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CRYSTALLIZATION PRODUCTS OF Fe-B-Si BASED METALLIC GLASSES

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АННОТАЦИЯ

Методами калориметрии и мессбауэровской спектроскопии исследовалась кристаллизация металлических стекол Fe-B-Si. Определены кристаллические фазы и изучена зависимость процесса кристаллизации от состава.

KIVONAT

Fe-B-Si fémüvegek kristályosodását vizsgáltuk kalorimetria és Mössbauer spektroszkópia segitségével. Meghatároztuk a kristályos fázisokat,és megvizsgáltuk a kristályosodási folyamat összetételfüggését.

ABSTRACT

The crystallization of FeBSi metallic glasses have been investigated by calorimetry and Mössbauer spectroscopy. The crystallization products have been identified and the composition dependence of the crystallization process is discussed.

INTRODUCTION

Fe-B-Si amorphous alloys are very interesting materials both from a practical point of view [1,2] and for understanding the factors which determine the thermal stability of amorphous metallic materials. Several recent reports [3-6] indicate that Si is very effective in increasing the crystallization temperature. It is well-known from these works that clearly resolved double stage crystallization can be observed at much higher total metalloid content than in the Fe-B system [7] and it is the b.c.c. (α-Fe) phase which appeares after the first crystallization step in the Fe-B-Si glasses. Inoue et.al. [6] noticed, that the lattice parameter of this b.c.c. phase is significantly smaller than that of a metalloid-free transition metal, indicating a substantial amount of Si dissolved in this phase.

In the present paper Mössbauer spectroscopy and Curie point determinations for several partly or fully crystalline FeBSi based alloys are used to idenfity crystallization products.

CURIE POINT STUDIES

The change in ferromagnetic Curie point /T_c/ on heat treatment in $Fe_{78}B_{12}Si_{10}$ amorphous alloys has been investigated by differential scanning calorimetry. *Fig. 1.* shows that the increase in T_c is proportional to the logarithm of heat treatment

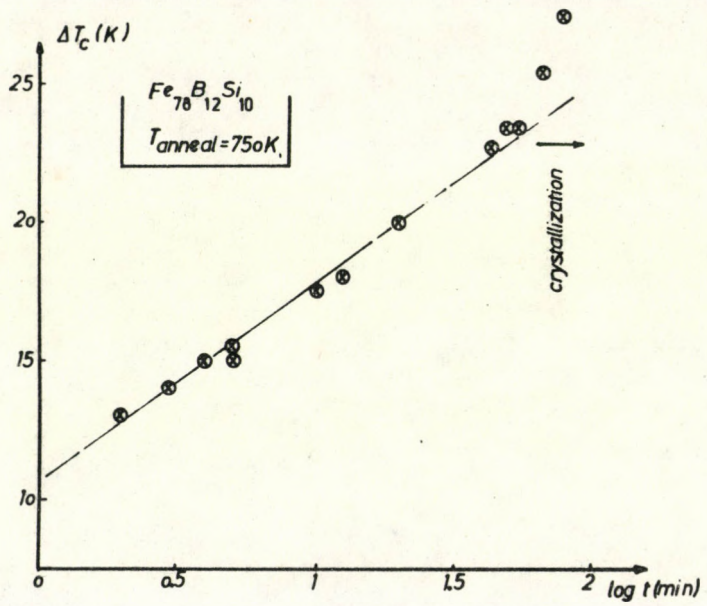


Fig. 1. Curie point change due to heat treatment

time for $t \lesssim 50$ min. Besides this variation, which has been shown to be connected with structural ralaxation [8,9] an extra T_c increase is detected after longer time heat treatments. Calorimetric studies indicate that the crystallization curve is not influenced by annealing for $t \lesssim 50$ min, but the first stage of crystallization is gradually eliminated by heat treatments in the region marked in *Fig. 1.*

The relation between crystallization and extra T_c increase can be established much better on samples where refractory additives enhance thermal stability [10] and depress T_c. $Fe_{76}X_2B_{12}Si_{10}$ with X=Mo and W glasses were heat treated at different temperatures, their T_c and heat of crystallization, ΔH were measured. The extra Curie point increase, ΔT_c^{extr} is plotted on *Fig. 2.* versus the crystalline fraction, $C_{cryst}=(\Delta H_o-\Delta H)/\Delta H_o$

where ΔH_o is the crystallization energy of the as-received material. From this T_c increase an estimation can be made of the Si content of the precipitated Fe-Si, assuming that the crystallization process is: $Fe_{78}B_{12}Si_{10} \rightarrow C_{cryst}/Fe_{1-z}Si_z/ + /1-C_{cryst}/\cdot /Fe_{1-x-y}B_xSi_y/$ as shown by Mössbauer experiments discussed later. We can measure the change in T_c of the remaining amorphous $Fe_{1-x-y}B_xSi_y$ phase as:

$$\frac{dT_c}{dC_{cryst}} = \frac{\partial T_c}{\partial x}\Big|_{y=const} \frac{dx}{dC_{cryst}} + \frac{\partial T_c}{\partial y}\Big|_{x=const} \frac{dy}{dC_{cryst}} \cdot$$

Using the results of Narita et al. [11]

$$\frac{\partial T_c}{\partial x}\Big|_{Si=const} = 900 \pm 200 \text{ K} \qquad \frac{\partial T_c}{\partial y}\Big|_{B=const} = 600 \pm 200 \text{ K}$$

and our measured value, $\frac{dT_c}{dC_{cryst}} = 65 \pm 15$ K

the Si content of the precipitated $Fe_{1-z}Si_z$ is estimated as $z=0.16 \pm 0.08$.

MÖSSBAUER SPECTROSCOPY

The Mössbauer spectra of $Fe_{80}B_{20-x}Si_x$ glasses after the first stage of crystallization clearly show the presence of $Fe_{1-z}Si_z$, where z depends on the initial Si content, and a significant enrichment of the metalloid in the remaining amorphous phase /total metalloid content increase up to 25±2 at%/. In the second crystallization stage Fe_3Si and Fe_2B are formed.

The composition dependence of the crystallization temperature [12] is shown on *Fig. 3.*, which indicates the persistance of single stage crystallization to much higher Si content than

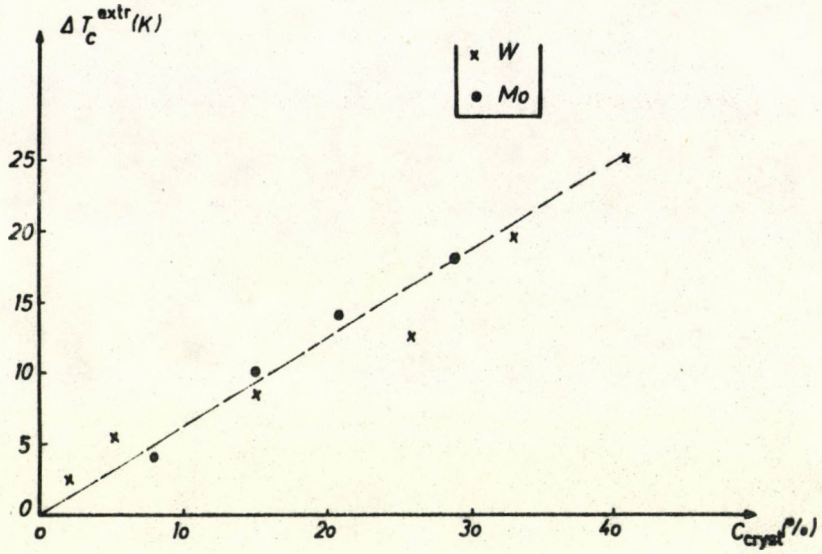


Fig. 2. Extra Curie point increase versus crystalline fraction in $Fe_{76}Mo_2B_{12}Si_{10}$ and $Fe_{76}W_2B_{12}Si_{10}$ glasses

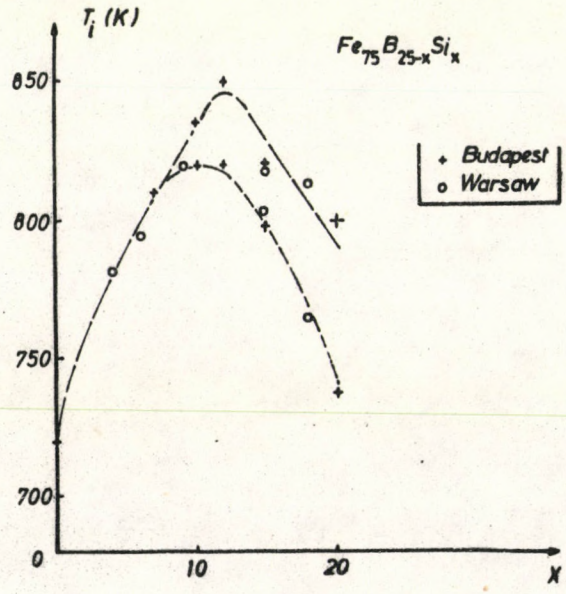


Fig. 3. Initial temperature of crystallization of $Fe_{75}B_{25-x}Si_x$ glasses determined from 10 K/min DCS measurements. Above 10 at.% Si a two-step process was observed

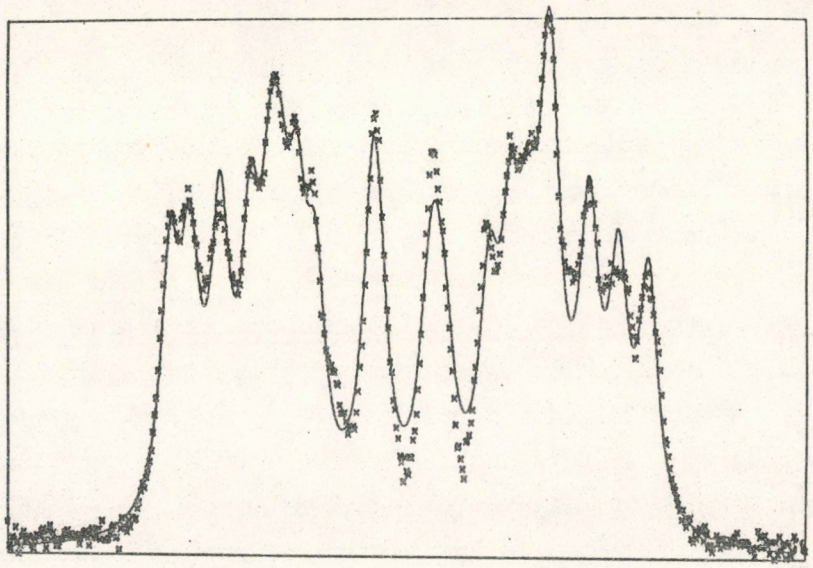
in $Fe_{80}B_{20-x}Si_x$ alloys.

Mössbauer spectra of the crystallized samples reveal the simultaneous formation of both $Fe_{1-z}Si_z$ and Fe_2B in the range of single stage crystallization. With increasing Si content, a second exothermic effect appeares but according to Mössbauer spectroscopy, no amorphous material can be detected after the first heat evolution stage as illustrated in *Fig. 4a*. After the first stage, the material is crystallized to Fe_2B and chemically disordered b.c.c. Fe-Si. The spectrum of the same material after the second heat evolution is characteristic /besides the Fe_2B/ of an Fe-Si alloy which is slightly off-stoichiometric but has a well-defined Fe_3Si, DO_3-type chemical order.

The measured Mössbauer spectra can be fitted adequately with four six-line patterns. The hyperfine field values of the final crystalline states are plotted on *Fig. 5.* versus the Si content together with the corresponding values for the Fe_2B, Fe_3B and Fe_3Si intermetallic compounds [13,7 and 14, respectively]. The coincidence of the hyperfine fields together with the agreement between measured amount of Fe_2B and Fe_3Si and those values calculated from the different Si content /continuos lines in *Fig. 6.*/ verifies this phase identification.

CONCLUSION

The significant differences between the crystallization of Fe-B and Fe-B-Si glasses are connected with the solubility of Si in Fe. The Si causes the metalloid enrichment of the matrix to be much slower and this contributes to the separation of the two crystallization processes of b.c.c. Fe-Si precipitation and the Fe_3Si, Fe_2B compound formation in most of the composition range below 25 at% metalloid. In $Fe_{75}B_{25-x}Si_x$ glasses Fe-Si and Fe_2B crystallize simultaneously and the second heat evolution stage must be connected with the appearance of Fe_3Si-type chemical order.



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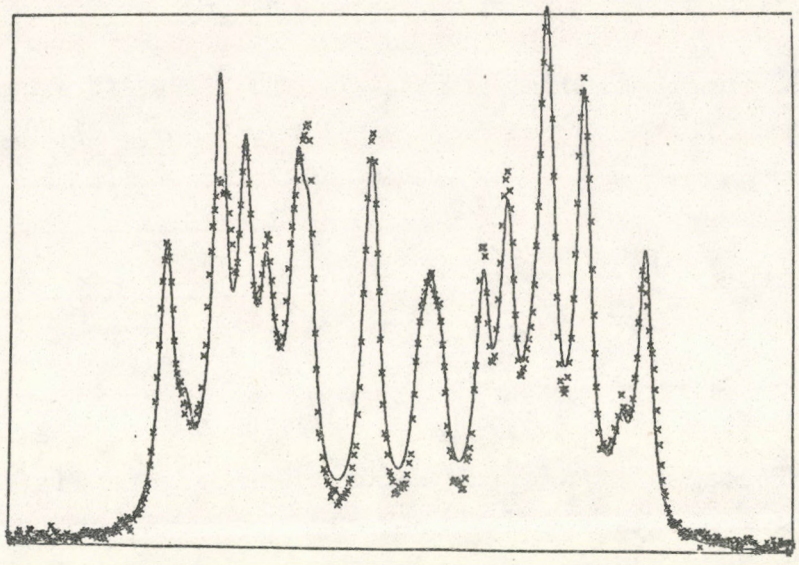

b,

Fig. 4. Room temperature Mössbauer spectra of crystalline $Fe_{75}B_{10}Si_{15}$ /the continuos curves are fitted ones/

a, Heat treated to the first heat evolution stage: it consists of a mixture of disordered b.c.c. $Fe_{78}Si_{22}$ and Fe_2B. No amorphous material is remaining.

b, After the second heat evolution stage: it is a mixture of ordered /DO_3-type/ off-stoichiometric Fe_3Si and Fe_2B

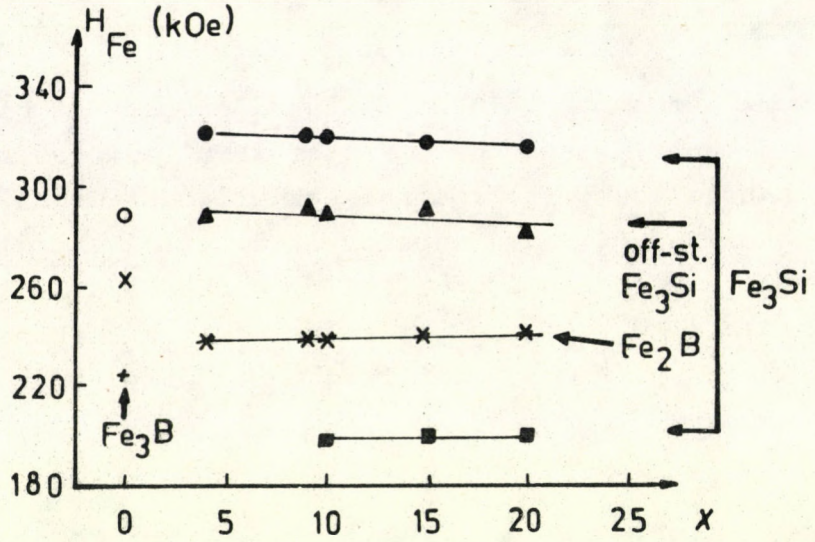

Fig. 5. Hyperfine fields of the final crystalline phases in $Fe_{75}B_{25-x}Si_x$ at room temperature. The hyperfine fields of the known intermetallic compounds Fe_2B, Fe_3B/2B,3B and 4B sites/ and Fe_3Si /8Fe and 4Fe,4Si sites/ are also shown. The off-stoichiometric Fe_3Si site corresponds to 6Fe,2Si nearest neighbours /13/. Because of the overlap of the lines, the 7Fe,1Si and 5Fe,3Si environments cannot be resolved

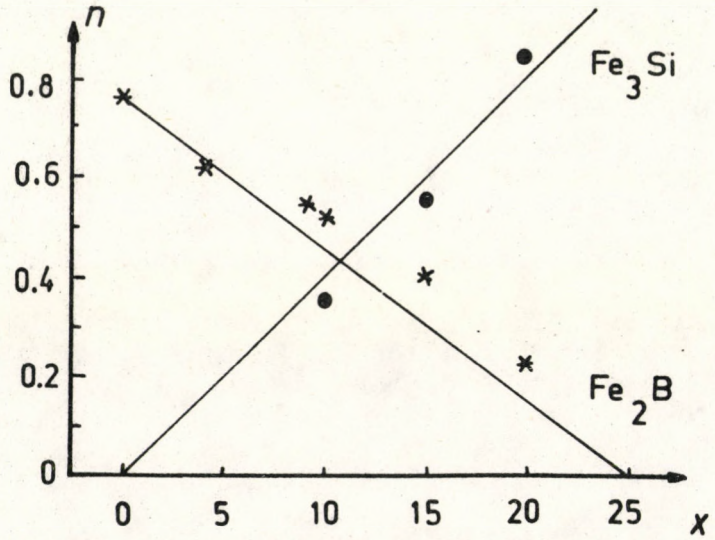

Fig. 6. The measured relative amounts (n) of Fe_2B and Fe_3Si in the $Fe_{75}B_{25-x}Si_x$ series. The continuos line is calculated assuming a decomposition for these phases.

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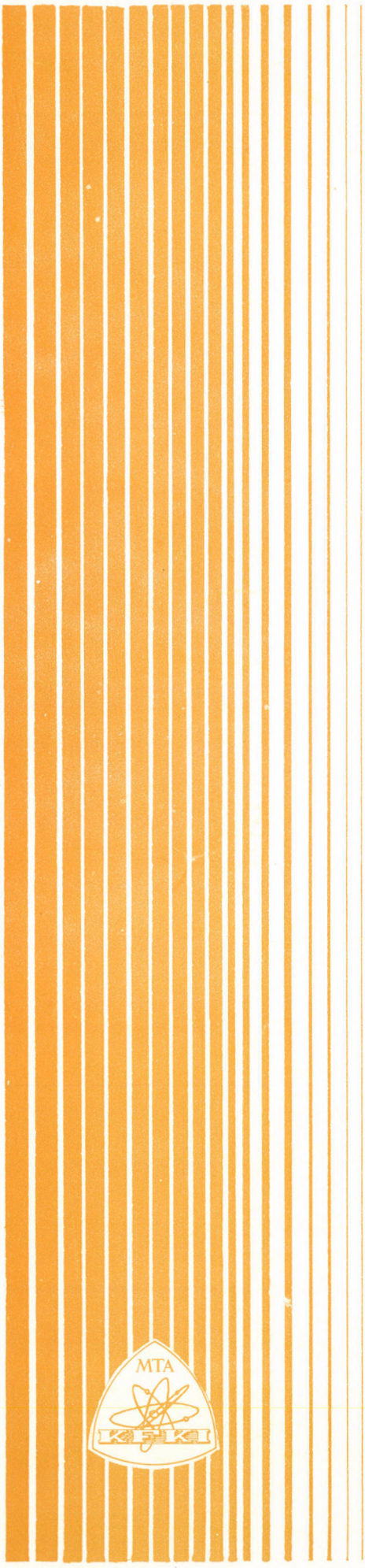

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