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ELECTRONMICROSCOPIC INVESTIGATIONS OF
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ELECTRONMICROSCOPIC INVESTIGATIONS OF TRANSITION METAL
BASED METALLIC GLASSES

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АННОТАЦИЯ

При помощи электронмикроскопии исследовалась кристаллизация металлических стекол Fe-Ni-B, Fe-Co-B, Fe-B-Si и Fe-B-C, особенно те случаи, когда процесс кристаллизации начинается с нуклеации металлического компонента. Замещение как металлических, так и стеклообразующих металлоидных элементов сильно влияет на процесс кристаллизации и одно- или двухфазный характер аморфно-кристаллического перехода. Показана возможность термодинамической интерпретации этих явлений.

KIVONAT

A Fe-Ni-B, Fe-Co-B, Fe-B-Si és Fe-B-C üvegfémek kristályosodását vizsgáltuk elektronmikroszkóppal, különös tekintettel azokra az esetekre, ahol a kristályosodási folyamat a fémes elem nukleációjával indul. Mind a fémes, mind az üvegeképző metalloid elemek cseréje erősen befolyásolja a kristályosodási folyamatot, az amorf-kristályos átalakulás egy-, vagy többlépcsős jellegét. Ezen jelenségek termodinamikai értelmezésének lehetőségére mutatunk rá.

ABSTRACT

The crystallization of Fe-Ni-B, Fe-Co-B, Fe-Co-Si and Fe-B-C metallic glasses has been studied by electron microscopy. Mainly those cases were investigated where the crystallization process starts with the primary nucleation of the metallic element. The exchange of both metal and metalloid can seriously influence the process of crystallization, resulting in single or multi-step transformation behaviours. A thermodynamic interpretation is suggested for these phenomenon.

INTRODUCTION

Being metastable, amorphous metals crystallize with the proper combination of temperature and time. Crystallization is generally complex, proceeding in stages that often include intermediate metastable crystalline phases. According to Mosumoto [1] the crystallization of the metallic glasses containing metalloid atoms, starts with the nucleation and growth of crystallites (MS-I) in the amorphous matrix, which according to the lattice parameter values, consist of nearly pure metallic element. In long-time heat treatments at low temperature the amorphous metals crystallize into a single phase having the same crystal structure as that of the major metallic element /see SS in *Fig. 1*/. It is an assembly of microcrystallites having diameters of about 50 to 100 Å and it is a supersaturated solid solution with the same composition as that of the matrix, according to the lattice parameter measurements. In further heat treatments, complex metastable phases appear /see MS-II, MS-III in *Fig. 1*/.

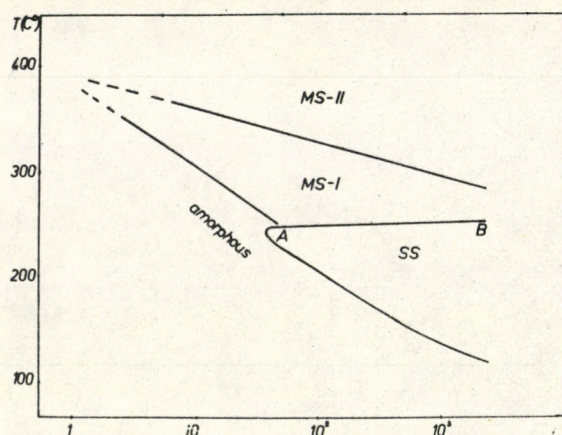


Fig. 1. TTT curve from annealing study of an amorphous alloy. MS-I and MS-II correspond to different metastable phases

metastable phase also was influenced by these changes.

In a large concentration scale the crystallization of the Fe-B system follows the scheme of Fig. 1. MS-I corresponds to the nucleation of α -Fe, and MS-II corresponds to Fe_3B /tetragonal/ [2,3].

It was investigated how the nucleation of α -Fe is effected by other alloying elements at a fixed ratio of metal and metalloid. On the other hand the crystal structure of $(\text{TM})_3\text{M}$

EXPERIMENTAL

The crystallization of metallic glasses has been studied by in-situ electron beam heating in a JEOL-100CX electron microscope.

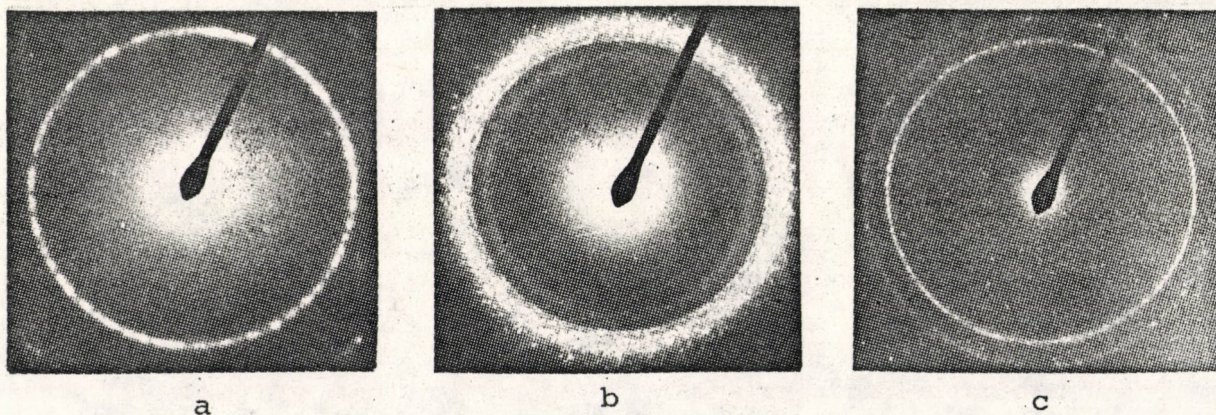


Fig. 2. The MS-I phase have been detected in the investigated systems a) α -Fe, b) α -Co, c) γ -Fe-Ni

The electron microscopic measurements of samples cooled down from different stages of the transformation helped us to clarify and separate the individual processes. The comparison with samples of well defined thermal history made it possible to set up a tentative temperature scale for in-situ microscopy observations. Part of the heat treatments was made in a DSC calorimeter, and others were followed by in situ electrical resistivity measurements. The

Table 1

The effect of exchange of B by C

Composition	MS-I (T _q)	MS-I structure	MS-II (T _q)	MS-II structure	MS-III (T _q)	MS-III structure
Fe ₈₄ B ₁₆	710 K	αFe+a'	740 K	αFe+Fe ₃ B _(t)	-	-
Fe ₈₄ B ₁₄ C ₂	730 K	^a αFe+a'	755 K	αFe+a' αFe+Fe ₃ B _(t) αFe+Fe ₃ B _(o)	780 K	αFe+Fe ₂ B αFe+Fe ₃ B _(o)
Fe ₈₄ B ₁₂ C ₄	715 K	αFe+a'	750 K	αFe+Fe ₃ B _(t) αFe+Fe ₃ B _(o)		
Fe ₈₄ B ₁₀ C ₆		αFe+a'		αFe+Fe ₃ B _(o)		
Fe ₈₄ B ₈ C ₈	695 K	αFe+a'	740 K	αFe+Fe ₃ B _(o)		
Fe ₈₄ B ₆ C ₁₀		αFe+a'		αFe+Fe ₃ B _(o)		

(t) indicates tetragonal and (o) orthorhombic structures, while a and a' refers to as-cast type and modified amorphous regions, respectively.

samples were thinned by electrochemical polishing at -40°C in a mixture of methanol and percloric acid with a ratio of 5:1. The composition of the investigated samples are shown in the first column of Tables 1, 2, 3, and 4.

The effect of exchange of B by Si Table 2

Composition	MS-I (T _q)	MS-I structure	MS-II (T _q)	MS-II structure
Fe ₈₀ B ₂₀	-	-	745 K	αFe+Fe ₃ B _(t)
Fe ₈₀ B ₁₅ Si ₅	790 K	αFe+a'	810 K	αFe+Fe ₃ (B,Si) _(o)
Fe ₈₀ B ₁₀ Si ₁₀	775 K	αFe+a'	822 K	αFe+Fe ₃ (B,Si) _(o)
Fe ₇₅ B ₂₅	-	-	765 K	αFe+Fe ₂ B
Fe ₇₅ B ₁₅ Si ₁₀	844 K	αFe+a' (?)	862 K	αFe·(SS-like)
Fe ₇₅ B ₁₀ Si ₁₅	825 K	αFe+a' (?)	860 K	αFe+Fe ₂ B
Fe ₇₅ B ₅ Si ₂₀	790 K	αFe+a' (?)	852 K	αFe+Fe ₂ B
Fe ₇₀ B ₂₀ Si ₁₀	853 K	αFe+a' (?)	863 K	αFe+Fe ₂ B
Fe ₇₀ B ₁₅ Si ₁₅	850 K	αFe+a' (?)		
Fe ₇₀ B ₁₀ Si ₂₀	830 K	αFe+a' (?)		

a' (?) indicates a possible amorphous phase inferred from the detected diffuse background only

The effect of exchange of Fe to Co, or Ni Table 3

Composition	MS-I (T _q)	MS-I structure	MS-II (T _q)	MS-II structure
Fe ₈₀ B ₂₀	-	-	745 K	αFe+Fe ₃ B _t
(Fe ₁ Ni ₁) ₈₀ B ₂₀	-	-	720 K	γ(Fe,Ni)+(Fe,Ni) ₃ B _(o)
(Fe ₄ Co ₁) ₈₀ B ₂₀	-	-	760	αFe+(Fe,Co) ₃ B _(t) αFe+(Fe,Co) ₂ B
(Fe ₃ Co ₁) ₈₀ B ₂₀	-	-		αFe+(Fe,Co) ₃ B _(t)
(Fe ₂ Co ₁) ₈₀ B ₂₀	-	-	765 K	αFe+(Fe,Co) ₃ B _(t)
(Fe ₁ Co ₂) ₈₀ B ₂₀	-	-	775 K	αFe+(Fe,Co) ₃ B _(t)
(Fe ₁ Co ₃) ₈₀ B ₂₀	-	-	760 K	αFe+(Fe,Co) ₃ (b)
(Fe ₁ Co ₄) ₈₀ B ₂₀	-	-	755 K	αFe+(Fe,Co) ₃ (o)
Co ₈₀ B ₂₀	700 K	αCo+a'	745 K	αCo+Co ₃ B _(o)
Fe ₇₅ B ₂₅	-	-		αFe+Fe ₂ B
(Fe ₃ Co ₁) ₇₅ B ₂₅	-	-	790 K	αFe+(Fe,Co) ₃ B _(t)
(Fe ₂ Co ₁) ₇₅ B ₂₅	-	-		αFe+(Fe ₁ Co) ₃ B _(t)
(Fe ₁ Co ₁) ₇₅ B ₂₅	-	-	795 K	αFe+(Fe,Co) ₃ B _(o)
(Fe ₁ Co ₂) ₇₅ B ₂₅	-	-	770 K	αFe+(Fe,Co) ₃ B _(o)
(Fe ₁ Co ₃) ₇₅ B ₂₅	-	-		αFe+(Fe,Co) ₃ B _(o)
Co ₇₅ B ₂₅	-	-		αCo+Co ₃ B _(o)

Table 4

The effect of exchange of Fe by other transition metals

Composition	MS-I (T _q)	MS-I structure	MS-II (T _q)	MS-II structure
Fe ₈₀ Ti ₃ B ₁₇	704 K	αFe+a'	768 K	αFe+Fe ₂ B
Fe ₈₀ V ₃ B ₁₇	736 K	αFe+a'	756 K	αFe+Fe ₂ B
Fe ₈₀ Cr ₃ B ₁₇	-	-	716 K	αFe+Fe ₂ B
Fe ₈₀ Mn ₃ B ₁₇	-	-	710 K	αFe+Fe ₂ B
Fe ₈₃ B ₁₇	-	-	696 K	αFe+Fe ₃ B _(t)
Fe ₈₀ Co ₃ B ₁₇	-	-	692 K	αFe+Fe ₃ B _(t) αFe+Fe ₃ B _(o)
Fe ₈₀ Ni ₃ B ₁₇	-	-	704 K	αFe+Fe ₃ B _(t) αFe+Fe ₃ B _(o)
Fe ₈₀ Cu ₃ B ₁₇	632 K	αFe+a'	696 K	αFe+Fe ₂ B

RESULTS

As it is well known, below 17% B content the nucleation of α-Fe is separable by calorimetric measurements, whereas the primer nucleation of α-Fe is observable by in-situ electron-microscopic measurements even at 20 at% B content, see. *Fig. 2a*.

The effect of the exchange of metalloid. In Fe₈₄B₁₆ the appearance of α-Fe is detected in samples heated to 710 K with 10 K/min heating rate. By exchanging B for C the temperature of the first transformation decreases, as the second column of Table 1 shows. C helps the nucleation of α-Fe in the amorphous matrix. At low C content (2-4 at%) this effect is not so obvious because the crystallization of α-Fe takes place inhomogeneously, causing three peaks in the thermograms [4,5]. Exchange of B to C causes the appearance of needle like α-Fe crystallites.

The crystal structure of MS-II phase has also changed already with the exchange of 2 at% C from Fe_3B /tetragonal/ to cementite-type orthorhombic.

The effect of Si was investigated for three different iron contents (70, 75, 80 at%, see Table 2). In the pure Fe-B system only one crystallization stage was detected by calorimetric measurements at this large /20-25 at%/ metalloid content. Exchanging 5 at% or more B to Si double stage crystallization has been observed /see Table 2/. After the first step the samples consist of α -Fe microcrystallites, probably containing the Si atoms in solid solution. It has a very strange structure, similar to that had been detected earlier [6] in silica glasses, due to a spinodal decomposition. This special crystallization is connected probably with the large solubility of Si in α -Fe.

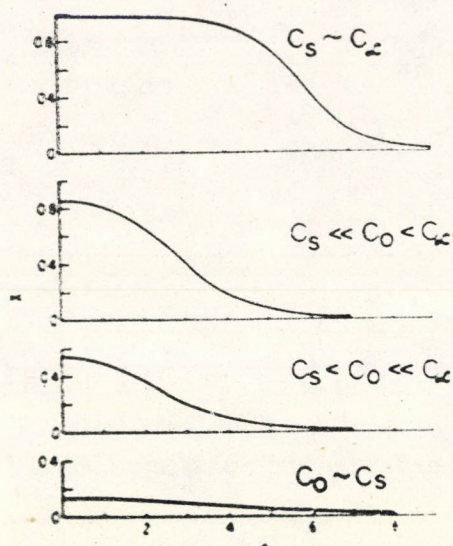


Fig. 3. Normalized composition profiles of the critical nucleus in the region $T \sim T_c$ [7].

$X = (C - C_0) / (C_\alpha - C_0)$; C_0 is the average, C_α is the equilibrium (A,B in Fig. 4), C_s is the spinodal (inflection point in Fig. 4) concentration.

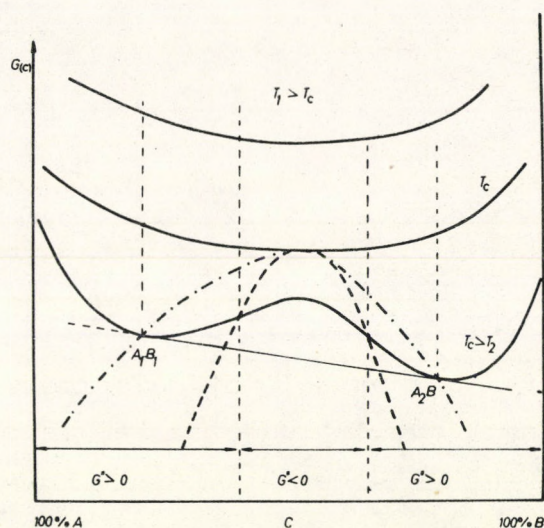


Fig. 4. Effect of temperature on the free energy-composition behaviour /schematic/ indicating the behaviour of ΔG for various fluctuations ΔC . In the range between broken lines (---) the phase transformation takes place with spinodal decomposition, and between --- and -.-.- with nucleation and growth

The effect of exchange of different transition metals. The influence of Co was investigated at two different B contents, 20 at% and 25 at% exchanging gradually Fe to Co; (Table 2). The effect is smaller than it was in the case of the exchange of metalloid. The nucleation of metallic element at 20 at% metalloid content is separable by calorimetric measurements only in the $\text{Co}_{80}\text{B}_{20}$. In these samples after the first crystallization stage the α -Co crystallites were detected in the amorphous matrix /Fig. 2b/. The crystal structure of MS-II phases changes to the orthorhombic one at a Fe-Co ratio of /75 at% / and /50 at% / in the samples containing 20 at% and 25 at% of B.

The effect of Ni was investigated in the samples with a composition of $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$. According to the in situ electron-microscopic measurements, the MS-I phase has the crystal structure of γ -Fe-Ni /see Fig. 2c/ and the MS-II phase was detected as an orthorhombic /Fe,Ni/₃B compound (Table 3).

As the effect of the exchange of the metallic element on the nucleation of α -Fe is smaller, a border case, $\text{Fe}_{83}\text{B}_{17}$ was chosen to investigate it /see Table 4/. Already 3 at% Ti, V or Cu is enough, for the nucleation of α -Fe to be separable by calorimetric measurements. These elements help the nucleation of the MS-I phase, causing a change in the free energy of the system.

DISCUSSION

In the cases shown here, the tendency is the crystallization of the major metallic element by nucleation from the amorphous matrix.

There is a well known model proposed by Cahn and Hilliard [7] to account for phase separation in binary systems, that has realistic "continuous" features. Phase transformation proceeds by the growth in size and amplitude of this critical fluctuations as nucleus. In contrast to classical theory, the nucleus has a smooth concentration profile that varies continuously

from c_n at the nucleus center to c_0 far away from it. Typical calculated profiles are shown in *Fig. 3*.

In the two limiting cases the Cahn-Hilliard nucleus tends to resemble the classical one exhibiting a constant concentration inside and a sharp interface /top curve in *Fig. 3*/. As the average concentration approaches this spinodal concentration /inflection points in *Fig. 4*/ the interface profile becomes increasingly diffuse and c_n decreases with decreasing temperature and size of critical fluctuation or nucleus.

Our opinion is that the formation of MS-I and SS phases are processes of the same type, and they are limiting cases of the crystallization of the metallic element by nucleation. The SS phase is a result of a spinodal-like decomposition. The size of the crystallites /about 100 Å/ corresponds to the spinodal wave length. According to the continuous Cahn-Hilliard [7] nucleation model, there is no sharp boundary between the MS-I and SS phase /A-B lines in *Fig. 1*/. It can only be a theoretical limit, similar to that of the equilibrium phase diagrams /*Fig. 4*/. Present experimental results also show that the primary nucleation of the metallic phase can be effected by the exchange of the metal, or metalloid elements by influencing the free energy of the system.

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