Characterization of Segregated Areas in Ferritic Steels by Thermoelectric Power Measurement

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Abstract. Based on the theory of coupled transport equations of heat and electricity in metals, we present a numerical method allowing us to calculate the ThermoElectric Power (TEP) (Seebeck coefficient) of a two-dimensional metal/metal composite structure. Depending on the thermoelectric properties of the components and their arrangement, the temperature and potential distributions are calculated. The apparent TEP is then deduced. A validation of the numerical approach was carried out on Copper/Solder composite samples that we fabricated. We applied the numerical model on a ferritic steel containing macroscopic segregated areas. We showed that this steel can be considered like a composite material, and that the TEP can be a helpful probe to characterize these segregations since measurement and simulation results show that TEP is very sensitive to the presence of these heterogeneities.

1 Introduction

The thermoelectric power (TEP) measurement of metallic materials has been used for many years to follow microstructural evolutions. This parameter is actually very sensitive to the microstructural variations that the materials can undergo. From a practical point of view, TEP measurement is relatively simple, fast, very precise and, unlike the resistivity (by the measurement of resistance), is independent of the geometry of the sample.
This measurement method is thus used to characterize precipitation kinetics of carbon [1] and nitrogen [2] in steels, and precipitation kinetics of copper in aluminium alloys [3]. If the effect of alloy elements on TEP measurement has been relatively well studied, it is not the case of the influence of the presence of many phases on the macroscopic TEP of a metallic material. In this work, we have studied a ferritic steel that contains macroscopic segregated areas enriched in alloy elements. These segregations make the steel similar to a two-constituent material. In the case of multi-constituent materials, the knowledge of the properties of each phase alone is not sufficient to determine the TEP of the structure. The proportion, the morphology and the distribution of each phase are, therefore, critical in the TEP that can be obtained at the end. These parameters which have to be taken into account are so numerous that an analytical expression of the TEP of such a structure is difficult to establish. Thus, a numerical approach is the only way to predict the macroscopic TEP of a composite material.
In the first section of this paper, we present the numerical simulation method, based on the resolution of the transport equations of heat and electricity, that have been developed. In a

second section, we apply this model to a ferritic heterogeneous steel. By the measurement and the numerical simulation, we highlight the effect of the segregated areas on the TEP.

2 Simulation of the TEP Measurement

2.1 Basic Concept and Theory

In this paper, we briefly recall the numerical procedure we used. A detailed description of the model can be found in [4].
Usually, to determine the TEP of a material in experiments, two junctions regulated in temperature are formed between the sample and the two metals (reference). Because of the Seebeck effect, a potential difference appears between the two junctions. The measurement of this potential difference and the knowledge of the two temperatures then make it possible to reach the TEP of the sample using the following relation :

$$S_{sample} - S_{reference} = \frac{\Delta V}{\Delta T} \qquad (1)$$

where $S_{reference}$ is the TEP of the reference material, which is supposed to be known. To increase the accuracy of the measurement, the samples are generally of rectangular shape and have a small section (figure 1).

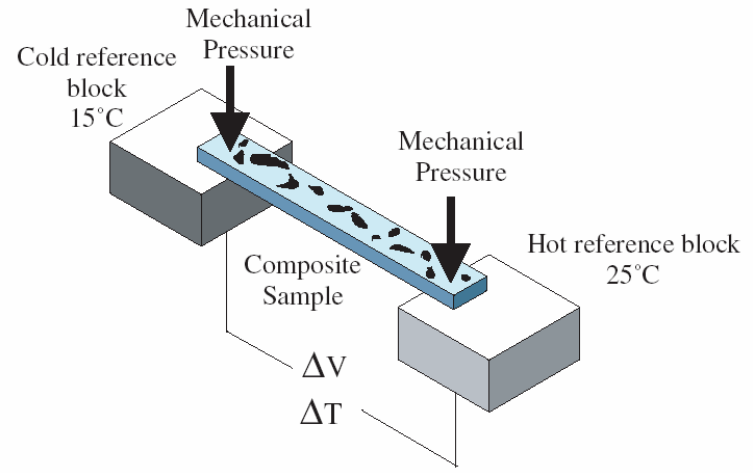


Figure 1. TEP (Seebeck coefficient) measurement schema

The aim of this study is to calculate the TEP of a composite structure made up of two metal phases, whose distribution and thermoelectric properties are known. The application of a temperature gradient along this structure induce, by the thermoelectric effect, a potential gradient and a very weak current which is distributed within the structure.

The macroscopic TEP of such a structure (figure 2), referred to the TEP of the copper block, then results from the following relation :

$$S_{composite} = \frac{\phi_1 - \phi_2}{T_2 - T_1} \qquad (2)$$

where ϕ_1 and ϕ_2 are, respectively, the average potentials of the cold and hot contact, and T_1 and T_2 the average temperatures of the cold and hot junctions. To determine the resulting TEP, it is thus necessary to calculate the temperature and the potential distribution within the structure.

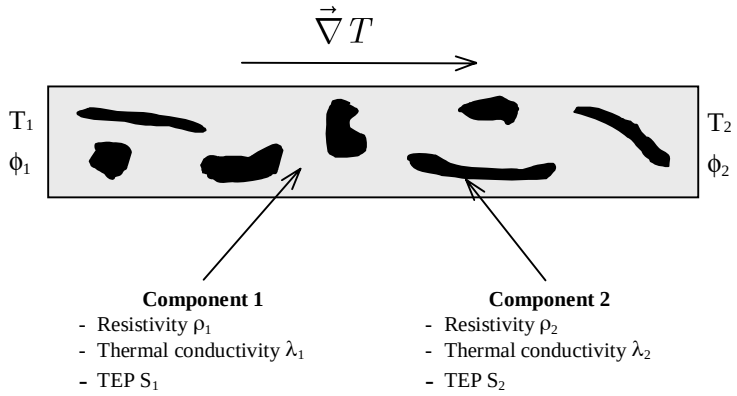


Figure 2. Two-dimensional composite sample made up of two different phases

The transport equations that govern the thermoelectric effects are coupled equations of heat and electricity in metallic materials. The electric current density **J** and the thermal flux **Q** are described by the following equations :

$$\begin{cases} \boldsymbol{J} = -\sigma.\boldsymbol{\nabla}\phi - \sigma.S.\boldsymbol{\nabla} T \\ \boldsymbol{Q} = U.\boldsymbol{J} - \lambda.\boldsymbol{\nabla} T \end{cases} \qquad (3)$$

with σ the electrical conductivity (isothermal), S the TEP (Seebeck coefficient) and λ the thermal conductivity (isothermal). ϕ and T are, respectively, the electrochemical potential and the temperature within the material. The term U can be expressed by the following relation : U=ϕ+ST.
In practice, to determine the temperature and potential distribution, it is enough to solve the transport equations (3). We will thus consider two assumptions :

- In steady state, we have conservation of heat and electricity within the sample, and therefore :

$$\begin{cases} \boldsymbol{\nabla J} = 0 \\ \boldsymbol{\nabla Q} = 0 \end{cases} \qquad (4)$$

- For metallic materials, which have a high electrical conductivity and a weak Seebeck coefficient (TEP), for the measurement conditions generally used (high thermal gradient), the term U.**J** can be neglected in the expression of the thermal flux. Therefore, we will assume that the term **Q** is equal to the thermal flux given by the Fourier law :

$$\boldsymbol{Q} = -\lambda.\boldsymbol{\nabla}\mathrm{T} \qquad (5)$$

By making these assumptions, the problem is simplified and the resolution can be carried out in two successive stages :

- Resolution of the thermal problem :

$$\begin{cases} \boldsymbol{Q} = -\lambda.\boldsymbol{\nabla} T \\ \boldsymbol{\nabla Q} = 0 \end{cases} \qquad (6)$$

then

- Resolution of the thermoelectric problem :

$$\begin{cases} \boldsymbol{-\nabla}\phi = \dfrac{1}{\sigma}.\boldsymbol{J} + S.\boldsymbol{\nabla} T \\ \boldsymbol{\nabla J} = 0 \end{cases} \qquad (7)$$

After the resolution, the temperature and the potential distributions are known. We can calculate the terms ϕ_1 and ϕ_2 in the expression of the TEP (equation (2)), and thus deduce the apparent TEP of the composite structure.

2.2 Numerical Resolution

In what follows , we will consider only the two-dimensional case. An extrapolation towards the three-dimensional case can easily be considered and does not present a major difficulty. We will consider the numerical problem by a finite difference approach. We discretize 2D space by building a grid with a square mesh of dimensions $h \times h$. Each mesh is represented by its co-ordinates (i,j) and delimits a surface in which the temperature $T_{i,j}$ and the potential $\phi_{i,j}$ are constant (figure 3). The thermoelectric properties of each mesh depend on the material considered at the point (i,j). The corresponding values are $\lambda_{i,j}$, $S_{i,j}$ and $\sigma_{i,j}$.

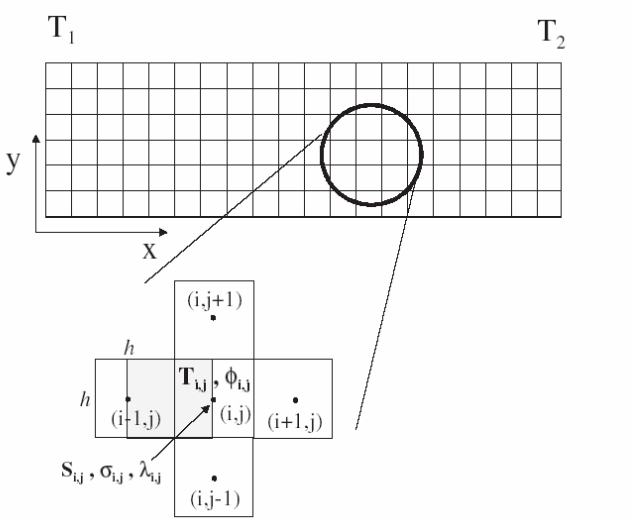


Figure 3. Discretization of the composite sample

First, we determine the temperature distribution within the sample using the conservation of thermal energy in each cell. By considering the Fourier's law (equation (5)), we obtain an expression of the temperature $T_{i,j}$ in each cell in the bulk of the material, which depends on the temperatures in adjacent cells and on the equivalent thermal conductivities of adjacent cells (see equation (11) in [4]). A special treatment is applied for the edges of the sample. Two types of boundary conditions exist : for the extremities of the sample which are temperature regulated, the temperature is imposed at a constant value on the surface corresponding to the surface in contact with the blocks. Dirichlet conditions are thus used. For the two other edges, we consider Neumann conditions, i.e. no energy flux will be allowed to leave the sample (the convection is neglected). By using the same method as for the bulk, the temperature in each cell on the edges can then be estimated. Finally, one gets a system of N equations with N unknowns, N being the number of nodes for which an equation must be solved. Instead of using classical methods of matrix inversion, we preferred to use the iterative method of Gauss-Seidel [4]. After solving the equations system, the temperature $T_{i,j}$ for each cell is known, and the potential distribution can then be evaluated.

We use a similar approach to determine the potential distribution within the sample. In steady state, the electric charge in the sample is conserved. We obtain an expression of the potential in each cell in the bulk, which depends on the temperatures and potentials in adjacent cells and on equivalent electrical conductivities and TEP between adjacent cells.

The knowledge of these parameters make it possible to calculate the electrochemical potential $\phi_{i,j}$. Since no potential is imposed on the sample, the only boundary conditions to take into account are the Neumann kind conditions, i.e. no current leaves the sample. The same algorithm of resolution as for the determination of the temperature distribution is employed (iterative method of Gauss-Seidel).
Since $T_{i,j}$ and $\phi_{i,j}$ are known in each point, we can calculate ϕ_1 and ϕ_2 by averaging the potential in the surfaces of contact block/sample, and then deduce the apparent TEP (equation (2)).

2.3 Validation of the Numerical Approach on Metal/Metal Composite Samples

In order to validate the results of numerical calculations, various composite samples were made using a copper sheet and lead/tin alloys (solder alloy with 38% of lead). As calculations are carried out in two dimensions, the thickness of these samples have been reduced to a few hundred micrometers. For the numerical resolution, the images of the samples were digitized using a numerical scanner, then binarized in order to separate the two components (copper and lead/tin). These images were used during the numerical simulation to define the three matrices $S_{i,j}$, $\lambda_{i,j}$ and $\sigma_{i,j}$ which correspond to the TEP and the thermal and electrical conductivity values on each node of the grid.

Table 1. Thermoelectric properties of the two components

	Lead/Tin alloy	**Copper**
S/Copper block ($V.K^{-1}$)	-2.9×10^{-6}	-0.01×10^{-6}
σ ($S.m^{-1}$)	5.85×10^{6}	56.7×10^{6}
λ ($W.m^{-1}.K^{-1}$)	51	376

The TEP values of each component were separately measured using the device described previously. The electrical conductivities were determined using an eddy-current device. The thermal conductivities were extracted from the literature for the solder alloy and from the Wiedemann-Franz law for copper [6]. All these values are given in table 1.
In order to validate the numerical model, different types of composite structure were fabricated, where the constituents form various patterns. The figure 4 presents the results of measurements and calculations, like some examples of composite samples. For calculations, a grid resolution of h = 160 μm was used.

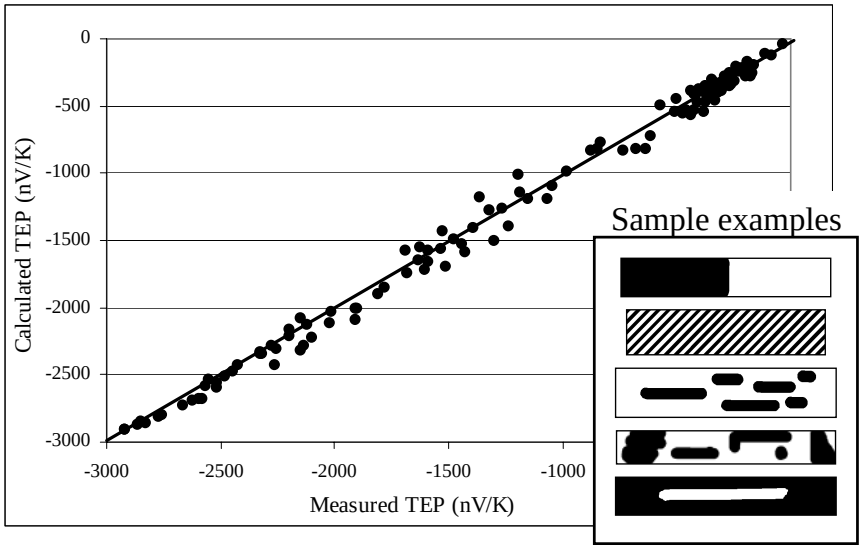


Figure 4. Comparison of measured and calculated TEP for Cu/Solder composite samples

In this graph are plotted the results for various positions of the sample on the blocks. Indeed, the TEP device allows us to make measurements with different contact width between the sample and the blocks. The figure 4 shows a very good agreement between numerical calculations and experimental results, that enable us to conclude to the validation of the numerical model on the metal/metal composite samples. Moreover, it shows that the simulation can take into account the position of the sample on the blocks of the TEP device.

3 Characterization of Segregated Areas

3.1 Description of the Steel and the Samples

The steel we studied is a ferritic low-alloyed steel. Because of its development process, it contains macroscopic segregated areas, which are enriched in alloy elements and impurities. The steel gets thus an heterogeneous character. It can be considered like a composite material made up of two constituents, a "matrix" constituent and a "segregation" constituent. Previous studies showed that the presence of these segregated areas has an effect on the TEP measurement of the steel [7]. The chemical composition of the two constituents, which have been evaluated by electron microprobe, is given in table 2.

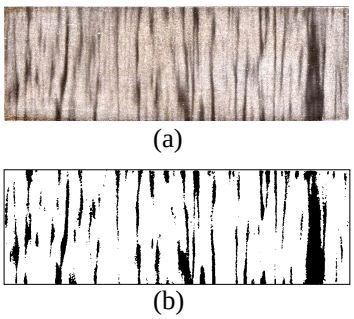
Table 2. Composition of the two constituents (wt.%)

Element	C	Mn	Ni	Mo	Si	Cr	Cu	P	Al	S	V
Matrix	0.16	1.32	0.74	0.51	0.14	0.18	0.06	0.01	0.01	0.008	0.015
Segregation	0.25	1.92	0.87	1.28	0.27	0.22	0.09	0.023	0.03	0.008	0.01

In order to apply our model, two types of samples were cut : samples which present segregated areas in the direction of their length, and samples with segregated areas perpendicular to their length. The first one, which have a distribution of the components close to a series connection are named S-samples, whereas the second one, close to a parallel connection between the two components are called P-samples. All these samples have a low thickness (a few hundred micrometers) so that we will consider that the phases repartition is the same along their thickness.

3.2 Phases Repartition

To determine the repartition of the components, and then deduce the matrix $\lambda_{i,j}$, $S_{i,j}$ and $\sigma_{i,j}$, we first revealed the segregation areas so that they are visible. The surface of each sample is thus polished, etched by Nital (5%vol nitric acid in ethanol), and then digitized using a numerical scanner. Thanks to a thresholding with an image treatment software, we separate the "matrix" phase from the "segregation" phase. The figure 5 illustrate these different stages for a S-sample.



(a) (b)

Figure 5. S-Sample (a) after polishing and etching (b) after binarization

3.3 Electrical Resistivity, Thermal Conductivity ant TEP

In order to carry out numerical calculations on the steel, we have to estimate the different input parameters that are used for the simulation.

The electrical resistivities of the two components were evaluated using an empirical relation established by Meyzaud [5]. This relation gives the electrical resistivity of a steel at 300 K according to its composition, and is given by :

$$\rho(\mu\Omega.cm)=9,9+30.(C+N)+6.Mn+12.Si+14.P-10S+Co+2,9.Ni \quad (8)$$
$$+5,5.Cr+2,8.Mo+1,3.W+3,3.V+6,4.Ti+3,9.Cu+13.Al$$

Thus, the electrical resistivities of the components are calculated thanks to equation (8) and by taking the chemical composition given in table 2.

The thermal conductivities are estimated thanks to the Wiedemann-Franz law, which links the thermal and electrical resistivities via the Lorentz constant (at constant temperature).

As we can not measure the TEP of the two components separately, we determined the TEP between the matrix and the segregated areas. To evaluate the TEP difference, we realised a TEP cartography using the hot tip TEP device in a region presenting a wide segregation.

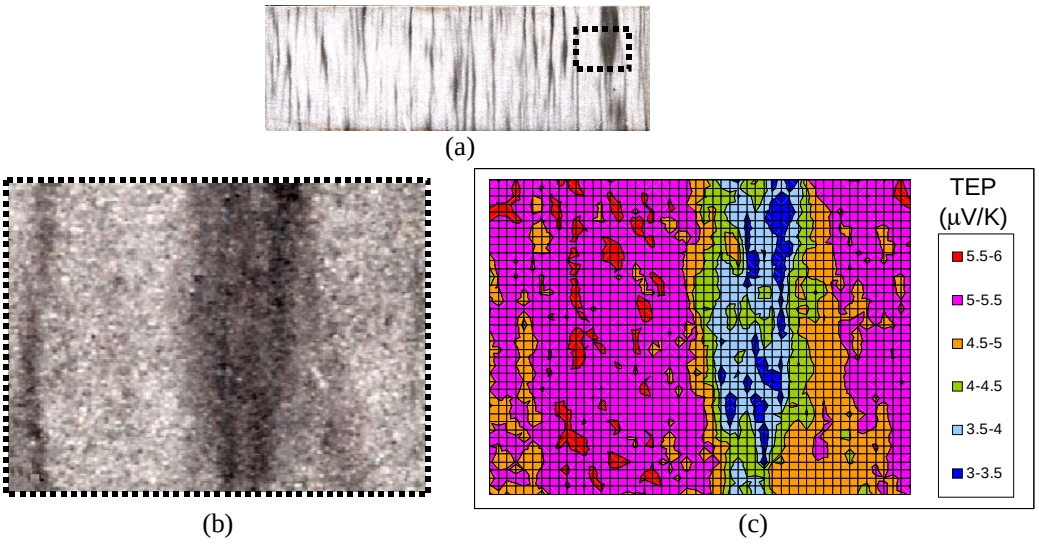


Figure 6. (b) Region of a S-sample (a) corresponding to the TEP cartography (c)

The figure 6 presents the scanned area (b) and the corresponding TEP cartography (c). If we compare these two images, we can see that the contrasts in TEP values correspond to the contrasts in chemical composition highlighted by the Nital etching. It confirms the possibility to detect segregation areas using the hot tip TEP device.
Due to a different measurement protocol (temperature, block), the absolute values given by the hot tip TEP device can not be used directly. Since only the TEP difference is important for the numerical simulations, we estimated it using the TEP cartography [4] [7] :

$$\Delta TEP = TEP_{matrix} - TEP_{segregation} \approx 2\ \mu V/K$$

All the thermoelectric properties that we took for the calculations are given in table 3. The TEP values of the two components used for the calculations were chosen in order, first to include most of the simulation results in the range of the measurements, and second to respect the TEP difference of 2 μV/K between the two components. A grid size of h = 100 μm was used.

Table 3. Thermoelectric properties of the two components

	Matrix	**Segregation**
S/Copper block ($V.K^{-1}$)	6.85×10^{-6}	4.85×10^{-6}
σ ($S.m^{-1}$)	3.4×10^{6}	2.5×10^{6}
λ ($W.m^{-1}.K^{-1}$)	27	19

3.4 Simulation Results

First, the TEP measurements were carried out using the classical TEP device (figure 1), using the smallest surface of contact that could be achieved between the sample and the copper blocks. The resulting measurements and numerical simulations are given in figure 7, plotted as a function of the surface fraction of segregated areas.

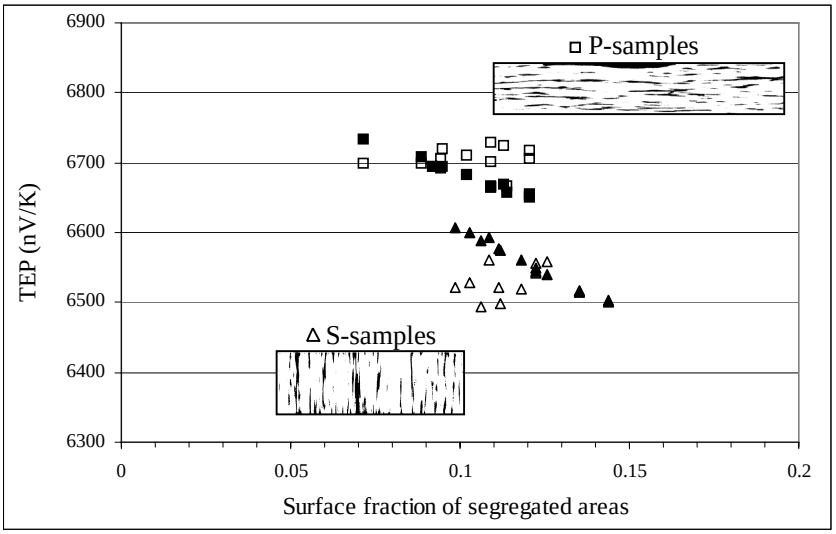


Figure 7. Comparison between measured TEP (hollow symbols) and calculated TEP (filled symbols) as a function of the surface fraction of segregated areas

Other measurements were carried out, for different positions of the samples on the blocks. The experimental and numerical values that we get, like these in the figure 7, are plotted in figure 8.

This figure shows a good agreement between measurements and calculations, since the maximal difference observed is about 100 nV/K. It confirms that the simulation can take into account the position of the sample on the blocks, which can have a non-negligible effect on the TEP measurement. Moreover, the distinction between the TEP values of the S- and P-samples, which present two different orientations of the segregation, is highlighted by the simulation.

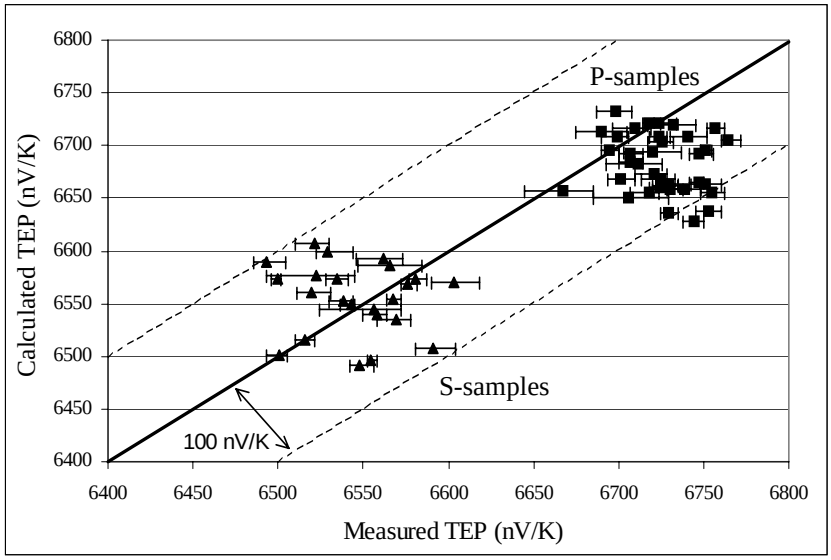


Figure 8. Comparison of measured and calculated TEP for ferritic steel samples

4 Conclusion

In this paper, we developed a numerical model which enable us to calculate the temperature and potential distribution within a composite structure made up of two constituents. If we know the thermoelectric properties and the arrangement of the two phases, we can estimate the apparent TEP of such a structure. The comparison of the TEP values calculated by the simulation method with the experimental values on metal/metal composite samples proved to be excellent.

We applied the numerical model on a ferritic steel containing macroscopic segregated areas. We have shown that the TEP measurement is very sensitive to the presence of these segregations. It is not only sensitive to the density of segregations, but also to their orientation compared to the direction of the temperature gradient. The simulation results confirmed this influence. Thus, either by measurement or by simulation, TEP proved to be a useful method to characterize such heterogeneities.

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