Thermoelectric power applied to metallurgy: principle and recent applications

Dedicated to the late Prof. Charles Crussard (1916–2008)

Thermoelectric power is the magnitude of an induced thermoelectric voltage in response to a temperature difference across a material. The thermoelectric power of metal alloys is strongly influenced by the presence of solute atoms. Measuring thermoelectric power is therefore an accurate technique for characterizing the microstructure evolution of alloys taking place during various phase transformations. The potentialities of this technique are illustrated through four examples: (i) the measurement of copper solubility limit in iron; (ii) the characterization of the strain ageing kinetics of extra-mild steels; (iii) the determination of precipitation kinetics of Mo2C in low alloyed steels; and (iv) the monitoring of ageing of neutron irradiated power plant steels.

Keywords: Thermoelectric power; Precipitation; Segregation

1. Introduction

Thermoelectric effects, namely Seebeck, Thomson and Peltier effects were discovered at the beginning of the 19th century. At the same time, their applicability to thermometry, power generation and refrigeration was recognized. Then, in the late 1930s, after almost a century of silence, began a new period of strong activity in the field of thermoelectricity. The pioneer work of Charles Crussard in the late 1940s opened a new field of investigation, regarding Thermoelectric Power (TEP) effects as a way of investigating precipitation, segregation, and recovery kinetics [5, 6].

In tribute to the exceptional career of Charles Crussard, and especially to his key contribution to microstructure characterization of alloys by means of TEP measurements, this paper aims at briefly presenting

i) the principle of such measurements,

ii) an original apparatus developed within the authors’ group and

iii) a few recent applications of this technique to metallurgy.

2. Principle and apparatus

Consider an open circuit B/A/B composed by two metals A and B (see Fig. 1a). If a temperature difference $\Delta T$ is created between the two A/B junctions of this circuit, a voltage difference $\Delta V$ will appear between the two B segments. The TEP $S_{AB}$ of such a circuit, also known as the Seebeck coefficient, is defined as:

$$S_{AB} = \frac{\Delta V}{\Delta T} \quad (1)$$

$S_{AB}$, referred as the relative TEP of metal A with respect to metal B, is the difference between absolute TEP of both metals: $S_{AB} = S_A - S_B$.

With such a circuit, applying a temperature gradient and measuring the voltage difference lead to the estimation of relative TEP. The absolute TEP of a metal can be determined using the Thomson effect, another thermoelectric effect that is more difficult to achieve from an experimental point of view. Roberts [7] determined with a great accuracy the absolute TEP of many pure metals (lead, platinum, copper). These metals and their associated absolute TEP can

![Fig. 1. (a) Principle of TEP measurement: two junctions are held at two different temperatures $T$ and $T + \Delta T$ within an open B/A/B circuit. The ThermoElectric Power (TEP), or Seebeck coefficient, is the ratio of the generated potential drop $\Delta V$ over the temperature gradient $\Delta T$. (b) Picture of the TEP apparatus commercialized by TechLab [10].](image)
serve as reference metal when using the Seebeck B/A/B circuit (Fig. 1).

The TEP experimental device is based on the former B/A/B circuit (schematized in Fig. 1). Rectangular or cylindrical samples (around 60 x 4 x 0.5 mm³) are generally employed. Samples are fixed at each end to reference metal blocks (e.g., copper). The two reference metal blocks are maintained at temperatures \( T \) and \( T + \Delta T \) (generally, \( T = 15^\circ C \) and \( \Delta T = 10^\circ C \)). The temperature of the two junctions is determined by ultra thin thermocouples located underneath the surface of the reference blocks. The relative TEP is given for the mean temperature of the sample \((T + \Delta T)/2 = 20^\circ C\). Each measurement takes about one minute (time required to get a stationary temperature profile within the sample). For homogeneous samples, TEP is independent of the shape and size of the sample, which is a noticeable advantage of this technique compared to the resistivity measurement technique, also used in metallurgy. For heterogeneous materials (macroscopic heterogeneities), the situation gets more complex and requires a specific analysis to treat the results [8].

Since the TEP is very low for metals, the voltage drop measurement requires great care. A specific amplifier (very low noise) has been developed at “Institut National des Sciences Appliquées” of Lyon: an accuracy of 5 nV on thermoelectric power device [11].

Finally, it is important to notice that TEP measurement can also be achieved on bulk materials using the hot tip thermoelectric power device [11].

3 Theoretical aspects

3.1 The absolute TEP of pure metals

The absolute TEP of a pure metal (\( S^\ast \)) is the sum of two components [12]: \( S^\ast = S^\ast_0 + S^\ast_x \) where:
- \( S^\ast_0 \) is the diffusion component which is associated with the conduction electron scattering and which varies almost linearly with the absolute temperature.
- \( S^\ast_x \) is the lattice component which takes into account the interaction between phonons and electrons. It presents a maximum at \( \theta_D/5 \) (where \( \theta_D \) is the Debye temperature) and it is generally negligible for \( T > \theta_D \). Therefore, in most cases, the absolute TEP of a pure metal at room temperature is essentially due to the diffusion component.

3.2 Influence of the microstructure

The absolute TEP \( S^\ast \) of a metallic material is affected, at different levels, by all the lattice defects (solute atoms, dislocations, precipitates, etc.) which may disturb the electronic or elastic properties of the material and subsequently, induce a TEP variation. Therefore, it can be written as follows:

\[
S^\ast = S^\ast_0 + \Delta S_{\text{ss}} + \Delta S_{\text{d}} + \Delta S_{\text{pp}}
\]  

where \( S^\ast_0 \) is the TEP of the pure metal (without defects) and \( \Delta S_{\text{ss}}, \Delta S_{\text{d}} \) and \( \Delta S_{\text{pp}} \) are the TEP variations due to elements in solid solution (ss), dislocations (d) and precipitates (pp), respectively.

The contribution of solute elements on the diffusion component of TEP is given by the Gorter–Nordheim law [13], which can be expressed as follows:

\[
\rho S = \rho(S^\ast_0 - S^\ast_i) = \sum_i \rho_i S_i = \sum_i \alpha_i C_i S_i
\]  

where: \( \rho = \rho_0 + \sum \rho_i \) is the resistivity of the considered material (given the Mathiessen’s rule), \( \rho_0 \) is the resistivity of the pure metal, \( \rho_i \) is the increase in resistivity due the solute atoms \( i (\rho_i = \alpha_i C_i \text{, where } C_i \text{ is the concentration of solute element } i \text{ and } \alpha_i \text{ is its specific resistivity}) \) and \( S_i \) is the specific TEP of solute element \( i \).

When the concentration of the alloying elements in solution is low (<10⁻⁴ at.%) or when the variations of the solute content are weak, the resistivity (\( \rho \)) can be considered as being constant, so that the Gorter–Nordheim law becomes:

\[
S = \sum P_i C_i \quad \text{where} \quad P_i = \frac{\alpha_i S_i}{\rho}
\]  

\( P_i \) is the coefficient reflecting the influence of solute element \( i \) on the TEP.

As far as precipitates are concerned, their effect, as a second phase, can be generally neglected, except if they are coherent or if their volume fraction is high (>10%). In this case, they may induce strong TEP variations, the magnitude and sign of which are difficult to predict. As an example, Crussard and Aubertin observed a significant effect of Fe precipitates in aluminium during the dissolution stage, which they called “TEP abnormality”. They assumed that it was due to the stress field surrounding precipitates [2]. Lastly, in most alloys, the dislocations have an effect on the TEP. For example, in iron alloys, they tend to decrease the TEP, leading to a TEP variation which seems to be related to the dislocation density.

4. Applications

The high sensitivity of TEP to crystal defects such as dislocations and solute atoms provides a powerful experimental tool for characterizing the kinetics of structural transformations taking place in various alloys. TEP has therefore been successfully used to measure the solubility limit of carbon in iron [14] and the nitrogen content in aluminium killed steels [15], to characterize the interaction between interstitial and substitutional atoms in low alloyed steels [16] and the ageing of ULC alloys [17], to study the precipitation sequence in 6061 aluminium alloy [18]. In this section, some recent applications will be detailed and discussed.

4.1 Solubility limit of copper in iron

Iron–copper alloys have received considerable interest in the last 50 years because copper is an excellent candidate for structural hardening of many industrial alloys. The knowledge of the thermodynamics of this system, namely the solubility limit and diffusion coefficient, is essential. Such properties have been precisely measured by macroscopic techniques such as diffusion couples [19]. These techniques involve long-range diffusion and are therefore limited to tem-
temperatures higher than 700 °C. Unfortunately, copper precipitation in steels is technologically relevant at temperatures ranging from 550 to 600 °C. For this temperature range, the copper solubility is generally extrapolated from high-temperature results, which may lead to important discrepancies.

To overcome this difficulty, the fine precipitation of copper in iron has been studied using TEP. Indeed, precipitation of nanometric copper occurs over a reasonable time scale even at relatively low temperatures (down to 500 °C).

The Gorter–Nordheim law (Eq. (3)) has been validated using Fe–Cu binary alloys of different compositions, leading to an estimation of the specific thermoelectric coefficient of copper in iron \( S_{Cu} = 23.4 \text{nV K}^{-1} \) [20].

Figure 2a shows the evolution of the TEP for different ageing temperatures ranging from 450 to 700 °C. For ageing temperatures higher than 500 °C, kinetics have been followed until the end of precipitation characterized by a stabilization of TEP at a final value which depends on the ageing temperature.

Two important points can be deduced from these results:

(i) the sigmoidal evolution of the TEP curves tells us how fast precipitation occurs: it can be seen that increasing the temperature accelerates the precipitation until 575 °C (above this temperature, the precipitation is slowed down by increasing the temperature (typical “C” curve));

(ii) the final TEP level is directly linked to the precipitate volume fraction (and therefore to the solubility limit of copper in iron taking into account Gibbs–Thomson effects [21]) through Eq. (3).

Figure 2b gives the solubility limit of copper in iron measured by TEP and compares it to

i) some results of the literature and

ii) a direct measurement performed with a tomographic atom probe [22].

TEP gives higher solubility limits than extrapolated results of the literature [23]. Actually, most of the solubility limits found in the literature come from extrapolation to low temperature of the measurements of Salje and Feller-Kniepmeier [24] or Speich et al. [25] that were performed at temperatures higher than 700 °C.

4.2 Segregation of interstitial atoms to dislocations

The TEP technique can also be used to follow the segregation kinetics of the interstitial atoms (C and/or N) to the dislocations in heavily deformed extra-mild steels. The principle is to deform the steel up to a given strain and to strain age the steel for different times \( t \) at the temperature \( T \) of interest. After each treatment time at \( T \), the TEP variation induced by the ageing, \( \Delta S_t \), has to be measured, so that the change of \( \Delta S_t \) can be plotted as a function of the ageing time at \( T \). As can be seen in Fig. 3a, the curve giving the variations of \( \Delta S_t \) presents a sigmoidal evolution. As was established in [26], as long as no recovery and precipitation phenomena take place in the steel, the variations of \( \Delta S_t \) are due to the segregation of the interstitial atoms to the dislocations and at time \( t \), the value of \( \Delta S_t \) is directly proportional to the amount of interstitial atoms which segregated to the dislocations. If carbon and nitrogen atoms are simultaneously in solution in the initial state of the steel, one can write that:

\[
\Delta S_t(t) = [P_C] \cdot [\text{C}_{\text{seg}}] + [P_N] \cdot [\text{N}_{\text{seg}}],
\]

where \( P_C \) and \( P_N \) are the coefficients reflecting the effect of C and N in solid solution in iron on the TEP. \([\text{C}_{\text{seg}}]\) and \([\text{N}_{\text{seg}}]\) are the amounts of C and N atoms segregated to the dislocations at time \( t \).

From the measurements of \( \Delta S_t \), the fraction of atoms segregated to the dislocations, \( Y(t) \), can be evaluated during an isothermal treatment, where \( Y(t) \) is a curve representative of the segregation kinetics. As an example, Fig. 3b illustrates the influence of the chromium content on the segregation kinetics of C or N to the dislocations at 120 °C and shows that the presence of 1 wt.% Cr tends to delay the segregation of N.

Furthermore, it has to be noted that the methodology described above can be used to evaluate quantitatively the interstitial content in solution [26]. Indeed, when the dislocation density introduced in the steel is high and when the ageing time is long enough to reach the end of the segregation process, all the interstitial atoms initially in solution can leave the solid solution and segregate to the dislocations. In these conditions, one can write that:

\[
\Delta S_t = [P_C] \cdot [\text{C}_{\text{ss}}] + [P_N] \cdot [\text{N}_{\text{ss}}],
\]

where \([\text{C}_{\text{ss}}]\) and \([\text{N}_{\text{ss}}]\) are the carbon content and nitrogen content in solution, respectively.

As was shown in [27], the quantitative evaluation of the carbon content in solution in extra mild steels by TEP or by Internal Friction (IF) is not equivalent. Indeed, TEP detects all the carbon atoms in solution whatever their environment may be, while the IF technique is not sensitive to
the presence of the carbon atoms which are in interaction with some substitutional atoms (such as Mn, for example). The two techniques are thus complementary and their combination can be interesting. In particular, it can lead to the determination of the binding energy of interstitial-substitutional dipoles, as was shown in [16].

4.3 $\text{Mo}_2\text{C}$ precipitation in iron

As mentioned above, TEP is highly sensitive to solute element concentration. Therefore, the precipitation kinetics of $\text{Mo}_2\text{C}$ carbides can be studied by TEP. In low alloyed steels with a sufficient amount of molybdenum, tempering at high temperature induce generally a secondary hardening mechanism. It results from the precipitation of molybdenum with carbon, forming $\text{Mo}_2\text{C}$ precipitate. This hardening may be large enough to compensate the softening of martensite.

In order to study $\text{Mo}_2\text{C}$ precipitation kinetics, a ternary Fe-2 wt.% Mo-0.25 wt.%C alloy was austenitized at 1050°C for 30 min and water quenched. Just after austenizing and water quenching, the structure of the steel is martensitic with molybdenum and carbon in solid solution. Tempering at low temperature (100–300°C) leads to $\varepsilon$ and $\text{Fe}_2\text{C}$ carbide precipitation. At higher tempering temperature, molybdenum carbides, more stable than cementite, induce a secondary hardening, as shown in Fig. 4.

During the first stages of tempering, precipitation of $\varepsilon$ carbides or cementite induces a loss of solute carbon atoms, and therefore, an increase in the TEP (see for example Fig. 3a), as carbon atoms have a negative effect on iron TEP. For longer times, since molybdenum atoms have a positive effect on iron TEP, the precipitation of molybdenum in $\text{Mo}_2\text{C}$ carbides decrease the TEP as can be seen in Fig. 4.

Using Gorter–Nordheim relation (Eq. (3)), it is possible to estimate, from TEP measurements, the amount of molybdenum atom involved in $\text{Mo}_2\text{C}$ carbides. A very good correlation between the amount of molybdenum atoms involved in precipitates and the peak hardness is also seen in Fig. 4 (see Ref. [28] for more details).

4.4 Industrial application: monitoring ageing of neutron irradiated steels

The high sensitivity of TEP to microstructural change in metallic materials give rise to numerous industrial applications. Monitoring thermal ageing under irradiation of steels in a reactor pressure vessel (RPV) is a typical example. Indeed, during the last decade important efforts have been made in order to find new and innovative ways of checking the integrity of nuclear power plant materials.

The RPV steel is a low alloyed steel 16MND5. The microstructure is mostly bainite. During ageing under neutron irradiation, a loss of ductility is generally observed. Indeed, neutron irradiation induces the formation of vacancies as well as precipitation of copper. As a direct consequence, the steel becomes more brittle, leading to a lifetime reduction. TEP measurements can then be realized on samples made of RPV steels and located near the reactor. Indeed, due to its high sensitivity to solute and vacancy content, TEP is a good candidate to follow such ageing.

1 Composition: 0.16 wt.% C-1.5 wt.% Mn-0.6 wt.% Ni-0.5 wt.% Mo
In Fig. 5, the TEP variation of RPV steels has been plotted as a function of the fluence (number of neutrons per unit time and area). The good correlation obtained between these two quantities validates TEP measurements for monitoring ageing under neutron irradiation.

Fig. 5. Variation of RPV steels versus the fluence (number of neutrons per unit time and area). The good correlation obtained between these two quantities validates TEP measurements for monitoring ageing under neutron irradiation.

5. Conclusion

TEP measurement is a powerful and “easy to use” tool for microstructure characterization: coupled to a local characterization technique (e.g. microscopy), it has demonstrated its efficiency in many applications. However, at the present time, the scientific community is coming up against the complexity of TEP fundamentals. Indeed, the TEP depends on both electrons and phonons and their coupling is far from being understood.

In the near future, this problem could be tackled by
i) improving and developing new TEP measurement devices: e.g. measuring the temperature dependence of TEP down to very low temperature might be very helpful for a better understanding of electron/phonon coupling, and
ii) building a multi-scale modelling framework (from electrons to atoms), based on first principles, that could take into account electron/phonon coupling and therefore shed light on the effect of temperature, stress and lattice defects.

Thus, and only thus, will the pioneer contribution of Crusard be finally achieved.

References


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Bibliography

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