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CRYSTALLIZATION AND RELAXATION PROCESS IN THE AMORPHOUS Fe-B ALLOYS STUDIED BY THERMOPOWER AND DIFFRACTION METHODS

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АННОТАЦИЯ

Методами измерения термического напряжения /S/ и дифракции исследовалось влияние различных термических обработок на быстроохлажденные металлические стекла $Fe_{100-x}B_x$ /x = 11,7-24,5/. Для измерения локального поверхностного термического напряжения вблизи комнатной температуры был изготовлен простой зонд "Термотест". Термонапряжение аморфного Fe-B выше комнатной температуры имеет отрицательный знак, и только в небольшой мере зависит от концентрации бора, температуры и релаксационной термообработки. После кристаллизации термообработки термическое напряжение около 300 К в доэвтектической области смещается в положительном направлении и в отрицательном направлении в гиперэвтектической области в соответствии с природой и количеством составляющих фаз /Fe, Fe_3B, Fe_2B/. Рентгеновские и электрондифракционные исследования фаз однозначно указывают на то, что метастабильная фаза Fe_3B является наиболее стабильной при концентрации бора в окрестности 20 ат%.

KIVONAT

Különböző hőkezelések hatását tanulmányoztuk $Fe_{100-x}B_x$ (x = 11,7-24,5) fémüvegeken termofeszültség (S) és diffrakciós módszerekkel. A termofeszültség lokális, felületi mérésére a szobahőmérséklet környékén egyszerü "Termoteszt" szondát készitettünk. Az amorf Fe-B termofeszültsége a szobahőmérséklet fölött negativ előjelü és csak kis mértékben függ a bór koncentrációtól, a hőmérséklettől és a relaxációs hőkezeléstől. Kristályositó hőkezelés után a 300 K fok körül mért termofeszültség pozitiv irányba tolódik el a hipo- és negativ irányba a hiper-eutektikus tartományban az összetevő fázisok (Fe, Fe_3B, Fe_2B) természetének és mennyiségének megfelelően. Röntgen és elektrondiffrakciós vizsgálatok egyértelmüen arra utalnak, hogy a Fe_3B metastabil fázis 20 at% B tartalom körül a legstabilabb.

ABSTRACT

Thermopower (S) and diffraction measurements have been made on rapidly quenched $Fe_{100-x}B_x$ (x = 11.7-24.5) metallic glasses after different heat treatments. For local measurements of S around the room temperature a simple surface probe "thermotester" has been designed. The thermopower of amorphous Fe-B alloys measured above the room temperature is negative and depends slightly on the boron content, on the temperature and on the relaxation process. The change in S measured around 300 K after crystallizing heat treatments is positive in the hypo- and negative in the hyper-eutectic range corresponding to the actual structure and fraction of phase components (Fe, Fe_3B, Fe_2B). X-ray and electron diffractograms clearly indicate an extrastability of metastable Fe_3B around 20 at% boron.

INTRODUCTION

In this paper we report an experimental study of the thermopower as a function of composition in amorphous as quenched, annealed and crystallized $Fe_{100-x}B_x$ samples. For rapid testing of the ribbons local, relative thermopower was measured with a home-made thermoelectric probe around the room temperature. In addition, in-situ absolute thermopower measurements were performed to study the crystallization process. The crystallization phases obtained after different heat treatments were identified by X-ray and electron diffraction measurements.

EXPERIMENTAL METHODS

The $Fe_{100-x}B_x$ amorphous samples were prepared in a wide concentration range (x = 11.7-24.5) by conventional chill block melt spinning.

The low temperature relaxation heat treatment were performed at 473 K in Ar atmosphere. The high temperature isothermal heat treatments of temperatures 673 K, 773 K and 1073 K were made in vacuum to avoid the solid-gas reaction with the minute amount of H_2O in the protecting Ar gas.

The temperature dependence of the absolute thermopower was measured in classic arrangement [1].

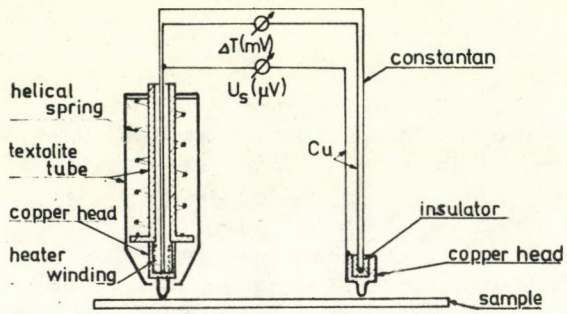

Fig. 1. The sketch of the thermoelectric probe

For the local, relative thermopower measurements around the room temperature a thermoelectric probe was designed (Fig. 1). The thermoelectric force sets up between the heated and cold copper heads pressed against the sample and it was measured with a Solartron μV-meter. The temperature difference ΔT was monitored on a digital mV-meter by a copper-constantan thermocouple and drifted around 70°C where the measurements were carried out, to avoid the temperature stability problem. The reproductibility of relative thermopower was better than $\pm$0.07 μV/K.

X-ray diffractograms were obtained in transmission mode with a Phillips XDC-700 Guinier camera using $Cr_{K\alpha 1}$ radiation. Transmission electron microscope (TEM) and selected area electron diffraction study was carried out using a JEOL 100-CX microscope.

RESULTS AND DISCUSSION

Thermopower measurements. The relative thermopower ($S-S_{Cu}$) of the as quenched amorphous Fe-B ribbons at room temperature is negative and shows a broad minimum near 20 at% as a function of boron content (see curve A in Fig. 2).

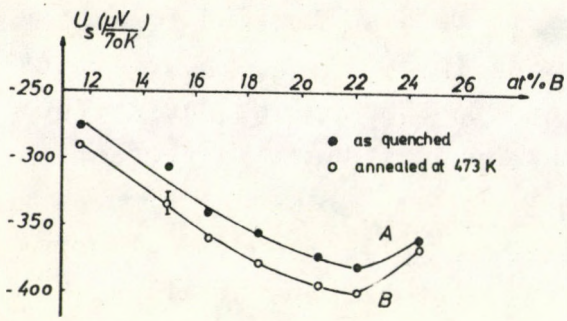

Fig. 2. *U_S vs c_B in the as quenched state and after relaxating heat treatment at 473 K/3 hours*

In the whole investigated range of concentration the thermopower decreases slightly after stress-relief heat treatment (473 K/3 h) as the curve B in Fig. 2 shows.

Similarly, above room temperature the absolute thermopower depends only slightly on the temperature in the concentration range x = 13-24.5. Larger changes show up only when the crystallization takes place (Fig. 3).

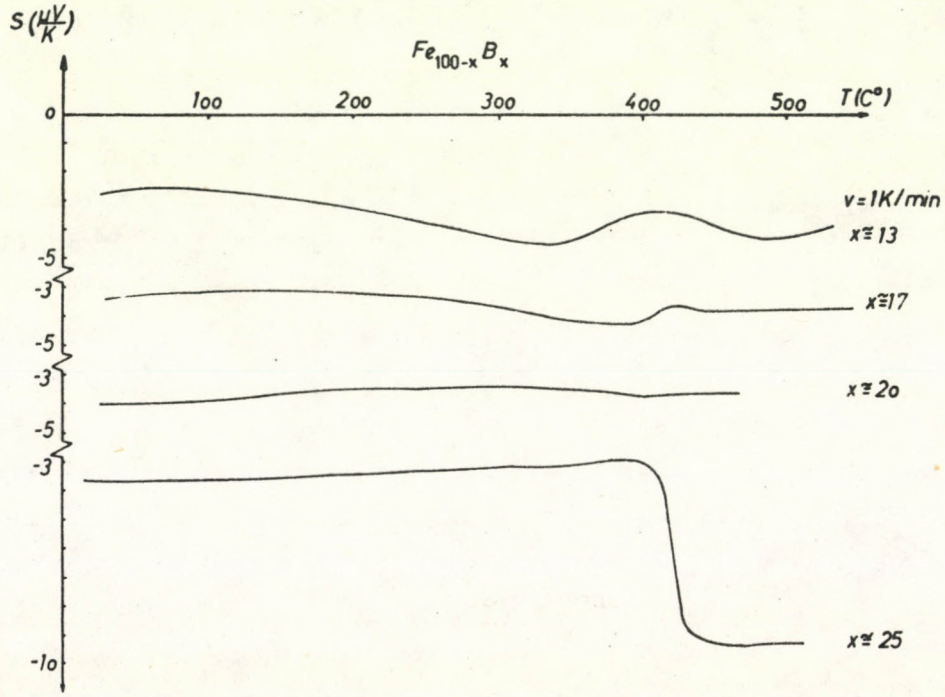

Fig. 3. *The temperature dependence of the absolute thermopower on $Fe_{100-x}B_x$ ribbons*

These findings concerning the high temperature behaviour and the positive temperature coefficient of resistivity seems to be explicable in the frame of extended Ziman model [2]. In the low temperature range, however, the thermopower has a broad minimum as a function of temperature [3]. The magnon drag contribution must be therefore also taken in to account beside the electron diffusion component.

Upon crystallization the thermopower shifts towards positive values in low concentration range and it is even lowered towards negative ones at the high concentrations (Fig. 3). At about 21 at% of B almost no change could be detected in thermopower during the crystallization implying that the thermopowers due to different phases compensate each other.

The thermopower of the crystallized samples measured at room temperature depend more strongly on the overall concentration than in amorphous state. For a better control of the phase composition three different isothermal heat treatments were carried out at 673 K/3 h; 873 K/3 h and 1073 K/3 h, respectively. The relative thermopower measured around the room temperature varies monotonously with the boron content from positive to negative values reflecting the phase composition of the samples (Fig. 4). All the plots intersect the as quenched curve around the eutectic point. The plot obtained for samples crystallized at 673 K/3 h differs from that obtained after 873 K/3 h heat treatment. Comparing the plots obtained after 873 K/3 h and 1073 K/3 h heat treatments no further change could be detected. Except the vicinity of x=20, the thermopower versus overall boron content plots for the fully crystallized samples and for the master alloys are very close to each other.

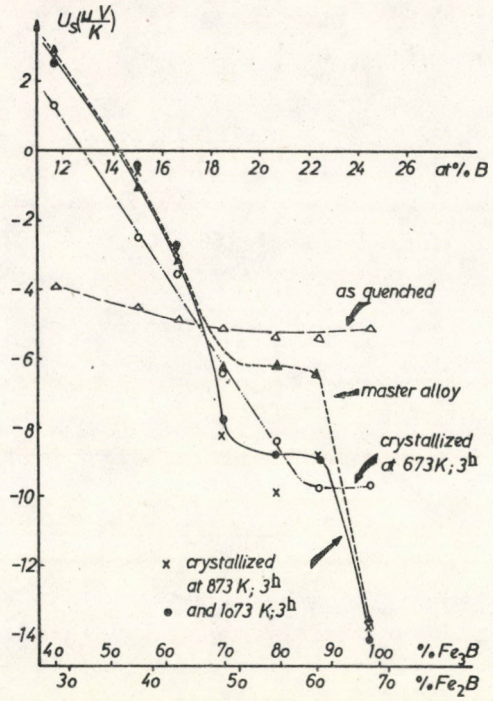

Fig. 4. U_S vs. c_B after different isotherm crystallization heat treatments

The high sensitivity of the relative thermopower measured around the room temperature to the crystallized fraction can be used as a rapid testing for amorphousness of the sample.

On the other hand, the characteristics of the ribbons in amorphous state can not be controlled by thermopower measurements. In addition to the low sensitivity of S to the composition of Fe-B alloys and to the relaxation heat treatment, it was found prac-

tically insensitive to the processing parameters the melt overheating and the quenching rate.

Diffraction measurements. In Table 1 the crystallized phases found after different heat treatments by X-ray diffractometry are summarized.

The low temperature heat treatment at 673 K was intended to produce α-Fe + Fe_3B, but for the lowest (c_B = 11.7 at%) and the highest (c_B = 24.5 at%) boron content already the equilibrium phases, α-Fe + Fe_2B were found.

After a heat treatment at 873 K/3 h the metastable Fe_3B decomposes in the whole range of c_B, however it persists at 20.7 at% of B. Even after 1073 K/3 h heat treatment traces of Fe_3B could be detected at this concentration.

In slowly cooled master alloys with low boron concentration instead of the stable boride Fe_2B the metastable Fe_3B was found. Only the slowly cooled sample with 24.5 at% boron consisted of the equilibrium phases; α-Fe + Fe_2B. After a 3 hours heat treatment at 1073 K all the master alloys show the equilibrium phases of α-Fe + Fe_2B and traces of Fe_3B except the sample of 24.5 at% B, where the Fe_3B reappeared in an amount comparable with that of Fe_2B.

The X-ray and electron diffraction results are in good agreement. Further information could be obtained by TEM and electron diffraction (noted by "1" and "2" in Table 1): "1" in the amorphous matrix traces of α-Fe appears, "2" in the crystallized matrix consisting mainly of α-Fe, and a new phase appears that are formed probably from amorphous boron [4] (Fig. 5a and b).

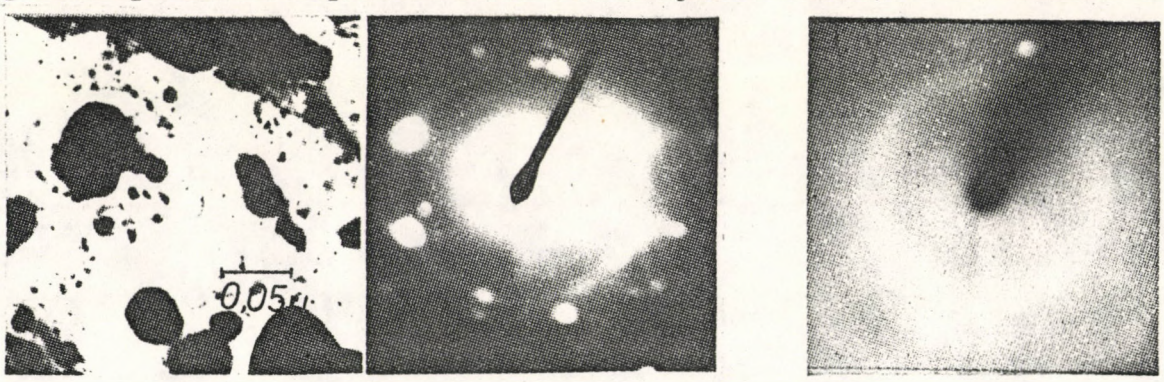

Fig. 5. TEM and diffraction patterns for sample with 18.5 at% B heat treated at 873 K/3 h. a/ α-Fe + Fe_2B; b/ α-Fe + amorphous B.

Table 1. Results of X-ray diffraction

c_B	Liquid quenched ribbons					Master alloys	
(at%)	as cast	473 K/3 h	673 K/3 h	873 K/3 h	1073 K/3 h	slowly cooled	1073 K/3 h
11.7	amorphous	amorphous[1]	αFe+traces of Fe_2B	αFe+Fe_2B	αFe+Fe_2B		
15.0	amorphous	amorphous	αFe+Fe_3B	αFe+Fe_2B+ +traces of Fe_3B	αFe+Fe_2B	αFe+Fe_3B	αFe+Fe_2B+ +traces of Fe_2B
16.6	amorphous	amorphous	αFe+Fe_3B	αFe+Fe_2B	αFe+Fe_2B	-	-
18.5	amorphous	amorphous	αFe+Fe_3B	α Fe+Fe_2B[2]	αFe+Fe_2B	-	-
20.7	amorphous	amorphous	αFe+Fe_3B	αFe+Fe_2B+ +Fe_3B	αFe+Fe_2B+ +traces of Fe_3B		
22.4	amorphous	amorphous	αFe+Fe_3B	αFe+Fe_2B	αFe+Fe_2B	αFe+Fe_3B+ +traces of Fe_2B	αFe+Fe_2B+ +traces of Fe_3B
24.5	amorphous	amorphous	αFe+Fe_2B	αFe+Fe_2B[2]	αFe+Fe_2B[3]	αFe+Fe_2B	αFe+Fe_2B+ +Fe_3B

The persistance of Fe_3B indicates on extrastability of this phase around 20 at% of B in accordance to thermomagnetic measurements of Tarnóczi et al. [5].

Finally, it should be emphasized the difference between the phase stability checked by such isothermal heat treatments and the stability of the glass expressed as the crystallization temperature at a given heating rate [6].

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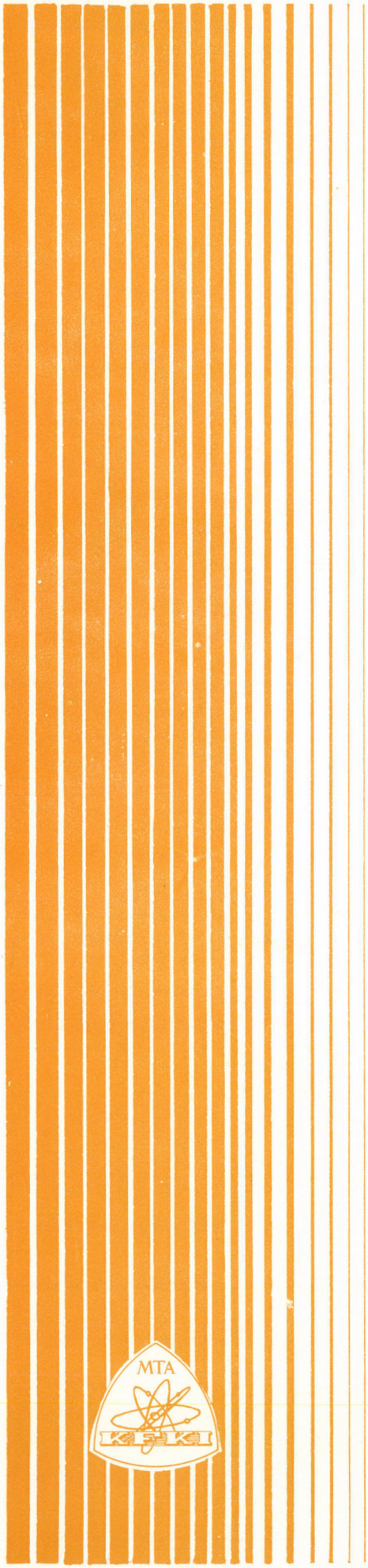

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