HIDDEN TRANSFORMATIONS IN FE-BASED GLASSY ALLOYS, DETECTED BY THERMOPOWER AND MICROHARDNESS MEASUREMENTS

Zoltán PÁL* and János TAKÁCS**

*Department of Vehicles Manufacturing and Repairing,
Budapest University of Technology and Economics,
Bertalan L. 2. 1111 Budapest, Hungary
Phone: +36 1 463 1694
e-mail: pal@kgtt.bme.hu,
**Department of Vehicles Manufacturing and Repairing,
Budapest University of Technology and Economics,
Bertalan L. 2. 1111 Budapest, Hungary Phone: +36 1 463 3466
e-mail: takacs @kgtt.bme.hu

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Abstract

The thermopower (S) measurements were carried out to detect the alloying effect (Cr addition) in Fe-B based glassy alloys. In spite of the single phase nature of the investigated glasses a non-monotonic shift in the thermopower was found versus the Cr-content which hints to the existence of a hidden transformation in amorphous state in the investigated alloys. The mentioned hidden transformation is also supported by the results of subsequent relaxation of heat treatments.

Keywords: hypo eutectic glasses, thermopower, hidden transformation.

1. Introduction

The main structural feature of metallic glasses is their single phase nature and the chemical homogeneity at least on the nanometer scale. This single phase nature manifests the appearance of a typical diffuse, single diffraction ring as structural information arising from the atomic disorder (the absence of crystal periodicity) [1]. However, the existence of chemical and physical short range order can be detected in these materials which is inherited from the structure of melts [2], from which the glass is formed during sufficiently fast cooling. In spite of the theoretical prediction of the physical homogeneity, the existence of anisotropy (arising mainly from the processing variables) can be often detected in many of the physical properties [3, 4]. Chemical inhomogeneity may also exist in certain glasses due to the gradient of quenching rate fulfilled locally inside the bulk of glasses or being induced by the addition of certain alloying elements (compositionally induced clustering in certain nanocrystalline precursors) [5].

Nevertheless, many physical properties can be regarded as a typical single phase manifestation, like the most electronic properties: electrical resistance or the thermopower [6].

In this paper some results will be presented which do support the existence of a hidden transformation in the "single phase" amorphous state of Fe-Cr-B alloys.

2. Experimental: Samples and Measuring Methods

Samples were prepared by melt spinning and planar flow casting [3].

2.1. Technical details of thermo-power measurements:

The thermo-electric measurement is sensitive to the fluctuation of the electron density near to the Fermi level.

In 1822 Seebeck demonstrated that electric current flows in a circuit which contains two different metals between the points „A" and „B" if the temperature of the two points is different T1, T2 ($T_1 \neq T_2$), see *Fig. 1*.

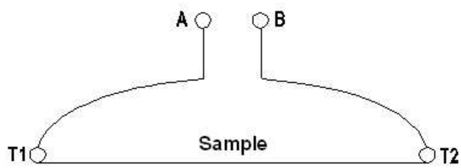


Fig. 1. Thermo-electric circuit

This is the Seebeck effect. The energy of electrons on the heated point is higher. Therefore the Fermi–Dirac distribution of the conduction electrons will modify: a small fraction will rise/get above the Fermi level. The electrons at the hot point on higher energy level want to reduce their energy, so they flow to the cold point. Consequently, the cold point will be negative and the hot point turns to positive, resulting a potential gradient and electric current in the circuit.

During the measurement the material surface will be touched with two different temperature contact points. One of them is the hot, the other is the cold one. The hot point is heated in 20 steps resulting in a gradual (3-7°C) temperature increase beyond the room temperature. The cold contact point is kept on room temperature. The potential is measured between the two contact points (see *Fig. 2.*).

2.2. The Reproducibility of Measurements

In order to ensure the sufficient reproducibility of the thermopower measurements several parallel experiments (See *Fig. 3:* Sign: 1., 2., 3., 4., 5.) were carried out to collect the informations concerning the detection of the alloying effect. Therefore,

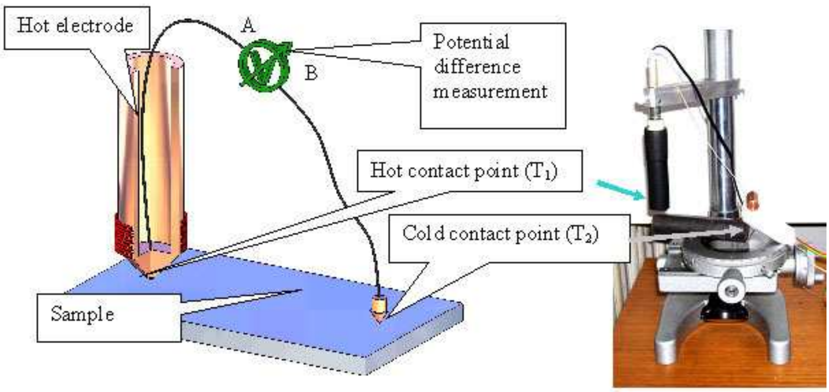


Fig. 2. The measuring principle of the thermopower and the photo of the equipment [7]

reproduction (error) of measurement was carefully controlled on several parallel measurements. The results are collected in *Fig. 3*, which contains several measuring runs carried out on the same series of samples.

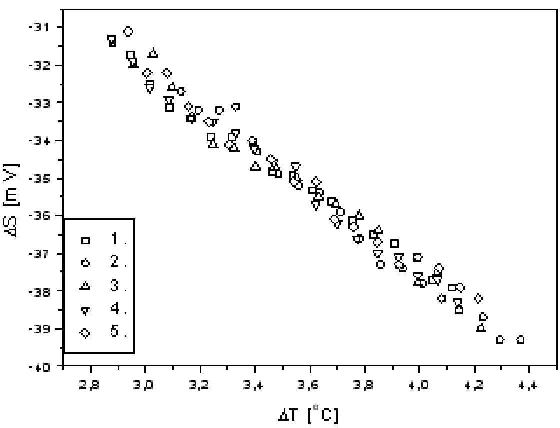


Fig. 3. The scatter of S values during five, independent measuring experiments on $Fe_{75}B_{25}$ sample and the resulting error bar.

3. Results and Discussion

In *Fig. 4* the thermopower (S) is plotted versus ΔT (the temperature difference between the hot and the cold point during the measurements, see in [7]). All of the data in *Fig. 4* refer to various FeB and FeCrB samples, in which the Fe host metal is substituted either by B (metalloid) or by Cr (TM, transition metal). So the Fe $_{100-x}$-B $_x$ alloy is the basic system. The ternaries (with Cr content) are hypo ($Fe_{85}B_{15}$), the binary (Fe_{75}-B_{25}) is hyper eutectic. The common feature of curves is their negative slope. Comparing the curves of $Fe_{85}B_{15}$ and $Fe_{75}B_{25}$one can recognize the significant shift towards the direction of negative S values due to the decreasing host metal content. As the B-content increases the d-electron density decreases at the Fermi level. Simultaneously, the covalent bonding character is also strengthened, what can be experienced in several mechanical properties [3]. The directions (sign) of the shift for S values due to the B-content increase in the case if binary curves are in qualitative agreement with [8].

On the other hand, when the host metal is replaced by Cr, (C_B is constant) the degree of the sp hybridizations can be supposed the same, hence the d-electron concentration (d electron/atom ratio) gradually decreases; a monotonic change in the thermopower would be also expected, as the Cr-content increases. This is not that case, however. The shift of S is positive in the low concentration range of Cr, then it turns to the opposite direction when the Cr content exceeds a critical value. There is no information about the exact value of the saddle point at present (concentration at which the change in sign occur). In order to support further the reproducibility plotted in *Fig. 1*, isothermal heat treatments were carried out on the same samples at 250 ^{0}C for various times (isothermal heat treatments). The results are summarized in *Figs. 4-7*. The slope of the curves remains the same. Again, the reversal of the sign versus the Cr-content can be observed in all cases. There is no significant influence of the applied heat treatments on the relative position, and on the slope of curves. Hence, the extraordinary concentration dependence of the curve position shown in *Fig. 3* is further supported by the results in *Figs. 4-7.* Based on the outlined results, the existence of a hidden structural change in the amorphous state is suspected at a critical value of Cr content.

The trace of crystallization can be excluded at this temperature. Structural relaxation of the glassy state takes place only, if short range atomic rearrangements occur (without long range diffusion, leading already to crystallization). The absence of crystallization is clear, when the sequence of S curves is compared (the slope and the concentration dependence). Only a small shift into the negative direction was observed due to the heat treatments, mainly on the binary samples.

It is remarkable, that both the reversal in the shift of S within a narrow concentration range (at low Cr content!) and other extraordinary property changes were noticed in these alloys. Similar discontinuity can be also observed in the crystallization temperature, enthalpy and the hardness change as it is illustrated in *Figs. 8-9* [9].

One can see that the rapid change in these properties is typical in the range

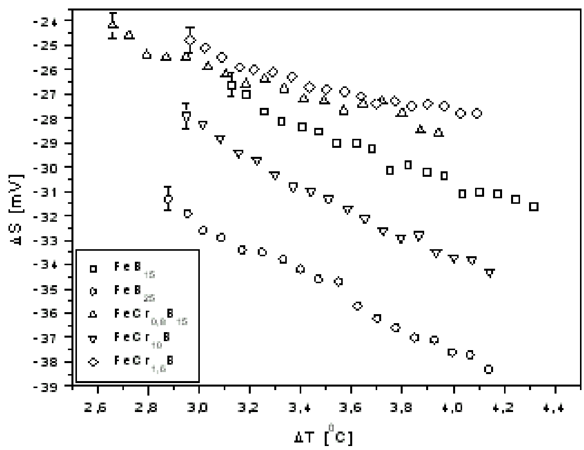


Fig. 4. Thermopower (S) for the $Fe_{100-X}B_X$, and $Fe_{85-X}Cr_XB_{15}$ as received samples

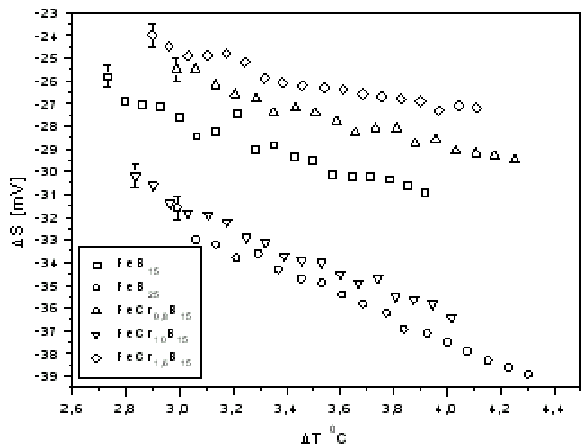


Fig. 5. Thermopower (S) for the $Fe_{100-X}B_X$, $Fe_{100-X}Cr_XB$ samples after heat treatments at 250 ^{0}C for 1 hour

of low Cr only. Beyond 4 at % Cr content the microhardness do not, or only slightly altered with the Cr content indicating, that besides the d-electron density

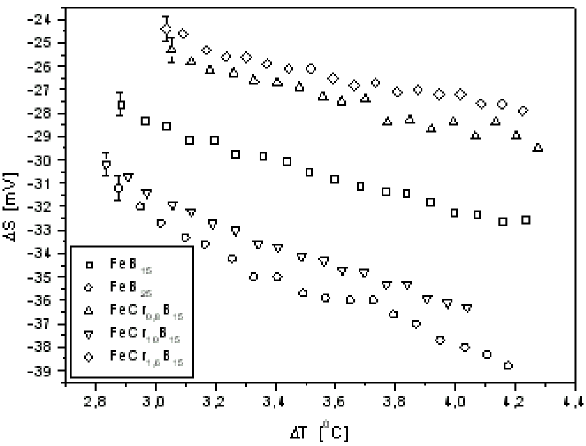


Fig. 6. Thermopower (S) for the $Fe_{100-X}B_X$, $Fe_{100-X}Cr_XB$ samples after heat treatments at 250 ^{0}C for 2 hours

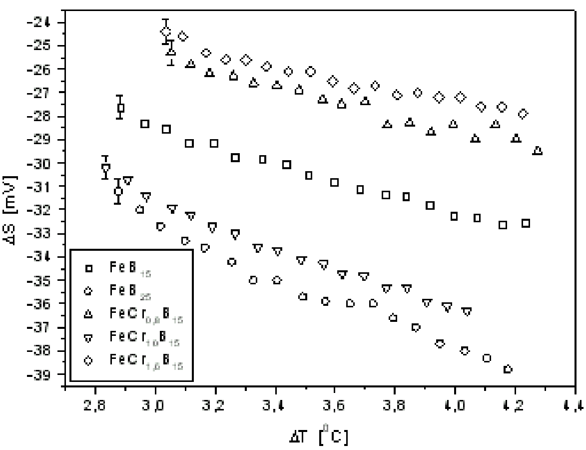


Fig. 7. Thermopower (S) for the $Fe_{100-X}B_X$, $Fe_{100-X}Cr_XB$ samples after heat treatments at 250 ^{0}C for 24 hours

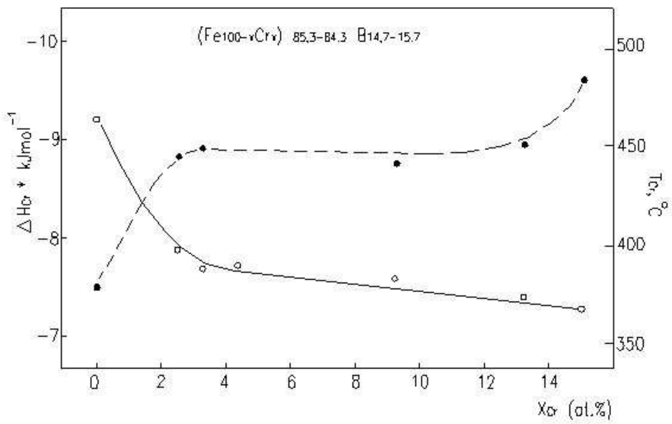


Fig. 8. Crystallization enthalpy, ΔH_{Cr}, crystallization temperature T_{Cr} hypo-eutectic Fe-Cr-B glasses ($14{,}7<X_B<15{,}7$ at.%) [9]

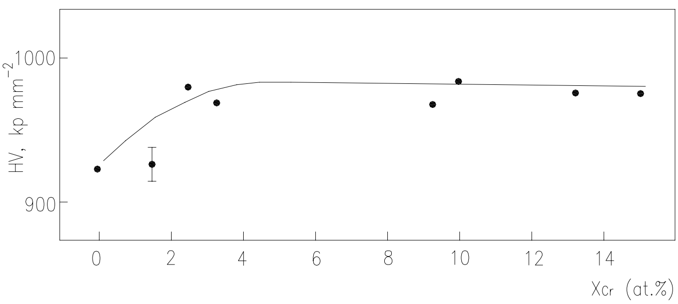
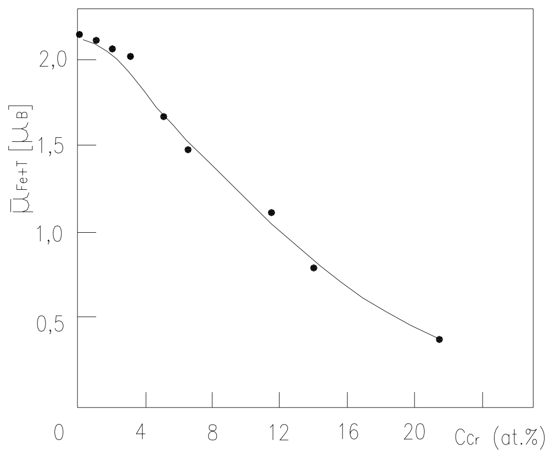


Fig. 9. Microhardness for hypo-eutectic Fe-Cr-B glasses ($14{,}7<X_B<15{,}7$ at.%) [9]

change, structural factors must also be taken into account, in the proper description of the evolution of these properties. The thermal stability (characterized by the crystallization temperature).

Discontinuities in the basic compositional dependent magnetic properties were also detected in early papers [10]. These results are cited in *Figs.* **??**. and 11. In *Fig.* **??** the magnetic moment/Fe atom is plotted versus the Cr concentration. The break of this curve at around 3-4 at% Cr is obvious. In *Fig. 10*, the exchange constant (responsible for the strength of ferromagnetic coupling) versus the Curie temperature is illustrated by the same authors. The concentration dependence of both quantities can be described by two, linear relation. The cross-section of the two curves lies also at around 3-4 at % Cr content, indicating the existence of two structural regions, in which the slope of property changes is different.



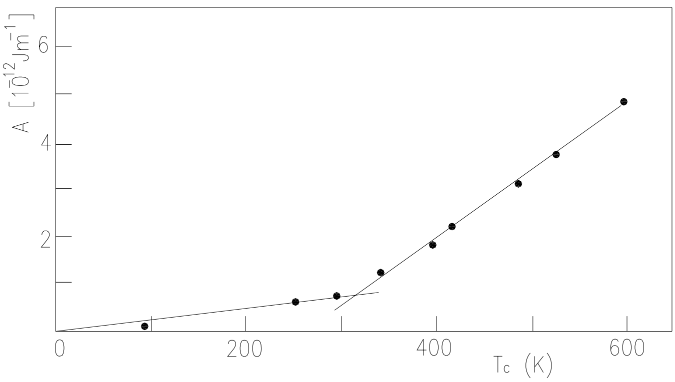


Fig. 10. Exchange constant as a function of Curie temperature for Fe-Cr-B [10]

4. Summary

Analysing the thermopower diagrams one can see that the sufficient reproducibility (error) of the thermopower measurements were carefully controlled on several parallel measurements. The thermopower diagrams show that a hidden structural change in the amorphous state is suspected at a critical value of Cr content. The curves of the hypo- and hyper eutectic Fe-based glassy alloys have got negative slope with a small shift into the negative direction due to the heat treatments, mainly on the binary samples.

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