



Composition, phase relations and stress state monitoring in technical alloys by thermopower measurement

booklet of PhD theses

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INTRODUCTION

The central phenomenon of thermoelectric power measurement (TEP) is the Seebeck effect, which is originally defined as a potential difference between the hot and cold junctions of bulk macroscopic conductors, according to the scheme in Fig.1. [1]

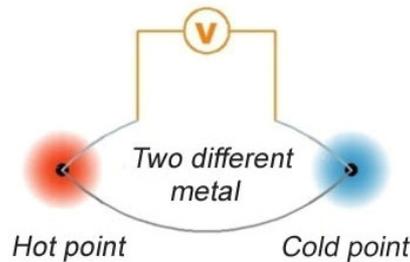


Fig. 1. The schematic arrangement for the detection of Seebeck coefficient (S) between two dissimilar metals [2]

This phenomenon is widely used over the past decades to measure temperature. Recently it is also applied as a non-destructive material testing in the engineering praxis: The thermoelectrical properties of thin films also have great theoretical and practical interest, by means of the information they offer about the material's transport properties and also about the possibilities of using them for thin-film sensors and transducers. [3, 4, 5]

TEP scan was recently used for monitoring the integrity of welds in multicomponent „INCONEL” alloy by plotting several $S(x)$ scan on the surface of the joined metallic plates, across the seam. [6]

TEP measurements were also proposed for judging the degree of quench-hardening in simple carbon-steels. Here the samples were compared after various heat treatments where the cooling rate was systematically altered. As the chemical composition of the samples was identical during these experiments, the only reason of the dramatic change could be the consequence of the change in phase relations only. [7]

In spite of the reported applications, still several details are open. There are still openings in the field of understanding the metallurgical background associated with this measuring method. There are also openings in the understanding of the contribution of phase relations and also the stress level of the measured sample. The significance of surface qualification also needs further re-investigations.

MEASURING ARRANGEMENT

The TEP measurement is sensitive to the thermal fluctuations of electrons which are around the Fermi surface. Seebeck discovered that the metals respond differently to the temperature difference, that creates a potential difference between the two junction of a conductor loop built from two different metal. [1]

If a closed conductive or semiconductor loop is built from two different materials, then an applied temperature difference releases charged carriers and they diffuse in material. 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 chargers 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. [8, 9]

To measure the Seebeck coefficient either dc or ac method are generally used [11], [12] and [13]. The dc method [10] is a relatively easier method for the transport measurements, which is used here to determine the Seebeck coefficient. In this technique a thermal gradient is established along the sample and both thermoelectric voltage (ΔU) and temperature difference (ΔT) across the length of the sample are measured. The Seebeck coefficient is calculated from equation(1) [15]:

$$S = \lim_{\Delta T \rightarrow 0} \frac{\Delta U}{\Delta T} \quad (1)$$

The principle of measuring the Seebeck coefficient is shown in Fig. 2.

Thermal gradient is generated by producing a temperature difference, across the sample. To produce the thermal gradient the temperature of the heaters raised slowly, typically at a rate of 2°C/min, which allows the steady state condition to be sustained during data collection and negate the error arising

from temperature drift. Thermometer attached to the copper block very close to the sample faces indicates the temperature T_1 and T_2 .

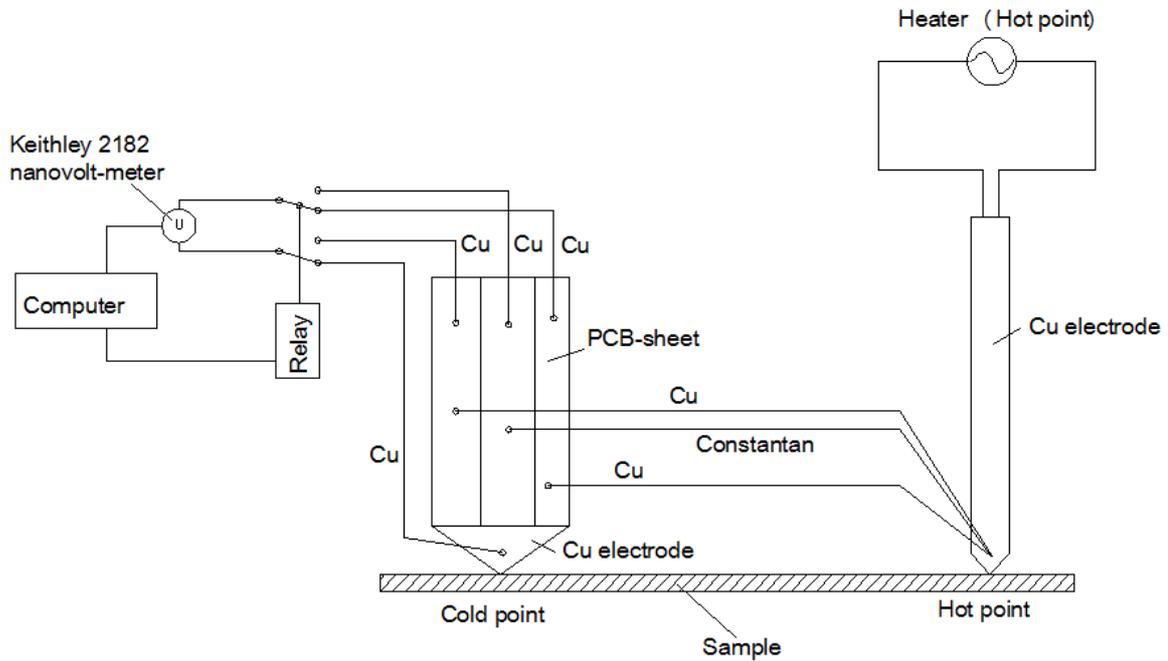


Fig. 2. The applied measuring system during the investigations

To measure the temperature Kiethley 2182 nanovoltmeter is used by which thermocouple signal can be converted directly into temperature values. Due to the temperature difference of $\Delta T=T_1-T_2$ a voltage ΔU_s is developed across the sample. To measure thermpower across the same Kiethley 2182 voltmeter is used.

RESULTS

The influence of the electron structure on thermopower

The thermopower of some selected metals and semi-metals

For the extension of the mapping of thermopower measurements, measurements were carried out on various pure metals and on $\text{Fe}_x\text{Ni}_{1-x}$ crystalline alloys as reference substances in order to reveal the metallurgical background of these measurements.

There are two possible ways to characterize the reference metals: in one hand, based on the sign of S (Seebeck coefficient, calculated from equation (1)) and in the other hand, based on the value of $|S|$. Now the discussion is continued by the distinction based on the sign of the individual slope.

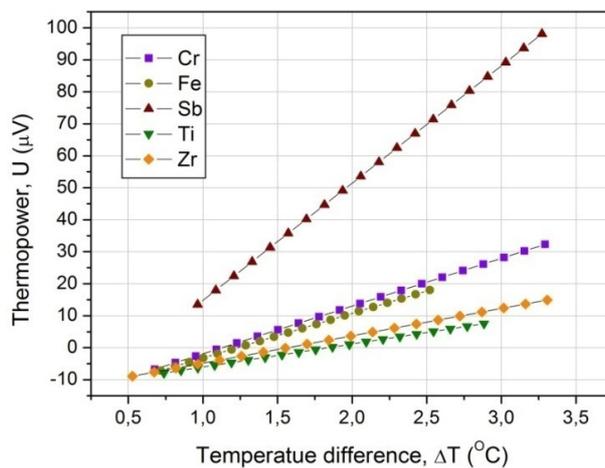


Fig. 3. Thermopower of different base elements versus the thermal gradient (ΔT) (positive slope)

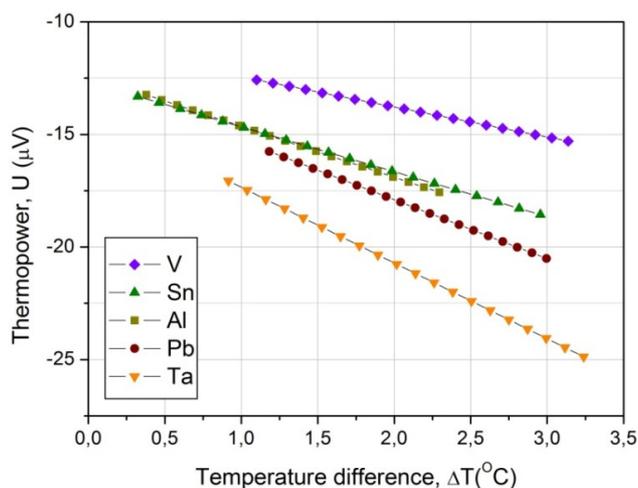


Fig. 4. Thermopower of different base elements versus the thermal gradient (ΔT) (negative slope)

The extremely small value of $|S|$ was found in those metals in which the s character is dominant in the valence electron structure. (see Al, Pb, or Ag, Cd). Slightly higher $|S|$ was observed by measuring $3d$ -metals in which both the s and d -electron state participate in the valence electron structure. It is remarkable however the slope of Ti, Cr, and Fe is the opposite (positive) of the slope of the Ni or Co (negative). This phenomena is probably connected to the increasing fraction of d -electron density in the valence band.

Finally, an extremely high slope can be observed in those metals (Bi or Sb), which exhibit higher electronegativity than the metallic average. In these metals an increasing participation of p -electron state in the valence band is typical.

It was found, that the slope of the S curve is negative, when $\Delta G_{(M-Cu)} \sim 0$, i.e the heat of mixing is nearly no-zero, but negative. This is the case of the formation of continuous series of solid solutions between two elements. In these interactions the heat of alloy formation is negligible, consequently, the contribution of entropy becomes significant in the total free energy change at mixing. These type of phase diagrams often exhibit ordering or the formation of intermetallic compound-like phases at low temperatures.

Opposite to the previously outlined cases, the another type of slopes are positive. This type of behaviour can be observed, when the mutual solubility between Cu and M is limited at low temperatures (in phases, stable at low temperatures) but increasing with rising temperature. The heat of mixing is substantial and negative in such interactions ($\Delta G_{(M-Cu)} < 0$) (Cd, Fe, Ti,). The appropriate phase diagrams are usually eutectic, containing also intermetallic compounds.

The influence of alloy content on thermopower in the single phase region

Studying the manifestation of alloy formation in the evaluation of thermopower, the Fe-Ni system was chosen because of the well known and simple phase relation. The composition dependence is studied in wide range Fe/Ni ratio both in crystalline and glassy state.

An interesting example, how the TEP is altered when a solid solution is formed. In Fig. 5. the result of Fe replacement by 4 and 7 at% Ni is illustrated. The bcc (ferritic) α -phase inherited from the Fe.

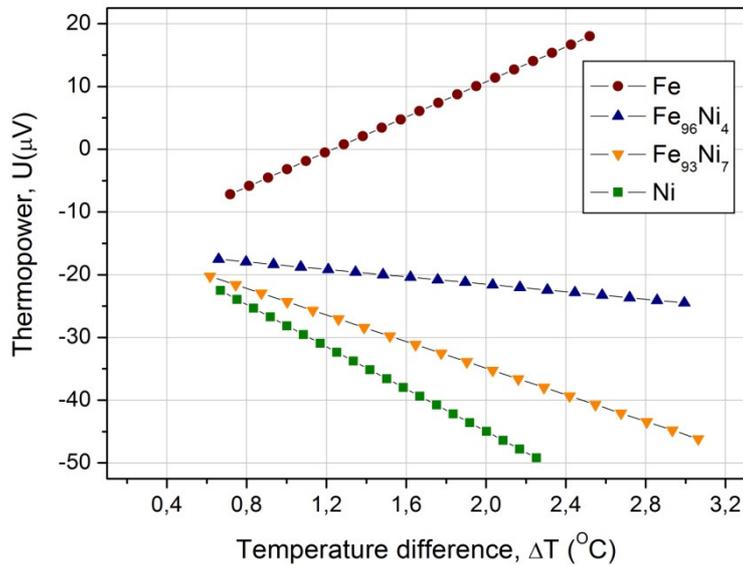


Fig. 5. Thermopower of crystalline Fe and Ni, $Fe_{96}Ni_4$ and $Fe_{93}Ni_7$ α -phase (bcc) solid solution

The electronic structure of Fe and Ni is similar. In spite of this, the sign of S is opposite for the two metals. The decreasing difference in $|S|$ in this range hints also to the similarity of band structure of these metals. Dramatic change of S (sign and $|S|$) can be observed, when 4 or 7 at% Fe is replaced by Ni. (Fig. 5.) The d-electron density (e/a) increases during the formation of this solid solution together with the increase of electron specific heat [14]. The α -phase is stable below this concentration range, (which is also supported by the X-ray check). It means that only the change in the electronic structure is responsible for the pronounced change of the thermopower.

The influence of phase transitions on thermopower

It was found, that investigating the FeNi alloys, the S-composition curve exhibits a minimum at around the formation of FeNi₃ compound phase. It is interesting to note, that the shape of the curve resembles to the character of heat of mixing curves. It is remarkable, that the concentration dependence of electrical resistance also exhibit maximum at around these concentration range. These behavior also typical for solid solutions.

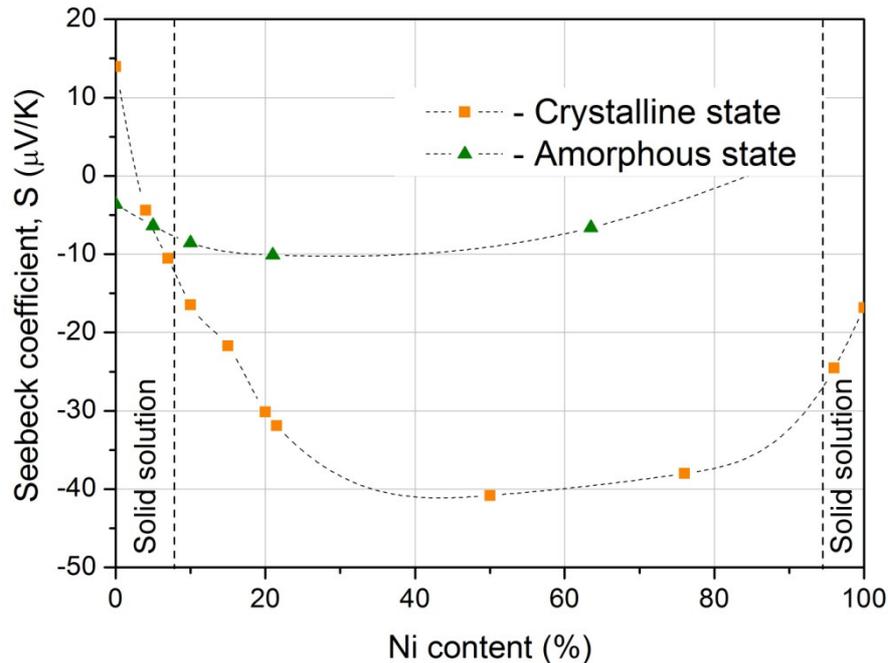


Fig. 6. The evaluation of Seebeck coefficient in the case of crystalline and amorphous phase alloys

The first remarkable feature of S is the rapid drop in the diluted concentration regime (both sides) taking a look on Fe-Ni crystalline curve. The Fe-side, three points – including the pure Fe lies in the ferrite range (bcc solid solution) – S drops rapidly with the concentration (solid solution). At the opposite (Ni) side the slope of S(T) curve is less steep and – opposite to the Fe-side – starts from negative value (pure Ni). So in the diluted region the alloying effect is not symmetric: it means, that alloying effect in the fcc or in bcc solid solution is not equally strong even in the case of the identical alloying partners.

It is also important to make clear the huge difference between the thermopower of amorphous and crystalline phase alloys near the same composition.

The value of S is composed by the density of occupied electron state at the Fermi level and also depends on the Fermi energy, which has a crystal structure dependence. In the single phase region the electron density (which is mostly determined by the concentration of solute element) has a dominant role. In the two phase region both phases are represented by individual Fermi level (different crystal structure).

Hence the total energy of electrons is distributed between the Fermi energy of the individual phases. It means, that both the magnitude and the net slope of TEP curve will depend on the individual density of states in the coexisting phases.

The influence of internal and external stresses

It is well known, that the hardness of Fe and the low-alloyed carbon steels (Fe-C alloys mainly with pearlitic structure) increases either by cold working (work hardening) or via rapid quenching (quench-hardening). Although, both types of hardening are bulk effects and their mechanisms are different. The origin of work hardening is essentially a dislocation pile up mechanism. In contrast, the quench hardening is induced by phase transformations (the tendency of increasing martensite phase formation is supported by the literature) where the generated internal stress is responsible for the hardness increase.

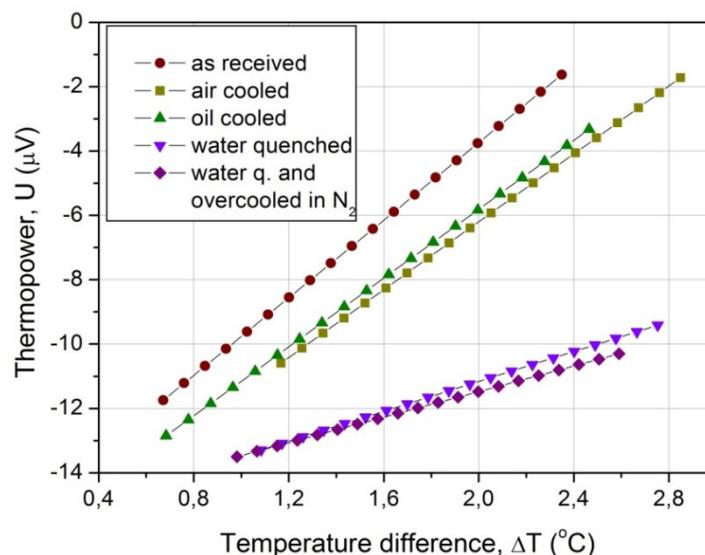


Fig. 7. Influence of heat treatment on the evaluation of thermopower in C70S6 steel

The thermopower shift clearly demonstrates the simultaneous contribution of phase transformation and the stress level increase in the quench hardening process. (see Fig. 7.)

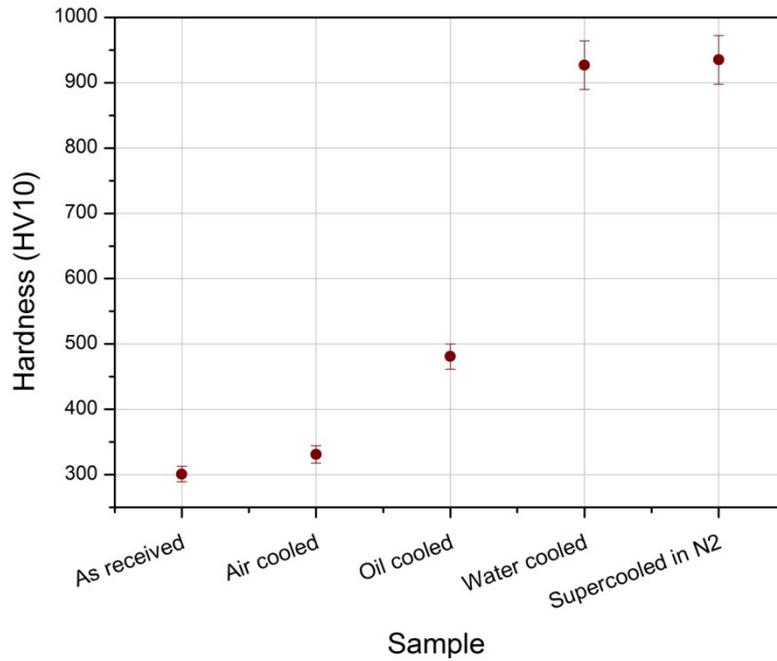


Fig. 8. The evaluation of micro hardens versus the cooling rate in C70S6 steel

The same increasing bulk stress state is clearly reflected in the trend of micro hardness values, measured on the same sample. (see Fig. 8.) In this case, the resulting S change (gradual shift to negative direction), is a result of two effects: phase transformation and induced stresses.

A complex study of surface fatigue in carbon steels, caused by rolling contact and sliding friction

The formation of macroscopic defects (cracks) near the surface of structural elements – suffered either by rolling or sliding processes – has an outstanding economic and safety significance. Therefore, the discovery (localization) of these defects – which mostly appear as microscopic crack formation (Fig. 9.) – has great practical interest.

Most of crack-detection methods are based on direct, optical observation. Only a very few experiments are based on indirect measurements, which are able to discover principally the embryonic state of crack formation or even the pre-existing stress accumulation, which would be fruitful in the avoidance of catastrophic breaking phenomena. In the present contribution a complex study is proposed, where thermopower and static coercive force measurements, as well as micro hardness measurements were performed, and the results are compared. On this basis the very early state of damage evolution can be recognized.

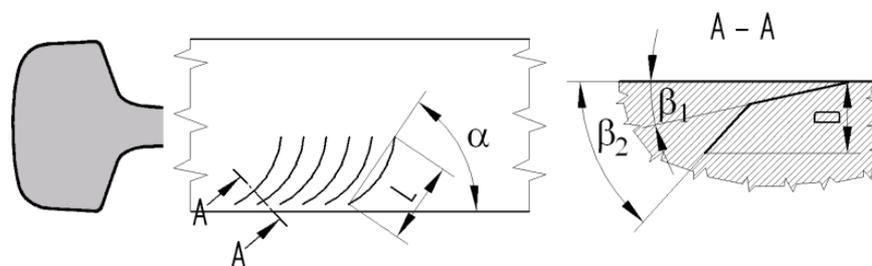


Fig. 9. Typical arrangements of crack formation, induced by rolling contact deformation
(A-A section: the crack propagation in the material)

Fig. 9. shows, that cracks are developed on the surface layer due to work hardening. Simultaneous coercive force (H_c) increase can be detected across the sample, depending on the rate of degradation. It is visible that right before crack formation, the H_c value suddenly increases (Fig. 10).

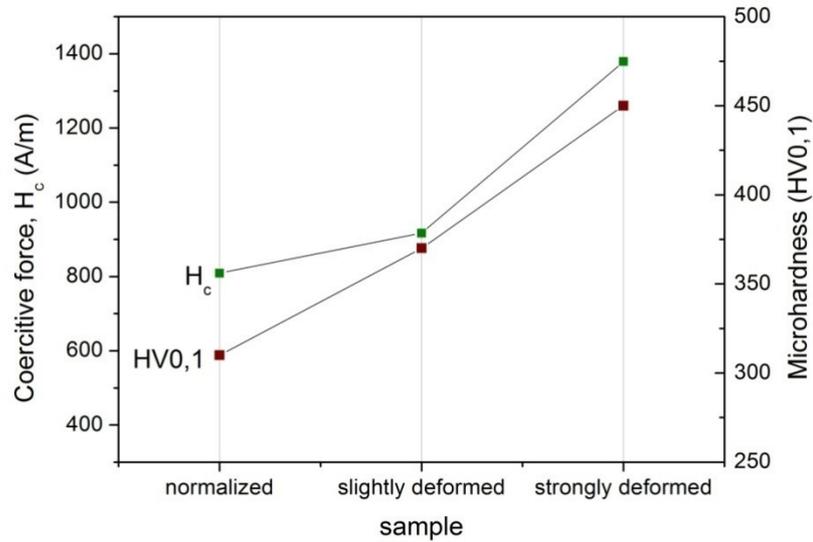


Fig. 10. The static coercive force and microhardness versus the deformation rate

The work hardening can also be supported by HV measurements, which was performed on the cross-sectional area of the sample (Fig. 10).

According to the metallographic micrograph, visible structural change can also be detected in the vicinity of surface along the rolling track.

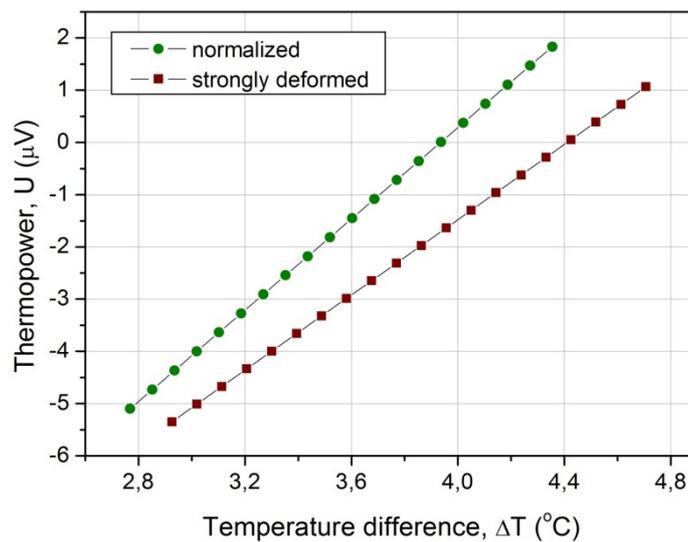


Fig. 11. The evaluation of thermopower versus the deformation rate

Fig. 11. shows, that parallel to the increasing H_c and microhardness values, there is a negative $S(\Delta T)$ shift in the thermopower.

THESES

Based on results achieved in the thermopower measurement of crystalline and amorphous alloys, the following thesis are formulated:

1. The effect of surface roughness and surface deformation on the evaluation of thermoelectric power has been determined: It was found that the surface roughness has no direct effect on the evaluation of thermoelectric power. If there is a local work hardening in the surface layer, then it is reflected in the results of the thermoelectric power. The reason is a local change in the electron free path due to work hardening. [S2, S9]
2. During the examination of metallic and semi-metallic elements the influence of electronic structure on the thermoelectric power has been determined: The evaluation of thermoelectric power depends on the electron density of states at the Fermi level. TEP is specifically determined by the s and p orbitals, but especially by the saturation of d orbitals. [S1, S10]
3. In crystalline phase FeNi alloys with low Ni ($\text{Ni} < 9\%$, single α -phase region) concentration, the influence of composition was determined from the point of view of thermopower: It was found, that with increasing nickel content (despite of the inheritance of bcc Fe matrix), the thermoelectric power takes up more and more negative value. The same phenomenon was found in the fcc nickel matrix doped by Fe atoms. The effect is interpreted as a stabilization of electron structure due to the formation of solid solution. [S4, S6]
4. Investigating Fe-Ni-B and Fe-Si-B amorphous alloys in a wide concentration range the influence of alloy component was investigated from the point of view of thermopower: At fixed Fe and (B-Si) content along with increasing B/Si ratio the Seebeck coefficient becomes more negative. The reason for this is the change in the s/p electron concentration. The change is not significant compared to the impact of the change of Ni content. The reason is the following: the influence of s and p electron concentration is less

significant compared to the change of d electron concentration in the determination of thermopower. [S11]

5. The effect of structural relaxation in Fe-Ni-B amorphous alloys and phase transformation in crystalline state C70S6 alloys has been determined. It was found that the formation of non-equilibrium phases have a strong influence on the evaluation of thermopower, however there is no change in the composition. The presence of amorphous phase turns the sign of the Seebeck coefficient. The reason is a change in the electron density of states at the Fermi level. [S11]
6. The thickness dependence of thermoelectric power of Cr, Ti and Ni thin film samples was studied. It was found, that increasing layer thickness causes a dramatic change both in the sign and the value of the Seebeck coefficient. At around and above the layer thickness of 4-500 nm the thermopower of thin-film and bulk samples are nearly identical. This behavior occurs because parallel with the increasing layer thickness, the electron mean free path also increases, and there is also a decrease in the epitaxial stress. [S12]
7. The role of external stress on Fe-Ni-Si-B metallic glass ribbons has been studied. It was found that in case of increasing tension there is a strong negative shift in the thermoelectric power, which change back if the load decreases. The process is partially irreversible, since the reversal of S is not complete. [S8]

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