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INFLUENCE OF Cu+Nb CONTENT ON THE CRYSTALLIZATION OF $Fe_{77.5-x}(Cu_{0.25}Nb_{0.75})_xSi_{13.5}B_9$ ALLOYS[1]

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Changes of phase composition and hyperfine splitting B_{hf} due to controlled crystallization by annealing in the range 475°C – 550°C were studied by means of Mössbauer spectroscopy. On the set of five alloys of x=0,1,2,3,4 the influence of Cu+Nb content was investigated. It was found that the atomic fraction of the intergranular phase changes with the Cu+Nb concentration and annealing temperature t_{an} in a complicated way. B_{hf} of the intergranular phase is controlled by iron contents, it decreases with substitution of Cu+Nb for Fe. For the crystalline phase B_{hf} does not change with the substitution and increases slightly with t_{an}.

Magnetic properties of the nanocrystalline materials Fe-Si-B-Cu-Nb prepared by controlled crystallization from the amorphous alloys depend on chemical composition, it influences, e.g., the temperature range of nanocrystalline state, size and orientation of nanocrystals [1, 2, 3]. Cu and Nb play an important role in formation of nucleation centres of the nanocrystals. Their number could be in connection with the grain size and amount of crystalline phase.

Results of x-ray and magnetic measurements of the $Fe_{77.5-x}(Cu_{0.25}Nb_{0.75})_xSi_{13.5}B_9$, x=0,1,2,3,4 alloys published by Müller et al. [3] have shown that annealing at temperatures between 475 °C and 550 °C caused formation of nanocrystals of $Fe_{(3+w)}Si_{(1-w)}$ phase. They found that the grain size and phase composition depend on the Cu+Nb content thus influence magnetic properties. The best soft magnetic properties were

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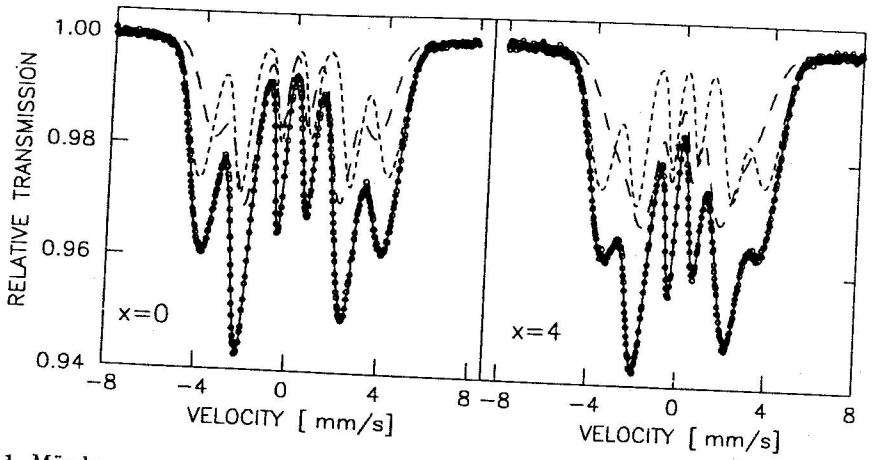

Fig. 1. Mössbauer spectra of the original amorphous ribbons for x=0 and x=4.

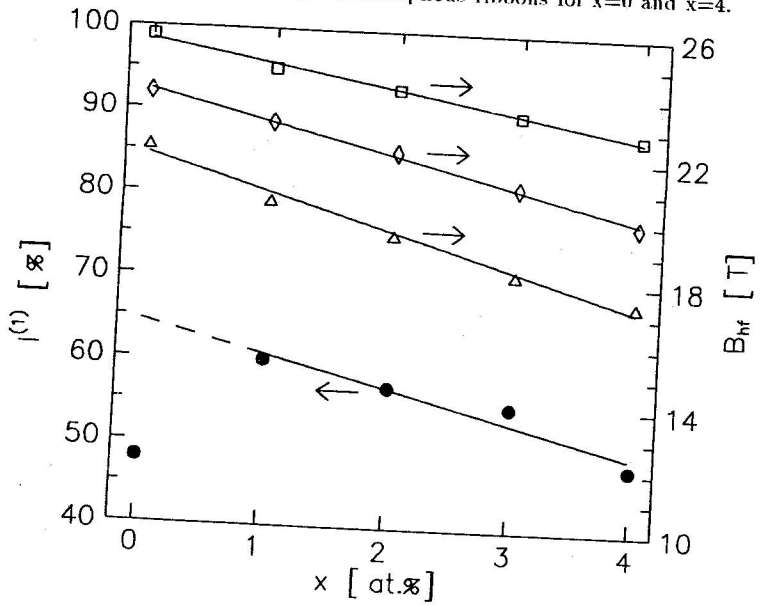

Fig. 2. Magnetic splittings B_{hf} of the first (□) and second (△) components, average B_{hf} (◇), and relative intensity $I^{(1)}$ of the first component of the amorphous phase (•) as function of content x of the Cu+Nb in amorphous ribbons.

obtained for x = 3, i.e. 0.75 at.% Cu and 2.25 at.% Nb, and an annealing at 550 °C for 1 hour in H_2. In this paper we have used Mössbauer phase analysis for investigation of changes in phase composition after crystallization at several temperatures close to the

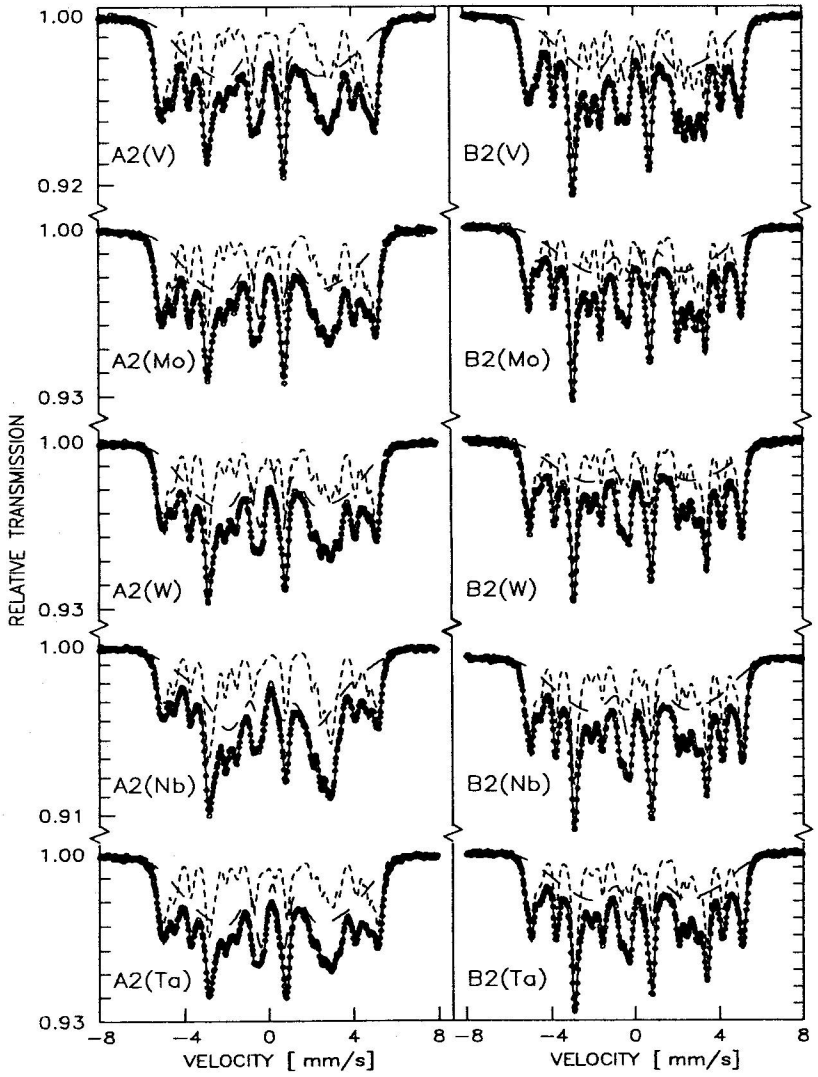

Fig. 3. Mössbauer spectra of the samples after annealing at 495°C and 515°C for 1 hour in $Ar+H_2$ atmosphere.

range of existence of nanocrystalline state due to the differences in Cu+Nb content.

The nanocrystalline samples of $Fe_{77.5-x}(Cu_{0.25}Nb_{0.75})_xSi_{13.5}B_9$, x=0,1,2,3,4 were

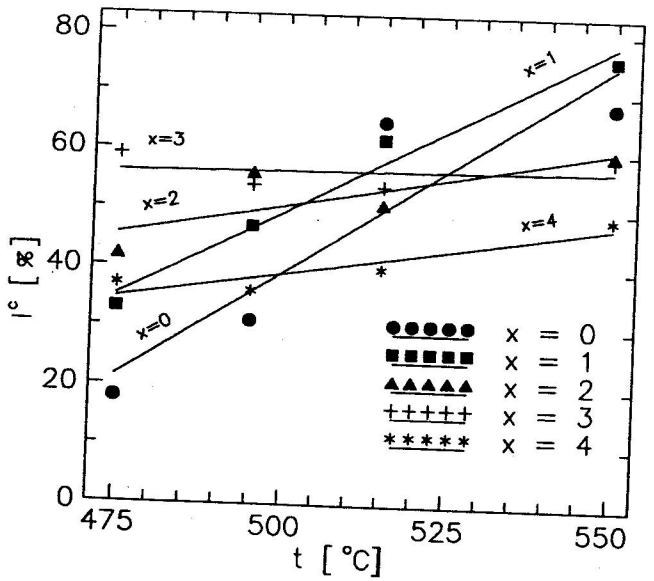

Fig. 4. Relative intensities of the crystalline phase I^c in dependence on the annealing temperatures for different contents x of the Cu+Nb (in at.%).

prepared from amorphous ribbons of the same origin as in [3] by annealing at t_{an} = 475, 495, 515, and 550°C for 1 hour in Ar+H_2 atmosphere. ^{57}Fe Mössbauer spectra of the original amorphous and nanocrystalline states were taken at room temperature in transmission geometry.

The spectra were deconvoluted in standard way supposing presence of crystalline and amorphous phases. This yielded intensities I of the components (taken as atomic fractions of phases) and their hyperfine parameters: magnetic splitting B_{hf} and isomer shift δ (given relative to α iron). Intensity ratio of the individual lines in sextets r, defined as ratio of the intensity of the second line to the first one, yields some information about the spin orientation. More details were given in [4, 5, 6]. The silicon content in Fe–Si nanocrystals was estimated in the same way as in [7].

Spectra of the original amorphous ribbons (Fig. 1) were fitted using two components represented by two sextets with Gaussian hyperfine field distributions. Relative intensity $I^{(1)}$ of the first component and B_{hf} of both components and mean B_{hf} of the samples are shown in Fig. 2. $I^{(1)}$ decreases with increasing x except the case with x = 0. It indicates that the presence of Cu+Nb influences also the amorphous state. The decrease in B_{hf} was expected because of dissolution of iron by Cu+Nb substitution. New information obtained from the spectra is that this substitution modifies also the distribution of iron atoms between the two components. With increasing x the content of the component with higher B_{hf} is decreased.

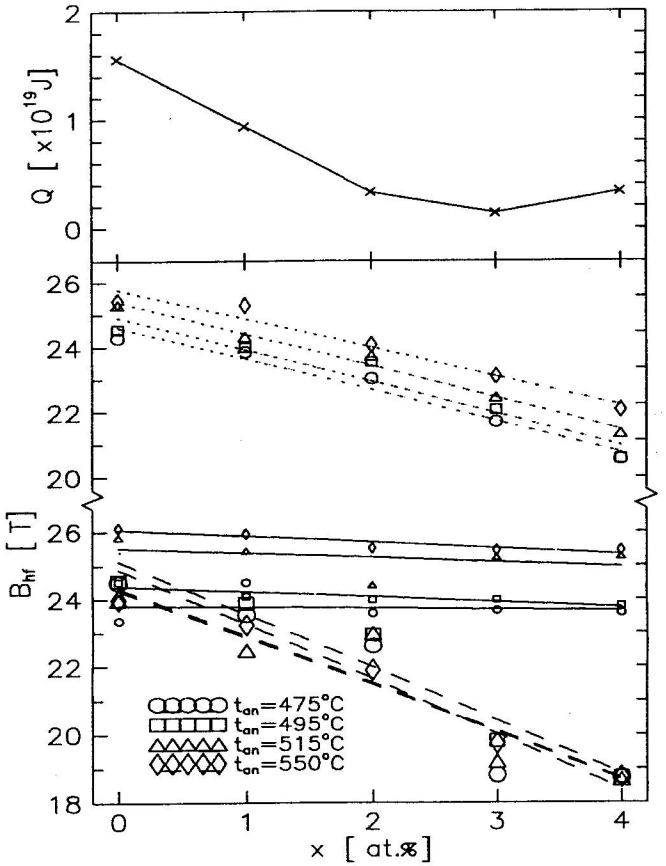

Fig. 5. Activation energy Q (above), the mean B_{hf} of samples (dotted), B_{hf} of the intergranular (dashed), and crystalline (solid) phases after different annealing temperatures in dependence on the Cu+Nb content.

Annealing at temperatures 475 ÷ 550 °C produces nanocrystalline state. Some examples of the spectra of the annealed samples are shown in Fig. 3. The content of the crystalline phase I^c increases with increasing t_{an} but with different slopes (see Fig. 4). Activation energy Q of formation of the crystalline phase derived from the ln(I^c) vs. 1/T dependence exhibits minimum for x=3 (see Fig. 5). Magnetic splittings of the intergranular B_{hf}^{ig} and crystalline B_{hf}^{c} phases are shown in Fig. 5. B_{hf}^{c} almost does not depend on chemical composition of the ribbons and increases with increasing t_{an}. Estimation of the content of Si in the crystalline Fe–Si phase using of $D0_3$ superstructure model [7] gives 20 ± 1 at.% Si for all samples. B_{hf}^{ig} exhibit important decrease with increasing x and negligible changes due to t_{an}. The mean B_{hf} increase with decreasing

x and with increasing t_{an}.

The results of the Mössbauer phase analysis show that the content of Cu+Nb as well as t_{an} influence the formation of the nanocrystalline state by annealing. The substitution of Cu+Nb for Fe influences B_{hf}^{ig} importantly but B_{hf}^{c} seems independent on these changes in chemical composition. It is in agreement with almost constant chemical composition of the Fe–Si nanocrystals as follows from our estimation and from x-ray results [3]. On the other hand it confirms the results obtained by Hono et al. [8] using atom probe field ion microscopy and high resolution transmission electron microscopy that the Cu and Nb atoms remain outside the Fe-Si phase.

Influence on the content of the individual phases is ambiguous. The increase of the mean B_{hf} with increasing t_{an} is in accordance with dependence of B_{hf}^{c} and relative intensity I^{c} of the crystalline phase on t_{an}. Müller et al. [3] have found the best magnetic properties for the sample with $x = 3$ and $t_{an} = 550°C$, for which Mössbauer phase analysis results exhibit 41% of the intergranular phase with $B_{hf}^{ig} = 19.73$ T and 59% of the crystalline phase composed of Fe–20 at.% Si with $B_{hf}^{c} = 25.45$ T. This sample is characterized by the lowest value of $\mathbf{r} = 0.32$, which is consistent with the preferred orientation of magnetization close to the normal direction to the sample plane. This is an indication of extremely low average magnetocrystalline anisotropy displayed by nanocrystalline materials with good soft magnetic properties [9, 10].

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