Thermovoltages under consideration of the thermal expansion

ABSTRACT

This contribution deals with the representation of the Seebeck- coefficient of simple non-magnetic metals like copper using a classical thermoelectric field model.
Other calculations leading to the same or similar results are based on Gibb's theory or on the Boltzmann-Fermi transport model.
The classical model can be expanded very simply to include the effect of the thermal expansion on both the total thermovoltage and of the total thermocurrent, using Fick's law. The thermal expansion reduces the thermal diffusion based Seebeck coefficient by a factor of (1- 4αZT), where α contains the linear expansion coefficient. Also it is shown, that the temperature course along the thermowire is regarded by a correction factor z.

INDEX TERMS

1. INTRODUCTION

We find various models for the determination of the absolute Seebeck-coefficient (ASC) vs. temperature curves in the literature [1,2]. Some of the results are based on the Gibb's relations [1] or others on the Fermi-Boltzmann statistics [3]. They are usually consistent for certain temperature regimes.

For the description of the ASC characteristic of standard thermoelectric metals one can also start with a thermoelectric field. However, one has still to discriminate between magnetic and nonmagnetic metals, s-band metals and s-d-band metals and between electron and hole conduction.

In what follows we consider only nonmagnetic-band metals, for example Copper (Cu).

Once a temperature gradient is applied along a metallic thermowire we observe a thermodiffusion of the charge carriers. i.e. the carriers which are already excited to the Fermi temperature move to the cold end of the thermowire, at least for simple metals. This leads to the build-up of a counter electrical field E(T) over the wire length (l) and with it to a thermoelectric voltage $U_{TE}(T)$ between the end faces of the wire.

Between the ASC and those thermoelectric quantities under a temperature gradient dT/dx along the wire we have the following relations:

(1) $ASC(T) = dU_{TE}/dT$

(2) $U_{TE} = \int E(T)dx$ integration over the wire length l

Eq's 1,2 now yield the temperature dependence of the ASC as :

(3) $ASC(T) = E(T)/dT/dx$

2. THERMOELECTRICAL FIELD AS OBTAINED BY THERMODIFFUSION, ETD(T)

If we have a temperature gradient dT/dx along the wire axis x, the charge carriers (electrons or holes) have slightly different electronic levels at a given x because of the temperature differences. This leads to a force F(T)

which in turn initiates a motion towards the cold end.

As we have an energy increment dW_e corresponding to a temperature increment dT along the path increment dx, we can write down the force F(T) as:

(4) $F(T) = dW_e/dx$ or expanded by dT : $F(T) = (dW_e/dT)\cdot(dT/dx)$

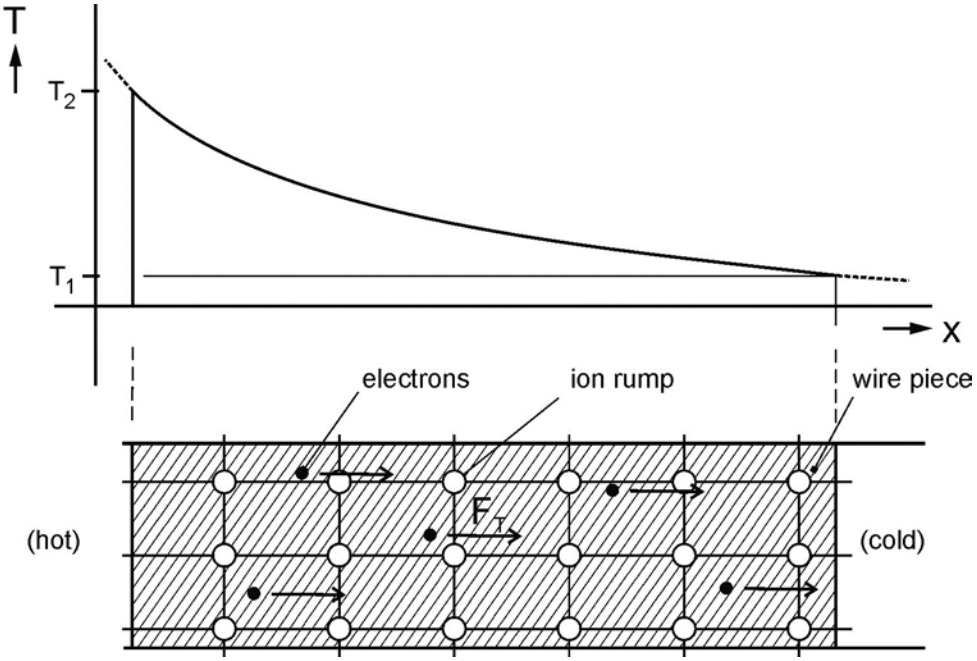

Fig.1 Generalized temperature gradient and electron diffusion in a metallic wire

The energy increment dW which is taken up by the thermowire can also be expressed by the total molar heat capacity $C_m = C_{em} + C_{gm}$, as in order to install the temperature gradient one has to heat both the lattice and the electron gas . The relation between dW and C_m reads:

(5) $dW = C_m N_M dT$

with C_m molar heat capacity, N_M mole number.

According to the literature [4], the molar heat capacity of a free electron gas reads:

(6) $C_{em} = (\pi^2/2)N_A k(T/T_F)$

with N_A electrons per mole, k Boltzmann's constant, T_F Fermi temperature, T Kelvin temperature.

Combining eq's 4,5,6 , one arrives at :

(7) $F_{TD} = (\pi^2/2)N_A k(T/T_F)N_M (dT/dx)$

with $N= N_A N_M$ the total electron number. The electrical field ETD which builds up according to the electron diffusion reads:

(8) $E_{TD} = (\pi^2/2)N_A k(T/T_F)N_M (dT/dx)$

if one considers that $F_{TD} = eNE_{TD}$ with e the elementary charge. According to eq.3, the ASC characteristic now reads:

(9) $ASC(T) = (\pi^2/2)(k/e)(T/T_F)$

in agreement with standard results [2,3]. This result implies medium temperatures and a contribution of all electrons at the Fermi surface. As according to eq.8 the thermoelectric field does not depend on the number of moles, the cross section and the wire length do not influence the value of the thermovoltage.
However, there is a number of factors which will influence the thermo-voltage, for example the thermal expansion.

The influence of the thermal expansion coefficient α has been investigated
in materials which are known to have an uniaxial tensor of expansion coefficients, making use of a correlation analysis [5]. α has been considered to have an influence on the ASC just as the heat and electrical conductivities.

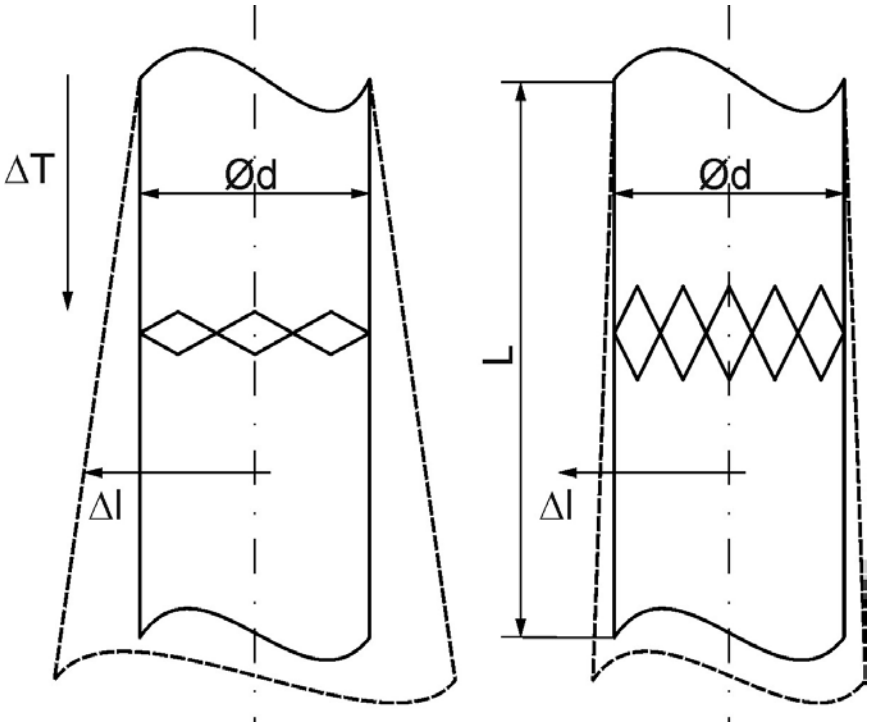

Fig.2 Uniaxial thermal expansion of thermoelectric materials, (a) short axis (b) long axis (c) table of α and ASC values for different materials.

Changes of the thermovoltage could also be observed in volume clamped thermowires (mounting in invar cylinders)[6].

The thermal expansion creates an increase in volume Thus, on gets a larger volume at the hot side of the thermowire as compared to the cold side. But under a constant number of charge carriers per unit volume, a volume change means a change in the carrier density Dn, which, however, will be equalized by diffusion, i.e. under Fick's law.

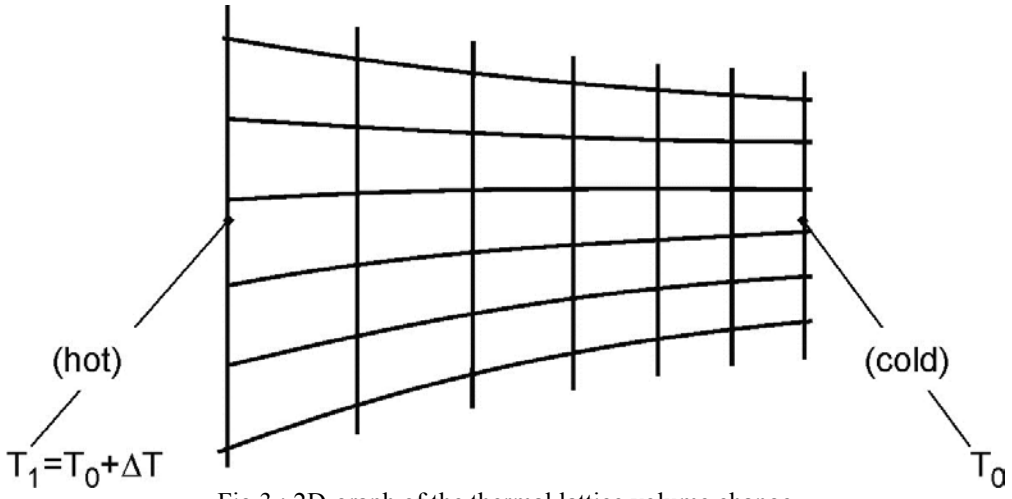

Fig.3 : 2D-graph of the thermal lattice volume change

3. CHARGE EQUALIZING CURRENTS UNDER THERMAL EXPANSION OF THE THERMOWIRE

Without thermal expansion, i.e. for $\alpha = 0$, all charge carriers at the Fermisurface, N_F with n_F the carrier density, contribute to the carrier diffusion. For $\alpha > 0$, the expansion created carrier density change at the hot end is $-\Delta n_F$. Carrier diffusion, ΔN_F , now sets in from the cold end - where the carrier density is higher - to the hot end. This number of carriers, ΔN_F, is now missing for the thermodiffusion which points to the cold end, i.e. only $(N_F-\Delta N_F)$ carriers thermodiffuse. As the thermodiffusion and the expansion created diffusion are opposite, the contributions ΔN_F compensate and in total we will have a loss of 2NF. This is true also for the carrier densities as $2\Delta N_F/N_F = 2\Delta n_F/n_F$. The same result is obtained if one argues with two independent thermally induced and opposite electrical field components along the wire axis.

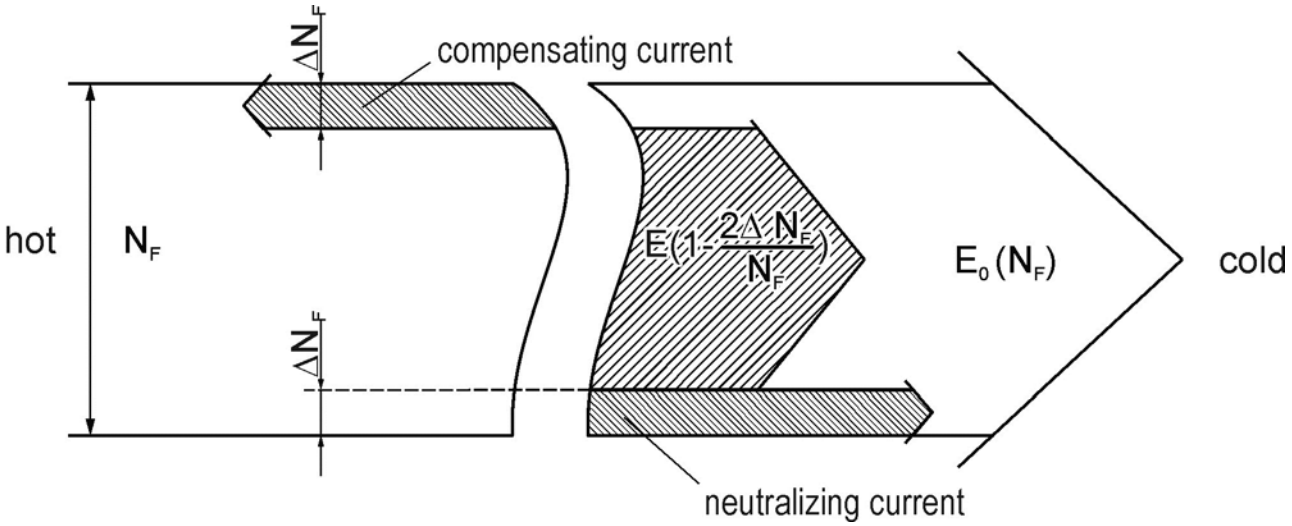

Fig.4 : Currents of carriers in the temperature field

Specifically, we find for the thermodiffusive force:

(10) $F_{TD} = eE_{TD}(N_F - \Delta N_F)$,

and for the expansion created force:

(11) $F_{TA} = eE_{TD}\Delta N_F$.

As the forces are opposite, the resulting force is the difference,

(12) $F_T = F_{TD} - F_{TA} = e\, E_{TD}(N_F - 2\Delta N_F)$ or per mole $f_T = eE_{TD}\,(1 - 2\Delta n_F/n_F)$.

In sum, the thermodiffusive field in a metallic wire is weakened by an amount $2\Delta N_F/N_F$ if there is a positive expansion coefficient $\alpha > 0$.

4. CALCULATION OF THE EXPANSION CREATED CHANGE IN THE ELECTRON DENSITY Δn

If there is a certain number of electrons per atom given to the electron gas of a metal, sometimes called the valence number z, the number of free electrons per atomic volume is constant even if the atomic volume gets larger under thermal expansion, if we take a volume which contains a constant number of atoms and call it the unit volume V, it would still get larger by thermal expansion while also having a constant number of electrons, N_o. However, the carrier density n would then get lower with increasing temperature as $n = N_o/V$ with V increasing (see also fig.5).

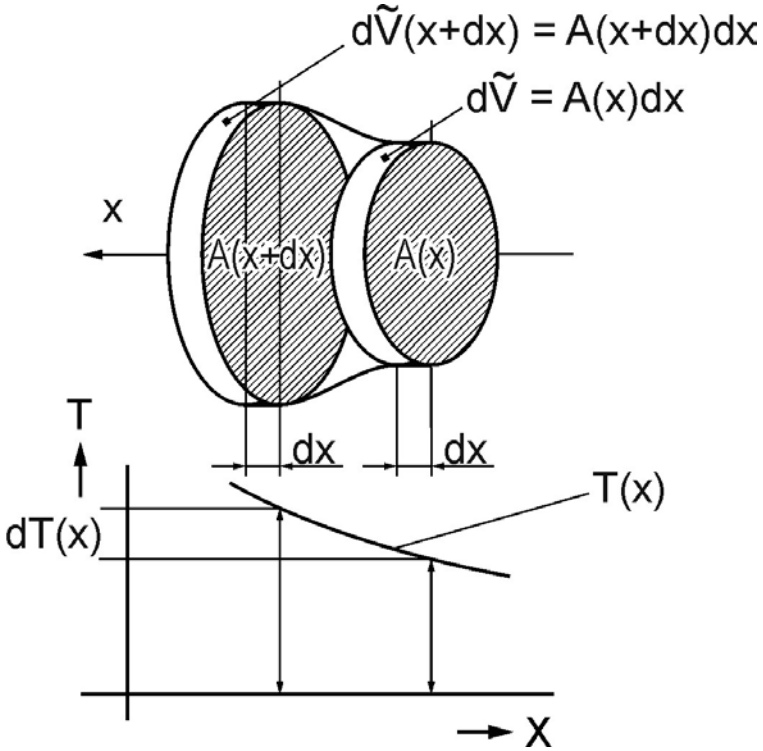

Fig.5: Incremental volume change with temperature change

Specifically, an incremental volume change dV at a position x of the thermowire which has the temperature T(x) can be expressed as dV(x) = A(x)dx, where A(x) is the cross section of the wire

at the position x. A neighbouring volume element , dV(x+dx) is larger if it is under a larger

temperature T(x+dx). Using the applied T-gradient , T', this temperature can be expressed as

$T(x+dx) = T(x) + (dT/dx)dx = T(x) + T'dx$. The volume increment the can be rewritten as :

(13) $\Delta V = dA \cdot dx$,

as $dA = A(x+dx) - A(x)$ and $\Delta V = dV(x+dx) - dV(x) = (A(x+dx) - A(x))dx$.
The total volume increase ΔV_l (per wire length) and an eventual non-linear T-gradient (see fig.6) is then obtained by integration:

(14) $\Delta V_l = 2\alpha A \int dT dx$.

because $dA = 2\alpha A.dT$ and $\Delta V_l = \int \Delta V$.

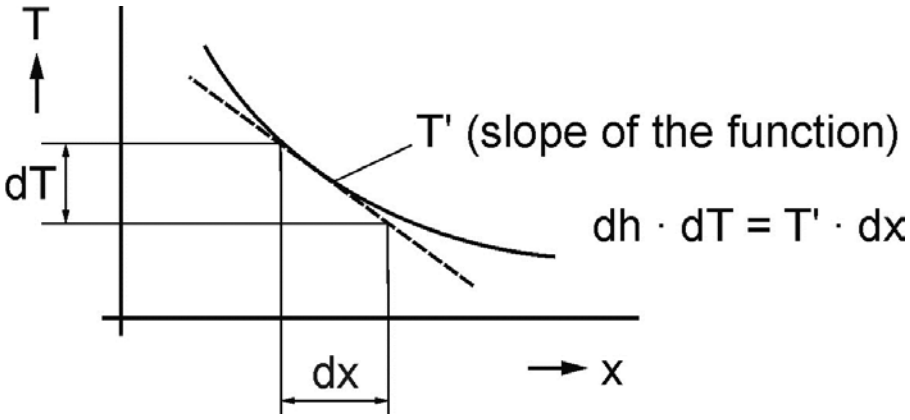

Fig.6: T(x) and its gradient.

Expressing the volume change in x-direction ,

(15) $dV/dx = 2\alpha \int T'dx$,

and expanding the differential of n(x):

(16) $dn/dx = (dn/dV)(dV/dx)$,

using the volume increment, one now has a chance to formulate a differential equation for n(x)on the basis of eq. (16) For that one has to add dn/dV. Since n = No/V, that differential is:

(17) $dn/dV = n/V$

Eq.'s 15-17 result in:

(18) $dn/dx = 2\alpha\, n\, (A/V) \int T'dx = (2\alpha n/l)T(x)$

, as the integral yields T(x) and A/V is just the wire length l. One can now introduce a temperature course correction term $Z{\cdot}T$. Z is defined by :

(19) $\Delta N = \int dn = (2\alpha n)(1/l)\int T dx = Z{\cdot}T$,or as $2\Delta n/4\alpha n = Z$.

$Z{\cdot}T$ is the area of T(x) over the full temperature and length interval (see fig.7).

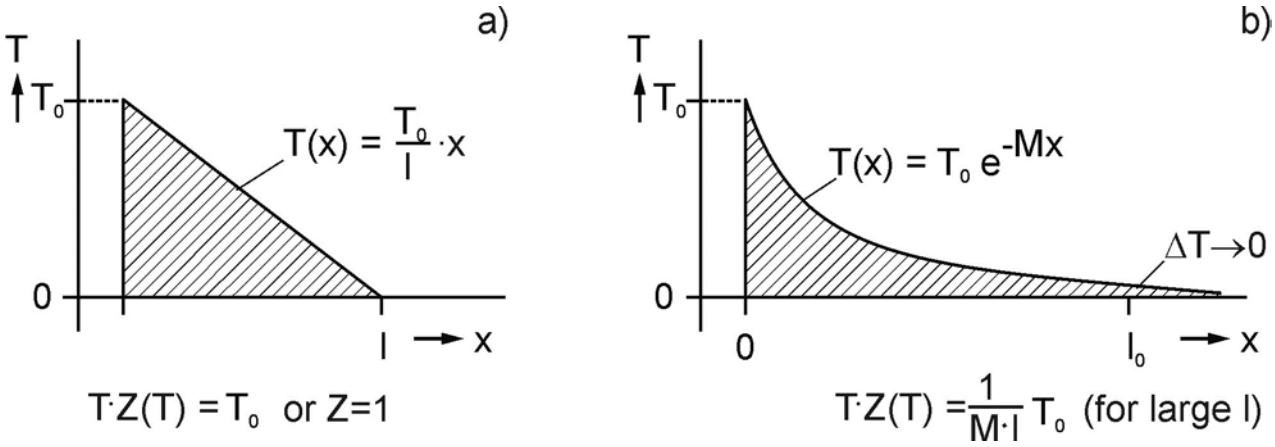

Fig.7 Linear versus exponential drop in temperature over the wire length T_o maximal temperature.

5. ABSOLUTE SEEBECK COEFFICIENT ASC(T) UNDER DIFFERENT TEMPERATURE COURSES

The temperature course T(x) along the wire can be different from linear, for example following Newton's cooling function or they are hyperbolic functions (see /8/). In such cases we have to use

the correction term, Following eq.(19) we have:

(20) $ASC(T) = (\pi 2kT/2eT_F)(1-4\alpha TZ)$,

where k is Boltzmann's constant, e elementary charge, T_F the Fermi temperature, Z the temperature course correction term, α the linear expansion coefficient.

Under the assumption that the temperature course is mainly determined by
the inner heat conduction, we have a linear slope and Z would be 0.5. That case would yield:

(21) $ASC(T) = (\pi^2 k/2eT_F)(T-2\alpha T^2)$.

Under consideration of the thermal expansion there appears a term in the ASC which is quadratic in T. Moreover, using the specific heat capacity of the electron gas one obtains another useful expression for the ASC: (22) $ASC(T) = (C_{em}/eN_A)(1-4\alpha TZ)$. The effect of the thermal expansion is found also in metals with s-d shells and for magnetic materials as Ni or Fe. Fig.8 shows that the ASC(T) -curves can indeed be curved, eventually representing the expansion related quadratic temperature term.

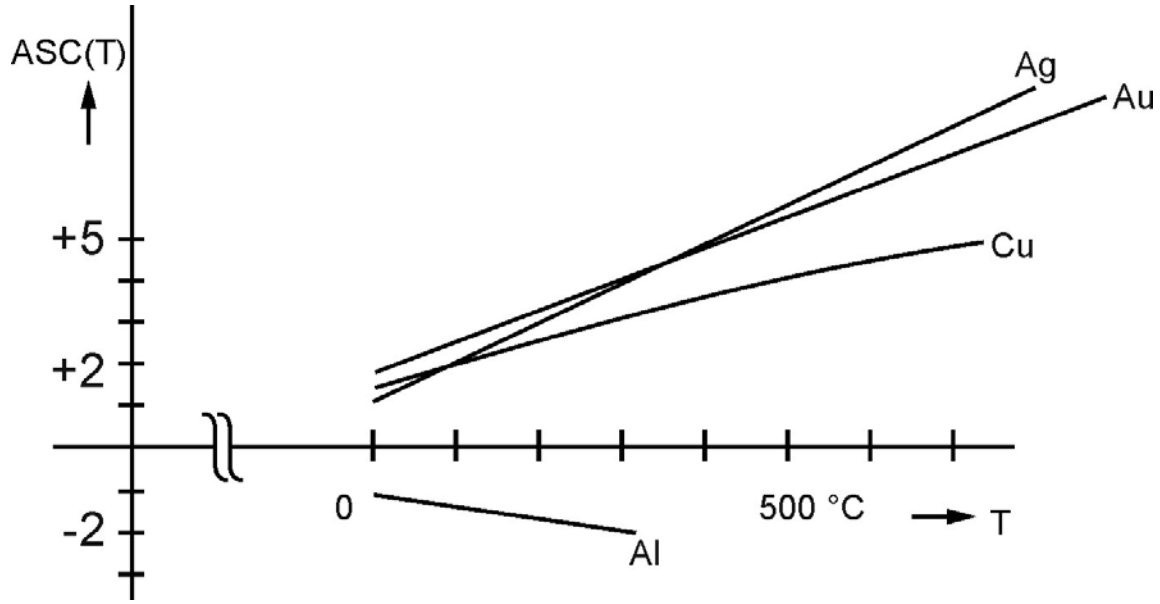

Fig.8: ASC(T) curves of Ag,Au,Cu and Al , acc. to [6]

The temperature course correction term Z introduced above is of fundamental importance. On one hand it is shown that a change of the temperature course along the thermo wire will alter the ASC value. In consequence, if the two thermocouple wires are exposed to a different temperature course respectively the Z values are different resulting in an error. Of course those errors are rather small and will appear for high temperatures only. But, it should be taken into account for precision thermo couple calibrations. In contrast to well-known inhomogeneity effects it occurs also for new unused thermo wires and remarkably, it can't detected by moving the thermocouple against the spatial temperature gradient into or out of the oven.

On the other hand we believe that this Z value calculation could be an explanation for the Benedickts effect which is for metals currently unproven. The author will pick up on this in a future paper.

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