and on the uranium content. The minimum value of H_c has been observed after annealing at 550 °C. Core losses of all alloys in the nanocrystalline state decrease with increasing uranium content.

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