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АННОТАЦИЯ

Методом калориметрии /DSC/ изучалось влияние легирования атомами 3d, 4d и 5d переходных металлов на стабильность эвтектического сплава металлического стекла Fe-B. 4d и 5d третий компонент чаще вызывает двухфазовую кристаллизацию, чем 3d-легирующие атомы. Установлено, что с повышением температуры кристаллизации увеличивается энергия кристаллизации и температурный коэффициент сопротивления.

KIVONAT

3d, 4d és 5d átmeneti fémek beötvözésének hatását vizsgáltuk Fe-B eutektikus fémüveg ötvözet stabilitására kaloriméter (DSC) segítségével. 4d és 5d harmadik komponens gyakrabban okoz kétlépcsős kristályosodást, mint a 3d-beli ötvözők. Megfigyelhető, hogy a kristályosodás energiája és az ellenállás hőfoktényezője csökken, ha a kristályosodás hőmérséklete nő.

ABSTRACT

The influence of 3d, 4d and 5d transition metals on the sta-
bility of FeB eutectic metallic glass has been investigated
by calorimetry /DSC/. Third component from 4d and 5d rows
yields more frequently the occurence of double stage crys-
tallization than that of 3d. A tendency is observed that
energy of crystallization, and temperature coefficient of
resistivity decrease with increasing crystallization tempera-
ture.

INTRODUCTION

Replacement of iron by other transition metals in the iron-
based metallic glasses may increase or decrease the thermal
stability of the amorphous state [1-4]. In spite of the recent
investigations there is no complete agreement in the literature
concerning the role of main stabilizing factors: relative
valence between the host and alloying transition metal
$/Z_{trans.metal} - Z_{Fe} = \Delta Z /$ or the electron/atom ratio, the size
effect and the role of chemical nature of the constituents.
For our investigations eutectic FeB alloy was chosen as basic
material and about 3 at% of the Fe atoms were replaced by 3d,
4d and 5d transition metals in order to have a series of
systematically changed bonding characters and atomic sizes.
Temperature of crystallization as well as the crystallization
energy have been measured by DSC. The thermal properties have
been correlated with electrical properties.

EXPERIMENTAL

Alloys were prepared from 4N vacuum-melted iron, high purity FeB master alloy and from the TM metals respectively. The homogenity was controlled by electron microprobe analysis [5]. Ribbons were prepared by the melt spinning method. The glassy state of the as-quenched ribbons were controlled by X-ray diffraction. The specimens were chemically analyzed by an atomic absorption spectrophotometer. All the investigated ribbons were quenched under the same processing conditions. It was observed that melting point of the binary FeB alloys were only slightly shifted by the alloying /within the accuracy of our optical pyrometer, appr. 30 K/.

RESULTS AND DISCUSSION

The crystallization behaviour of the binary glassy alloy /c_B = 15,9 at% $\pm$ O,5, slightly below the eutectic point/ was characterized by a single peak in accordance with earlier results [6, 7]. The ternary alloys in the 3d row also show a single-step crystallization kinetics if valence number difference $|\Delta z| \leqq \pm 2$./Fig. 1a./. This double crystallization were more pronounced with greater difference in the chemical nature between iron and TM. Double-step crystallization was observed in all cases due to 4d and 5d replacement except for the elements in the same column as Fe; ie. Ru and Os. /Fig.1b and 1c/.

The double crystallization may arise from the trivial shift of boron content below 16 at% during the alloying where the binary glasses themselves show a two-step crystallization mechanism [7], but there is no metallurgical reason for this type of systematic concentration shift. According to the chemical analysis the lowest boron content was found in the binary alloy. On the other hand the concentration of boron is
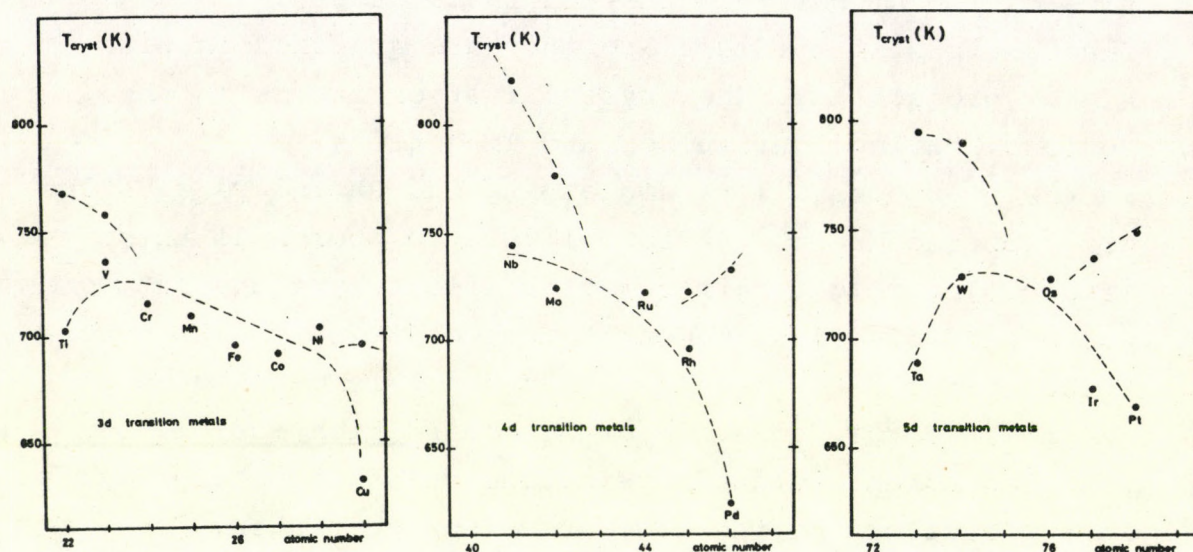
Fig. 1.a,b,c. The initial temperature of the crystallization
               steps vs atomic number in the transition metal
               series of the 3d, 4d and 5d periods.

the same within the experimental error of the chemical ana-
lysis in the 3d row. Consequently the appearance of the double
crystallization peak is caused by the alloying element with
growing difference in the chemical nature. The possible in-
terpretation of this behaviour is the clustering present al-
ready in the liquid state caused by the third element. This
presence of clustering is also plausible from the decreasing
value of static coercive force with increasing temperature of
the melt, measured on these alloys [8]. The clustering is also
supported by the fact of chemical ordering observed in other
types of melt-quenched amorphous alloys [9, 10]. Of Course
the nature of clustering may be different in this great variety
of chemical constituents. Two types can be considered:
a./ Alloys in which the TM has higher affinity to boron than
     that of Fe, clusters are considered as flexible associates

with $TM_mFe_nB_x$ compositions where m and x are higher and n is lower than the average concentration in the melt. Though these clusters are dynamic formations, their lifetime may be higher than that of the average concentration fluctuations in the melt, so they are quenched in with higher probability. The crystallization starts in the regions, having lower boron and TM-content.

b./ In the amorphous alloys containing Cu, Pt and Pd clusters are expected due to the low affinity of boron to these metals. Investigating the master alloys by electron microprobe analysis [5], the enrichment of these metals were found in the α-Fe phase. This tendency is manifested in the melt as the formation of Pt and Pd rich associates with low boron content. Again, the crystallization starts in the clusters having lower covalent character. Of course, this type of crystallization mechanism needs experimental verification by direct structural investigations /the work is under way/.

CRYSTALLIZATION TEMPERATURE AND ENERGY

A tendency is observed that energy of crystallization decreases with increasing crystallization temperature /Fig.2/. The TM substituents influence the crystallization temperature through the changed binding character, resulting in a temperature lowering of α-Fe precipitation on the right side of the periods and in the hindering of the compound-formation on the other side. In the case of Pd, Pt ... the change in the temperature of the α-Fe crystallization can be result of the weakend chemical bondings appeared due to the presence of atoms with noble metal character.

The temperature coefficient of resistivity vs. initial temperature of crystallization shows the same tendency as the crystallization energy /Fig. 3./. Those additives which raise

the "chemical bonding character" in the FeB metallic glass decrease the coefficient of resistivity.
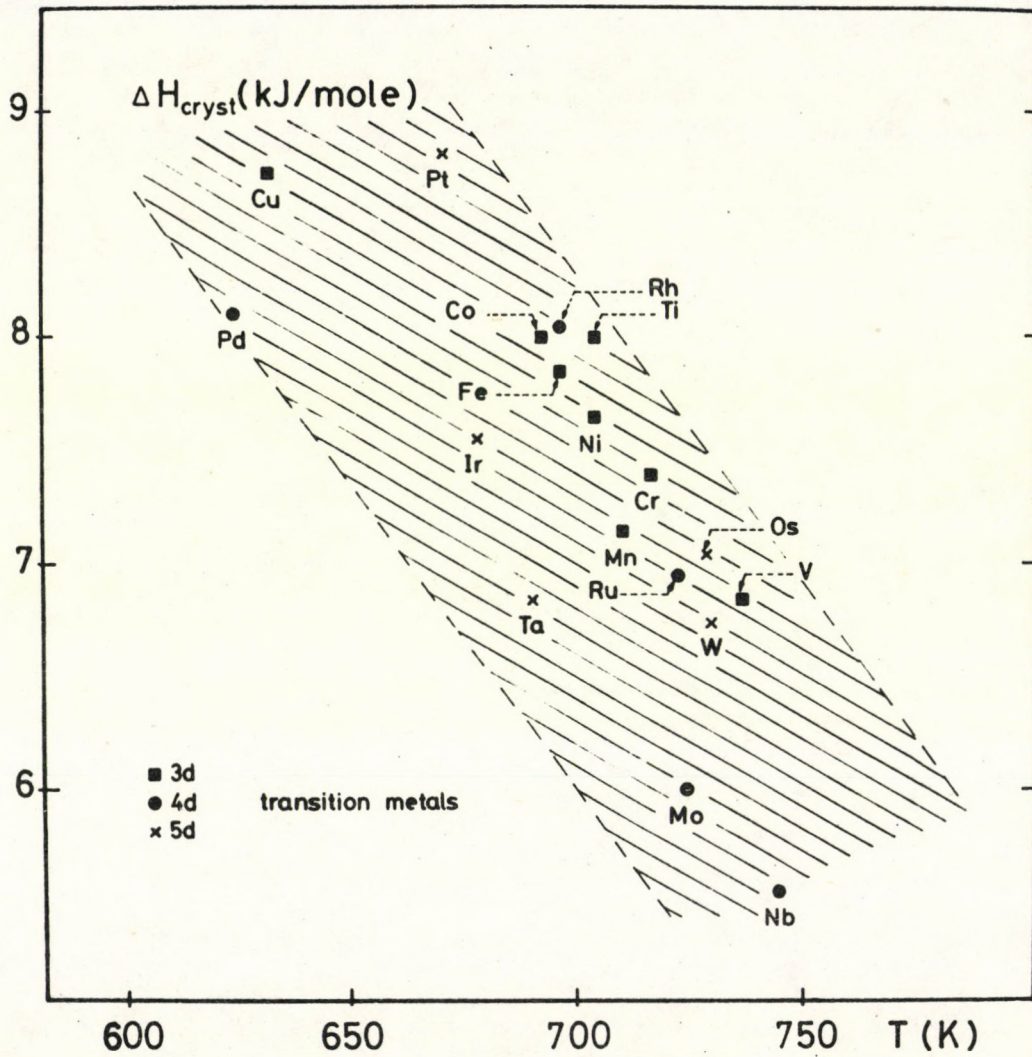

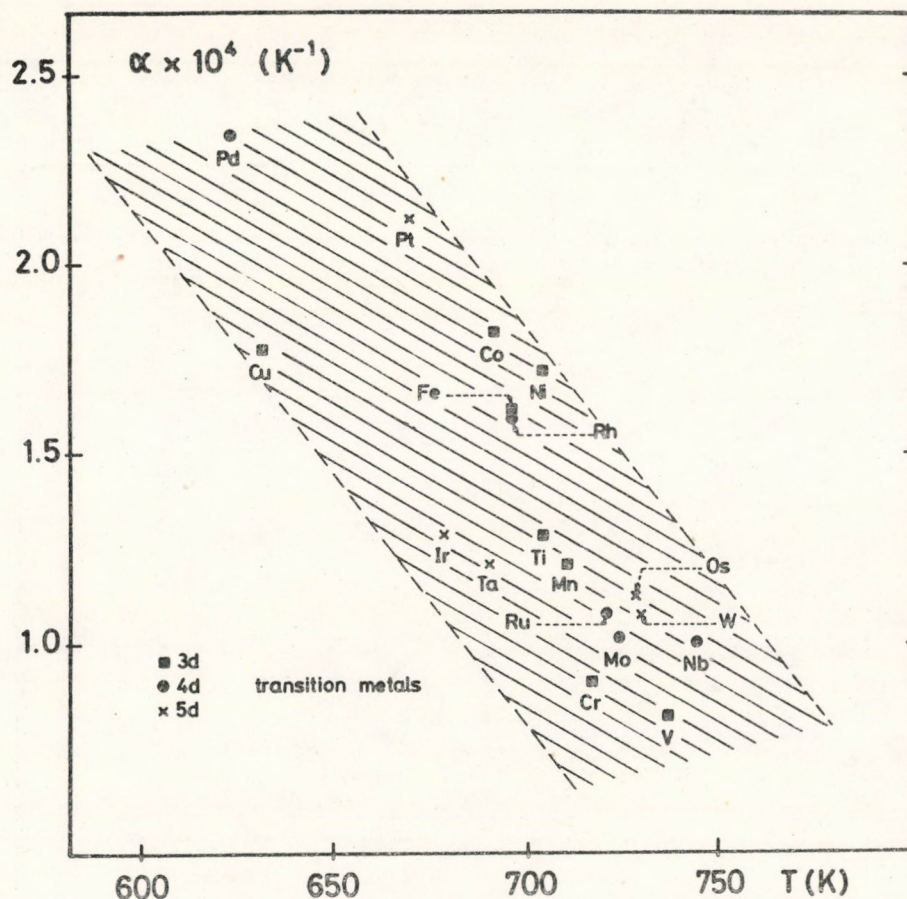Fig. 2. The crystallization energy vs the initial temperature of crystallization.

Fig. 3. The temperature coefficient of resistivity vs initial temperature of crystallization

CONCLUSIONS

1. The number of crystallization steps depends upon the relative valence number in the $Fe_{80}TM_3B_{17}$ quasi-eutectic metallic glasses.

2. There is a tendency-like correlation between the crystallization energy and the initial temperature of the crystallization, moreover a similar connection is detected between thermal stability and the temperature coefficient of resistivity. This behaviour is presented on a great number of alloys changing systematically the transition metal component.

3. The initial temperature of crystallization is effected by the transition metals. The TM-s which have more stable borides than Fe_2B, and high negative mixing enthalpy /H_{mix}/ with Fe increase the crystallization temperature /Nb, Mo, W/. Those, which form borides of nearly the same stability as Fe_2B and have slight negative H_{mix} do not effect on the T_{cryst} /Co, Ni/. The others forming unstable borides and having slight negative H_{mix} decrease the T_{cryst}. These facts suggest that T_{cryst} changes can be correlated with the bonding character of TM-s.

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