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MICROSTRUCTURE AND MAGNETIC PROPERTIES OF Fe-Zr-U-Cu-B ALLOYS*

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Influence of U and Cu on the crystallization process and magnetic properties of the amorphous $Fe_{86}Zr_6U_1Cu_xB_{6-x}$ (x =0; 1) after heat treatment were investigated. Structural measurement techniques showed the different course of crystallization process for both alloy systems. The positive influence of Cu on the crystallization of homogeneous nanocrystalline structure was observed as well as on magnetic properties.

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1 Introduction and Experimental

Besides the well known system of the Fe-rich Fe-Cu-Nb-Si-B alloys also the family of Fe-M-B-X (M=Zr, Hf, Nb,... and X = Cu) nanocrystalline alloys demostrate excellent soft magnetic properties [1-7]. The aim of this work was to study the influence of U and Cu on the crystallization process and magnetic properties in the amorphous $Fe_{86}Zr_6U_1Cu_xB_{6-x}$ (x =0; 1) after heat treatment.

Amorphous $Fe_{86}Zr_6U_1Cu_xB_{6-x}$ (x=0; 1) ribbons were prepared by melt spinning technique. To obtain onset crystallization temperature of the phase transition temperatures the differential thermal analysis (DTA) has been performed with heating rate of 10K/min. The heat treatment of the samples for further structural investigations were performed at 450, 530, 580, 650°C for 1 hour in hydrogen atmosphere. Structural observations were carried out by transmission electron microscopy (TEM) and Mössbauer spectroscopy at room temperature. The coercivity was determined from the differential hysteresis loops.

2 Results and Discussion

DTA results show a different way of crystallization process for samples with $x = 0$ and $x = 1$. The values of DTA characteristic temperatures are shown in Tab.1. It can be seen that Cu decreases temperature T_{x1} and increases T_{x2}. Temperature range between T_v and T_{x2} signifies stability of the existing nanostructure and the wider temperature range, the better stability of nanocrystalline state.

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Alloy	T_{x1}[°C]	T_p[°C]	T_v[°C]	T_{x2}[°C]
$Fe_{86}Zr_6U_1B_6$	537	579	605	608
$Fe_{86}Zr_6U_1Cu_1B_5$	499	520	547	625

Table 1: DTA charakteristic temperatures: T_{x1} - onset temperature of crystallization of bcc-Fe, T_p - temperature at which the value of heat flow during phase transition reaches maximum, T_v - temperature assigned to the end of phase transition, T_{x2} - onset temperature of borides formation or grain coarsening.

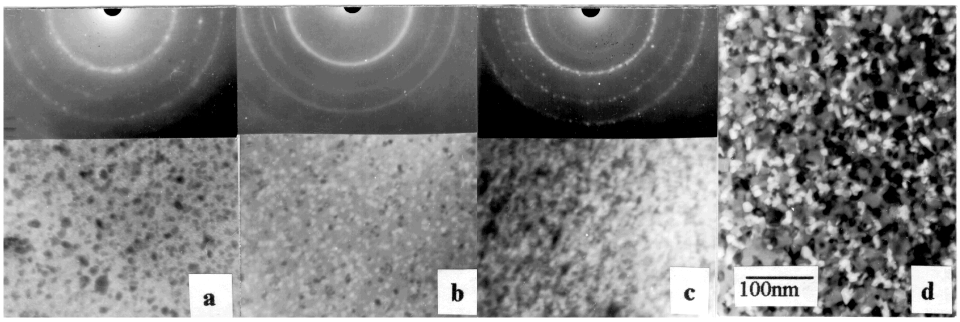

Fig.1. TEM micrographs and diffraction patterns

TEM investigations confirmed the amorphicity of the prepared samples and no influence of the annealing at the temperature up to 450°C on the crystallographic structure was observed only for $x = 0$ sample. The annealing at 530°C changed crystallographic structure of both samples significantly. Fig.1a shows structure of the sample without Cu consisting of bcc-Fe phase embedded in amorphous matrix. However, it is seen that the created bcc-Fe phase is not homogeneous and in micrograph small regular grains (15 nm), highly dendritic crystals (up to 50 nm) as well as a kind of aglomerations of the crystals embedded in the residual amorphous matrix were observed. The similar results were obtained by Greneche et al. [8]. On the other hand, homogeneous nanocrystalline structure consisting of bcc-Fe crystals with mean grain size of about 10 nm was observed for the $x = 1$ sample (Fig.1b). Temperature 580°C caused crystallization of all residual amorphous matrix of the FeZrUB sample and the structure seems to be more homogeneous. Moreover, the first diffraction points from precipitated Fe_3B phase have been observed (Fig.1c). This temperature did not change the structure of FeZrCuUB sample, only diffraction pattern of the sample signifies the increase of crystalline fraction [3]. After annealing at 650°C the formation of borides (Fe_3B and $Fe_{23}B_6$) was observed. Intensive grain coarsening of FeZrUB sample leads to transition to polycrystalline structure (Fig.1d). The sample FeZrCuUB remains nanocrystalline, but with the lower volume fraction of the above mentioned borides than in the sample without Cu.

Mössbauer spectroscopy supports previous TEM investigations (Fig.2). It can be seen that initial stage of crystallization for the $x = 1$ sample was already observed at 450°C. Moreover, the sooner formation of borides has been proved for $x = 0$ sample (530°C). Volume fraction of crystalline bcc-Fe phase of the samples derived from Mössbauer phase analysis is given in Tab.2.

The values of H_C, determined from the differential hysteresis loops obtained after heat treat-

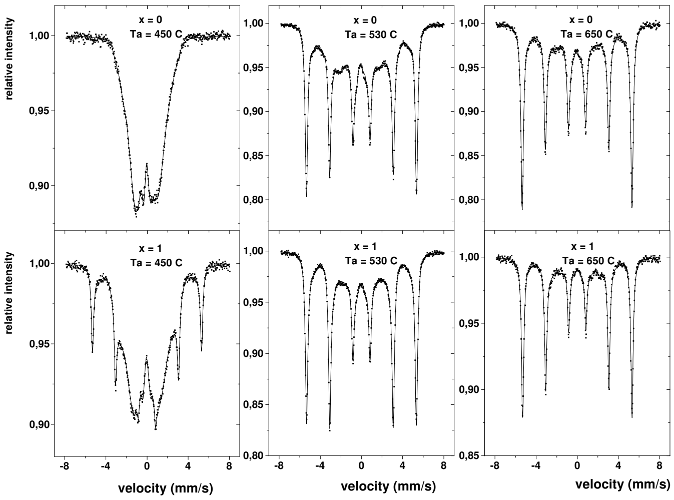

Fig.2. Room temperature transmission Mössbauer spectra of $Fe_{86}Zr_6U_1Cu_xB_{6-x}$ (x=0;1) samples annealed at 450°C, 530°C and 650°C for 1 hour.

alloys	as-quenched		T_a=450°C		T_a=530°C		T_a=580°C		T_a=650°C	
	H_C	V	H_C	V	H_C	V	H_C	V	H_C	V
$x = 0$	5.1	0	6.8	0	55.4	49.7	69.3	56.6	113.0	64.6
$x = 1$	3.2	0	5.5	17.7	4.4	58.8	5.7	65.2	118.0	77.6

Tab.2. Coercivity - H_C (in A/m) and volume fraction (V in %) of crystalline bcc-Fe phase of as-quenched samples and samples annealed at temperatures T_a for 1 hour.

ment, of both the samples are given in Tab.2. These results confirm the structural investigations. We suppose that higher value of H_C for FeZrUB sample in as-quenched state might be caused by non-homogeneous chemical short-range order caused by influence of U. Similar problems with non-homogeneous chemical content of the prepared alloys after U addition we have already observed [9]. The increase of H_C at 450°C indicates formation of clusters which play a role of domain pinning centres [9,10]. Temperature dependence of H_C typical for nanocrystalline materials, was observed only for FeZrCuUB sample with minimal value of H_C at 530°C. Strong increase of H_C after annealing at 650°C is caused by precipitation of borides and grain coarsening.The above mentioned non-homogeneous structure of FeZrUB sample annealed at 530°C caused impairment of exchange interaction between grains and consequently the high value of H_C.

3 Conclusions

We can conclude that crystallization process of Fe-Zr-U-B alloy can be modified by adding of Cu. Different course of crystallization process for the sample without Cu ($x = 0$) and with Cu ($x = 1$) was observed. Structural analysis of the sample with $x = 0$ confirmed that annealing at 530°C caused crystallization of bcc-Fe phase embedded in amorphous matrix, but created bcc-Fe phase is not homogeneous. It consisted from small regular grains (15 nm) and highly dendritic crystals (up to 50 nm). Moreover, Mössbauer spectroscopy proved the initial stage of formation of borides.

As for the $x = 1$ sample, homogeneous nanocrystalline structure consisting of bcc-Fe crystals, with mean grain size of about 10 nm, was observed. It has been proved that Cu decreases onset temperature of crystallization of bcc-Fe - T_{x1}, and increases the temperature of borides formation and grain coarsening - T_{x2}. Nanocrystalline structure for the $x = 1$ sample is stable up to 650°C when precipitation of borides was observed. Typical dependence of H_C on annealing temperature, as for nanocrystalline materials, was observed only for FeZrCuUB sample with its minimal value at 530°C.

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