# THE STUDY OF TRANSFORMATIONS IN GLASSY AND CRYSTALLINE ALLOYS USING THERMOELECTRIC POWER MEASUREMENTS

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## ABSTRACT

*Thermo-electric power (S) measurements were applied to detect the compositional change in $(FeNi)_{80}B_{20}$ glasses. It was found, that S does not alter monotonically with the Ni content, which hints to the existence of a hidden structural change in amorphous state. The S measurement was also applied to detect non-diffusive (martensitic) phase transformations in crystalline FeNi alloys.*

***Keywords:*** *non-destructive, TEP, thermoelectric power, FeNi, amorphous*

## 1. INTRODUCTION

The measurements of thermoelectric power (TEP) have been succesfully applied for nondestructive testing of several metallic materials, e.g. TEP scan has been used recently for monitoring the integrity of welds in multicomponent „INCONEL” alloy by plotting several S(x) scans on the surface of the joined metallic plates, across the seam [1]. TEP measurements have been recently also proposed for estimation of the degree of quench-hardening in simple carbon-steels. Correlations have been reported between the degree of quench hardening and the TEP value [2]. Here the samples were compared after various heat treatments where the cooling rate was systematically altered.

Since the chemical composition of the samples was identical during these experiments, the only reason of the dramatic change in S(T) could be only the change in the ratio of phase. As a consequence, the separation of compositional (chemical) and structural factors (ratio of phases) is inevitable for the correct understanding of S(T) evolution. An early attempt to overcome the outlined difficulties was made in [3], approaching this problem from the TEP characterisation of metallic glasses. These materials are inherently of single phase nature. On the other hand, the chemical composition can be altered in a wide range without affecting single phase character of material that makes possible to study compositional effects easily. Continuing the earlier activities described in [1,2] further measurements were carried out on various pure metals and on $Fe_xNi_{1-x}$ crystalline alloys as reference samples in order to reveal the metallurgical background of these measurements.

Although the above mentioned measurements were carried out successfully, TEP is not a popular material testing method because it is difficult to assign the results obtained by this method to the structural properties of material. Actually this is the reason why this material testing method is still in the background.

At the same time this method offers attractive opportunities for the examination of complex physical conditions. Non-destructive material testing methods provide mostly qualitative material parameters and they are used predominantly in the cases where the applications of destructive material tests are expensive or impossible.

## 2. BASE MATERIALS

Prior to the measurements, the samples were embedded into DENTAKRYL resin. Subsequently, the surfaces were cleaned and polished, in order to provide thermal contacts between the electrodes and the investigated samples.

## 3. METHODS

The TEP measurement is sensitive to the fluctuations of electrons which are around the Fermi surface. In 1821 Seebeck discovered that the metals respond differently to the temperature difference that creates a current in a closed conductive loop.

If a closed conductive or semiconductor loop is built from two different materials then an applied temperature difference releases charge carriers in the materials (electrons in metals, electrons and holes in semiconductors, ions in ionic conductors) and they diffuse in material. Hot carriers diffuse from the hot end to the cold end, since there is a lower density of hot carriers at the cold end of the conductor. Cold carriers diffuse from the cold end to the hot end for the same reason. This phenomenon is similar to the gas that expands when heated. If the conductor were left to reach thermodynamic equilibrium, this process would result in heat being distributed evenly throughout the conductor (see heat transfer). The motion of heat (in the form of hot charge carriers) from one end to the other is called a heat current. Since it is motion of charge carriers, it is also an electrical current.

In a system where both ends are kept at a constant temperature difference (a constant heat current from one end to the other), there is a constant diffusion of carriers. If the rate of diffusion of hot and cold carriers in opposite directions were equal, there would be no net change in charge. However, the diffusing charges are scattered by impurities, imperfections, and lattice vibrations (phonons). If the scattering is energy dependent, the hot and cold carriers will diffuse at different rates. This creates a higher density of carriers at the one end of the material, and the distance between the positive and negative charges produces a potential difference; an electrostatic voltage.

During the measurement the surface of the material is touched with two individual copper contactors. One of them is the hot point of the above mentioned measuring loop, and the other one is the cold point (see Fig. 1). The hot point is heated up to the temperature difference of 3-7 ºC with respect to the cold point. During the warm up the electronic system is sampling, and measuring 20 different TEP values at 20 different temperature differences. The cold point is at room temperature.

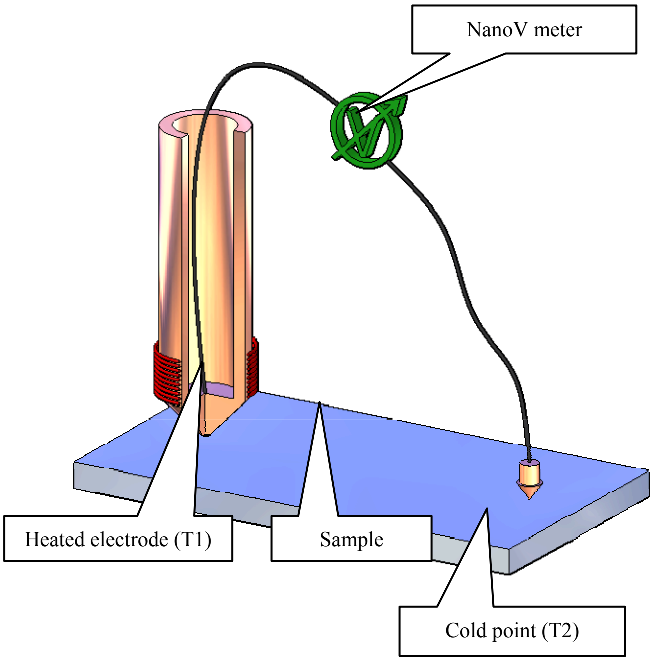

**Fig. 1** The principle of the TEP measurement and the scheme of the experimental setup

The results obtained by this measuring system depend neither on surface quality nor the distance.

### 3.1. Results

The results obtained for amorphous $Fe_{80-x}Ni_xB_{20}$ alloys in “as quenched” state (without heat treatment) are presented in Fig. 2. It is important to mention that the S does not exhibit monotonic change versus the Ni content. Slight shift into positive direction is observed between the 10-50 at% Ni-content, which is in contrast to the fact, that Ni has definitely negative S character (in contrast to the pure Fe with positive S). The TEP values of the base elements in crystalline state are either positive or negative. One should take into account that metalloid content (B) is the same in these alloys, and that the Fe/Ni ratio changes only. As can be seen in Fig. 2 increasing Ni content causes increasing TEP value. On the other hand, if we take into account, that S is significantly negative when Ni content is 70% in alloy system, one can expect, that singularity exists between the two concentration ranges. The reason can be a hidden phase reminiscence in amorphous state, similar to that reported in [4].

After 15 hours of isothermal heat treatment there is no significant change in the tendency of TEP values measured in $FeNi_{10}B_{20}$, $FeNi_{40}B_{20}$, $FeNi_{50}B_{20}$.glasses, only the TEP value for $FeNi_{70}B_{20}$ changes significantly.(Fig. 3) The S values shift in positive direction, however, not only the absolute value is changed but also the slope of the curve is decreased. The reason is the following: the crystallization has already started because the thermal stability is lower in the Ni-rich sample. If only structural relaxation takes place during heat treatment, the S shifts slightly in negative direction. This effect is observed in several Fe and Ni based glasses. The reason is not clear so far.

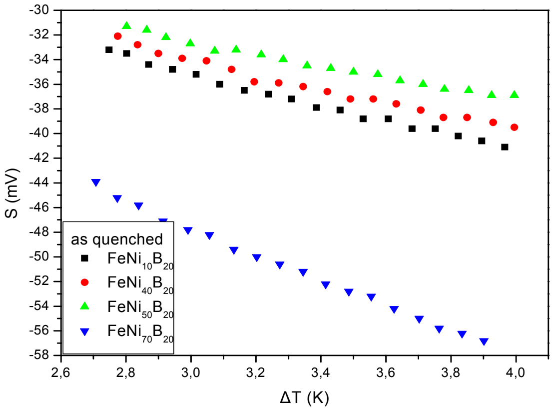

**Fig. 2** $FeNi_{10}B_{20}$, $FeNi_{40}B_{20}$, $FeNi_{50}B_{20}$ $FeNi_{70}B_{20}$ as quenched

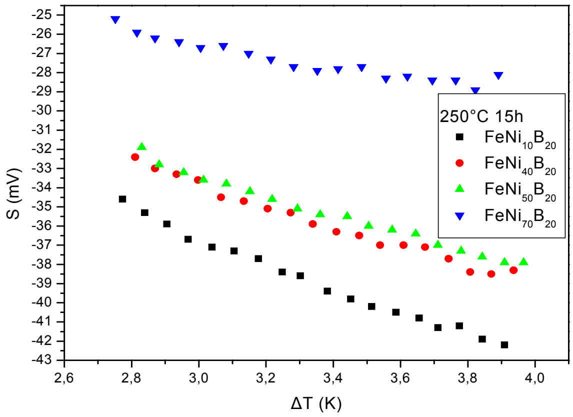

**Fig. 3** $FeNi_{10}B_{20}$, $FeNi_{40}B_{20}$, $FeNi_{50}B_{20}$ $FeNi_{70}B_{20}$ heat treated

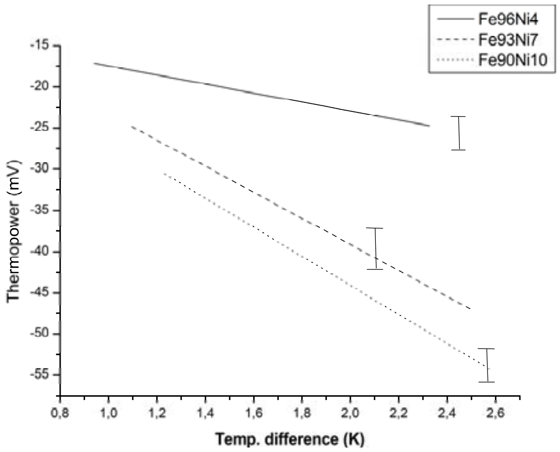

**Fig. 4** Thermoelectric power of $Fe_xNi_{1-x}$ alloys after slow cooling

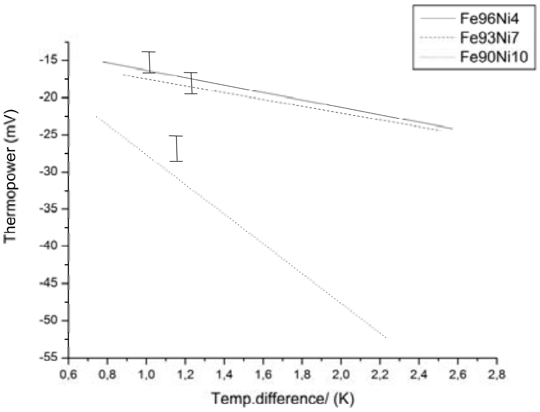

**Fig. 5** Thermoelectric power of $Fe_xNi_{1-x}$ alloys after quenching (water quenching)

In Ref. [2] the role of phase ratios on the S(T) was studied in simple carbon steels. Accordingly, the S(T) significantly altered due to the change of the ratio of phases at a fixed steel-composition that made possible to deduce thermal history of steels (non-destructive detection of quench-hardening).

Both the slope and the (S) is positive in this type of (Fe-based) alloys being in qualitative agreement with [5]. On the other hand, the S(T) curves shift to negative direction by applying increasing quenching rate, when the increasing fraction of martensite or the residual austenite phase formation is expected. Similar experiments were performed in the present work in various FeNi alloys as it is illustrated in Fig. 4 and 5. The S(T) was determined on FeNi4, FeNi7 and FeNi10 crystalline alloys after austenization at 900 ºC by applying slow cooling rate, or water quenching respectively.

Fig. 4 shows the thermoelectric power of the above mentioned alloys, on which slow cooling rate was applied after 900 ºC preheating (austenization). The (S) value shifts gradually into negative direction with increasing Ni content. Note, that not only the absolute value of (S), but also the slope of S(T) exhibit gradual increase with increasing Ni content. This tendency is common with the tendency depicted in Fig. 2. This tendency depends not only on the compositional change but also the phase ratios are reflected in the results of measurements, especially when the Fig. 4 and Fig. 5 are compared.

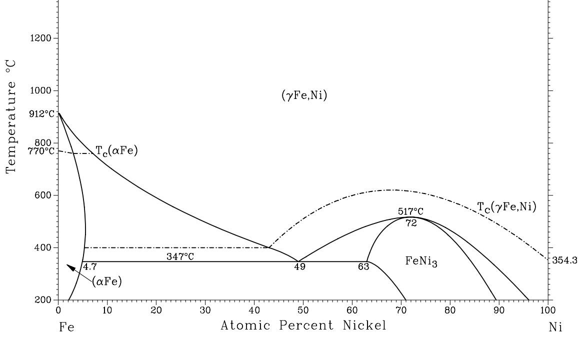

**Fig. 6** Fe Ni phase diagram

Neither the value of (S) nor the slope of S(T) is affected by the change of cooling rate (slow cooling to room temperature or water quench) using $Fe_{96}Ni$ alloy. The sample $Fe_{96}Ni_4$ is in α-phase, because at this composition this phase is stable according to the Fig.6. It means that no phase transformation occurs at 900 ºC (autenization). In the case of $Fe_{90}Ni_{10}$, the /S/ changes slightly. The change is negligible. However, the probable reason is the insensitivity of the $\alpha \rightarrow \gamma$ (diffusionless) transformation to the applied cooling rate, i.e., in FeNi10 alloy extremely slow cooling rate (such as 3-5C/h) is required to get stable phase distributions. In our experiment, higher (40C/h) cooling rate was applied, so consequently non stable phases come up in Fig. 4 as much as in Fig. 5. Testing the sample $Fe_{93}Ni_7$ shows that after quenching the slope of the TEP curve is much lower than after applying low cooling rate. The reason why this result turned up is the low but sufficiently high Ni content. Using low cooling rate a stable phase structure was developed. If the cooling rate is fast enough, the given phase is not stable. In other words in the $Fe_{93}Ni_7$ sample the $\alpha \leftrightarrow \gamma$ transformations proceed more rapidly in each direction allowing to gain different $\alpha/\gamma$ ratio within the applied range of cooling rates.

## 4. SUMMARY

The results of thermoelectric power measurements reported in this paper confirmed that this method can be used for detection of compositional change in the glassy state, which is of a single phase in nature. It was also proved that this method is sensitive enough to detect the phase transformation such as the amorphous phase - devitrification. It is also useful to follow martensitic transformation in crystalline Fe-Ni, i.e, when composition of material does not change.

## ACKNOWLEDGEMENTS

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## BIOGRAPHIES

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**Antal Lovas** was born in 1938. In 1967 he graduated from Eötvös Lorand University as a chemist. Then he spent a year at FORTE in Vac. In 1967 he got a new position in the Central Physical Research Institute at the Department of Solid State Physics (MTA SZFKI). Since then he has been working in the field of unstable and glassy alloy systems. In 1989 he got PhD. degree. Since 1994 he has been working at the Budapest University of Technology and Economics Department of Transportation Engineering, since 1997 in position of associate professor.
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