Measurement and Simulation of Surface Tension of Liquid NiCr alloys

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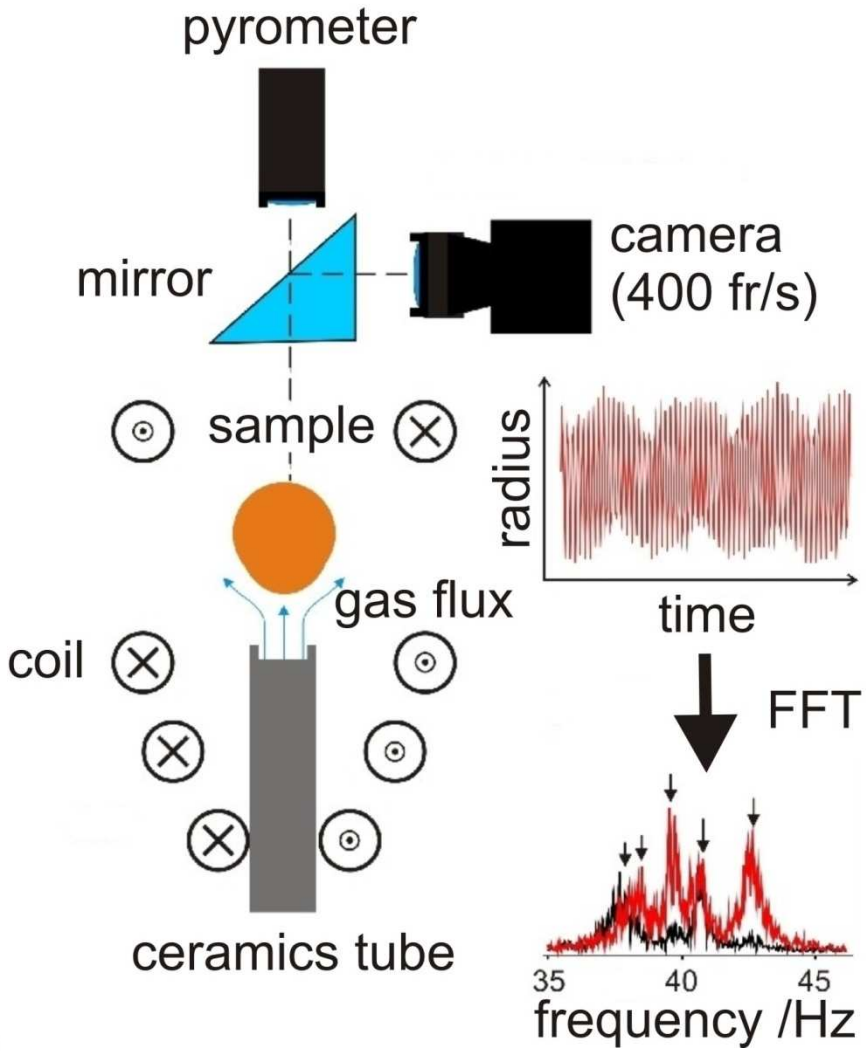
Motivation:

Thermophysical properties: density, surface tension, viscosity

- Important quantities in steelmaking (casting processes)
- Important input parameters for simulation of e.g. casting processes

➔ Aim of the project: Development of a software able to calculate surface tensions of multicomponent metallic alloys, creation of a database containing thermophysical data

Electromagnetic Levitation - Oscillating Drop



levitated liquid drop

Electromagnetic Levitation - Oscillating Drop

oscillating spherical force-free liquid drop[1]:

$$\omega_l^2 = l(l-1)(l+2)\frac{\sigma}{\rho R^3}$$

levitation experiments: ***l*** = 2

$$\Rightarrow \quad \omega_2^2 = \omega_R^2 = \frac{8\sigma}{\rho R^3}$$

Rayleigh formula

under terrestrial conditions: drop is not force-free !

ω_R Rayleigh frequency
σ surface tension
R radius of the liquid sample
ρ density of liquid sample (temperature dependent)

[1]J.W.S. Rayleigh , Proc. Roy. Soc. **29** (1873) 71

Electromagnetic Levitation - Oscillating Drop

correction of Cummings and Blackburn[2], sum rule:

$$\omega_R^2 = \frac{1}{5}\sum_{i=-2}^{2}\omega_{i,2}^2 - \overline{\omega_\tau^2}\left(1.90 + 1.2\frac{g^2}{4\left(\overline{\omega_\tau^2}\right)^2 R^2}\right)$$

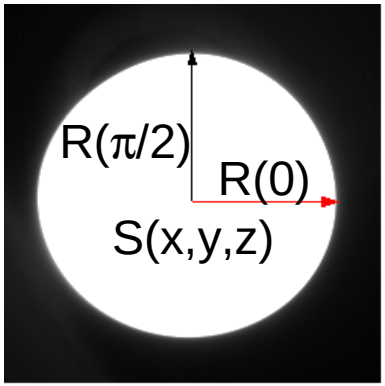
Rayleigh frequency ω_R splits up into 5 not degenerated frequencies:

$$\overline{\omega_{osc}^2} = \frac{1}{5}\sum_{i=-2}^{2}\omega_{i,n}^2 = \left(\omega_0^2 + \omega_{-1}^2 + \omega_1^2 + \omega_{-2}^2 + \omega_2^2\right)$$

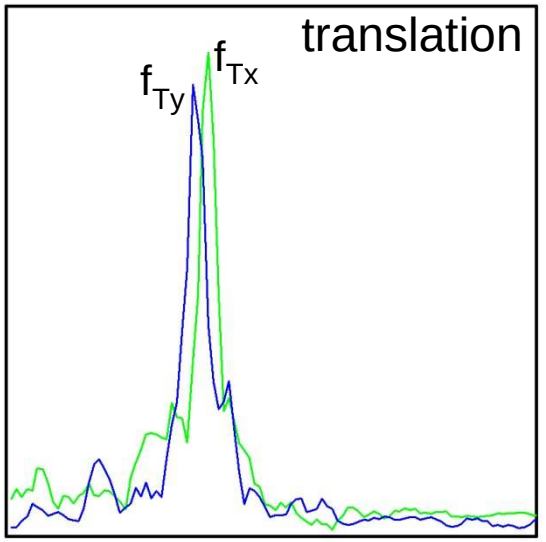
$$\overline{\omega_\tau^2} = \frac{1}{3}\left(\omega_{\tau x}^2 + \omega_{\tau y}^2 + \omega_{\tau z}^2\right)$$ mean square translation frequency

[2]D.L. Cummings, D.A. Blackburn, J.Fluid. Mech. **224** (1991) 395

Oscillating Drop

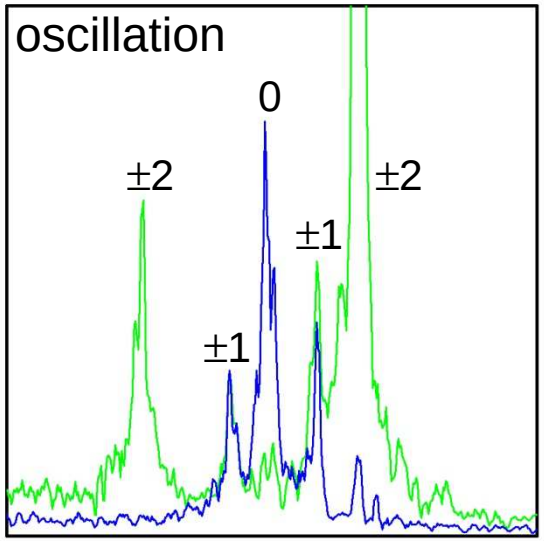


fft {R(0)}, fft{R(π/2},
fft {A}



frequency /Hz

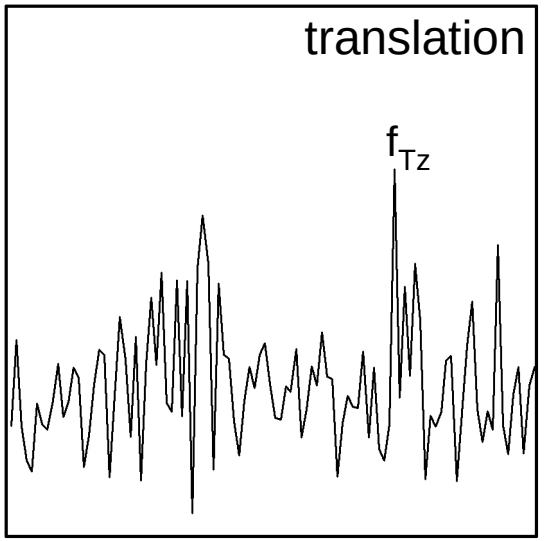
fft {R(0) - R(π/2)}
fft {R(0) +R(π/2)}



selection rules:

Peak	*fft* (sum)	*fft* (difference)
$m=0$	+	-
$m=\pm1$	+	+
$m=\pm2$	-	+

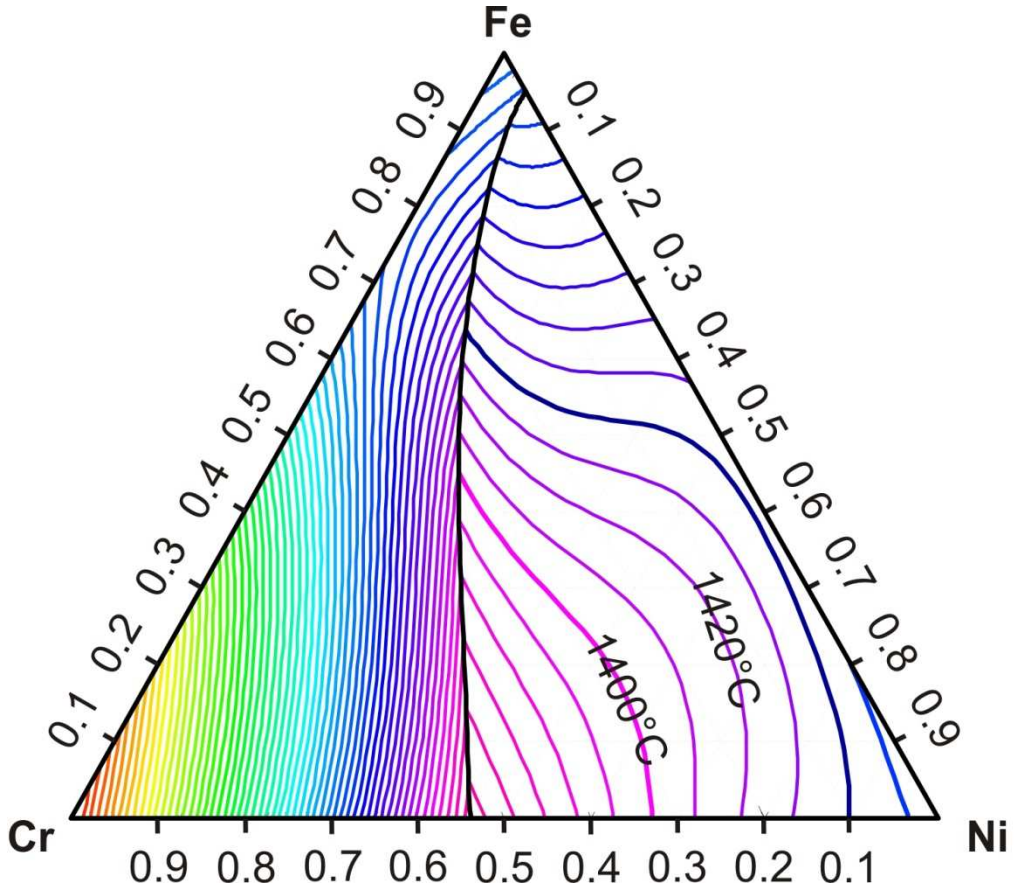
+ visible, - not visible



frequency /Hz

Model system for steels: FeNiCr

Calculated melting temperatures:



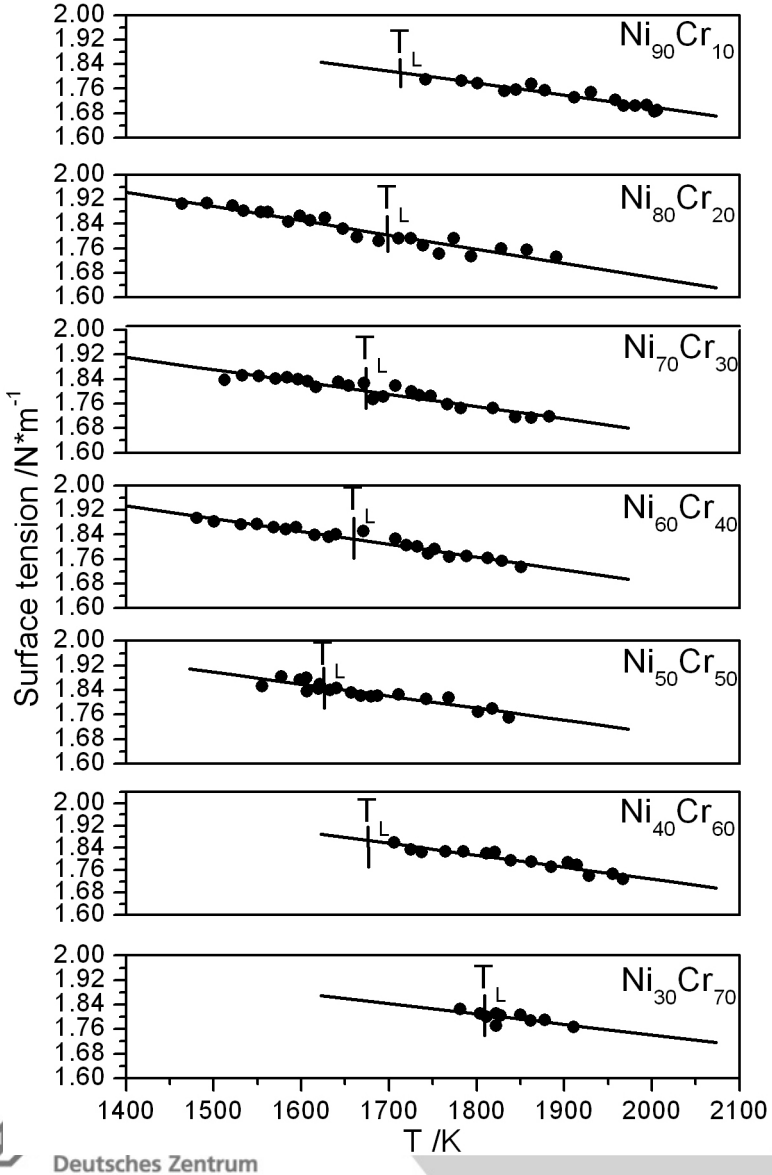
Cr rich side (left):

- high melting temperatures
- strong evaporation of Cr (large exp. error)

⇒ started with binary alloys

Surface Tension –

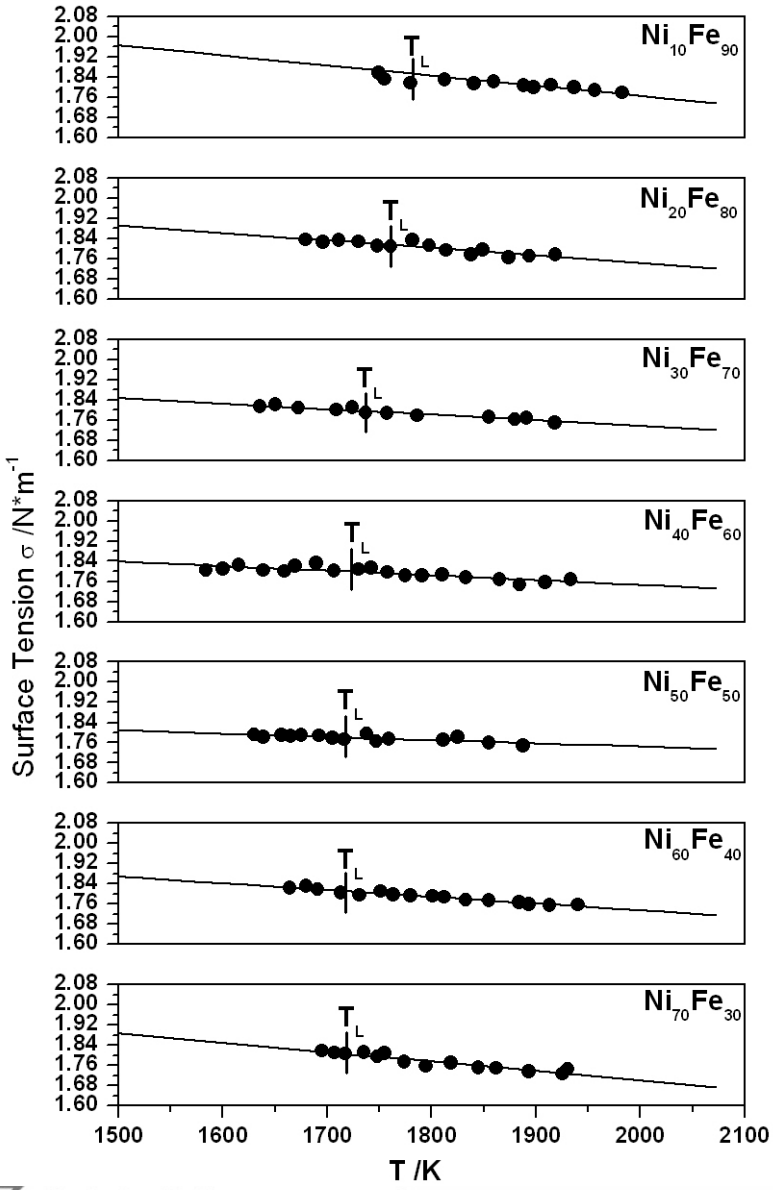
Example: NiCr



x	σ_T	σ_L	T_L
Ni_xCr_{100-x}	$/ 10^{-4} N \cdot m^{-1} \cdot K^{-1}$	$/ N \cdot m^{-1}$	/ K
0[*3]	-3.20	1.7000	2180
10			
20			
30	-3.42	1.8071	1808
40	-4.30	1.8645	1683
50	-3.91	1.8471	1631
60	-4.17	1.8273	1657
70	-4.01	1.7990	1680
80	-4.63	1.8058	1696
90	-3.90	1.8128	1713
100	-3.85	1.7784	1728

[3]T. Tanaka, T. Iida, Steel Research **65(1)** (1994) 21

Surface Tension – Measurements NiFe



x	σ_T	σ_L	T_L
Ni_xFe_{100-x}	$/ 10^{-4} N \cdot m^{-1} \cdot K^{-1}$	$/ N \cdot m^{-1}$	/ K
0	-3.04	1.833	1811
10	-4.00	1.855	1779
20	-2.99	1.815	1759
30	-2.24	1.795	1738
40	-1.87	1.798	1742
50	-1.25	1.7816	1715
60	-2.67	1.811	1715
70	-3.77	1.807	1718
80			
90			
100	-3.85	1.778	1728

Surface Tension – Butler equation

Surface tension calculation method based on Butler´s equation[4]

for binary solution of components 1 and 2:

$$\sigma = \sigma_1 + \frac{RT}{A_1}\ln\frac{(1-c_2^S)}{(1-c_2^B)} + \frac{1}{A_1}G_1^{E,S} - \frac{1}{A_1}G_1^{E,B}$$

$$= \sigma_2 + \frac{RT}{A_2}\ln\frac{c_2^S}{c_2^B} + \frac{1}{A_2}G_B^{E,S} - \frac{1}{A_2}G_2^{E,B}$$

σ_1, σ_2 surface tensions of components 1, 2 with molar free surface A_1 and A_2

$G_1^{E,B}$, $G_2^{E,B}$, $G_1^{E,S}$, $G_2^{E,S}$ partial excess Gibbs energies of 1 and 2 in the bulk (B) and in the surface (S)

c_1^B, c_1^S, c_2^B, c_2^S concentrations of 1, 2 in the bulk (B) and the surface (S)

[4]T. Tanaka, K. Hack, T. Ida, S. Hara, Z. Metallkde **87** (1996) 380

Surface Tension – Constrained Gibbs Energy Minimisation

Butler´s equation is difficult to handle for multi-component systems ⇒ Generalisation[5] starting from Gibbs:

$$G = \sum_i n_i \mu_i + A\sigma$$

$$n_i = n_i^B + n_i^S, \quad A = \sum_i n_i^S \cdot A_i$$

$$G = \sum_i n_i^B \mu_i + \sum_i n_i^S (\mu_i + A_i \sigma)$$

μ_i^B μ_i^S

μ_i = chemical potential of *i*,
n_i = mole fraction of *i*
A = surface area, σ = surface tension

μ_i^B = chemical potential of *i* in the bulk,
μ_i^S = chemical potential of *i in the surface*

[5]P.Koukkari, R. Pajarre, K. Hack, Int. J. Mat. Res. **98** (2007) 10

Surface Tension – Constrained Gibbs Energy Minimisation

System	Constraint	Conjugate Potential
System with chemical equilibrium	$\sum_{\alpha=1}^{\Omega}\sum_{k=1}^{N_\alpha} a_{kj}\, n_k^\alpha = b_j$ mass balance	$\sum_{j=1}^{l} a_{kj}\,\pi_j = \mu_k$ chem. potential
Systems with surface/interface equilibria	$A = \sum_{i=1}^{N_S} n_i^s\, A_i$ surface area	$\pi_l = \sigma \cdot A_0$ surface energy for unit area

G calculated and minimised for equilibrium
(code based on *ChemApp*)

Surface Tension – Constrained Gibbs Energy Minimisation

Prerequisite data for calculation:

- *Chemical potentials* μ of the pure liquid components, i.e. the G-values $\Rightarrow$ equilibrium calculations

- *Excess Gibbs energies* of the liquids (L-terms of Redlich-Kister formalism or other models)

- Temperature dependent *density values* of the pure liquid components $\Rightarrow$ molar surface area

- Temperature dependent *surface tensions* of the pure liquid components

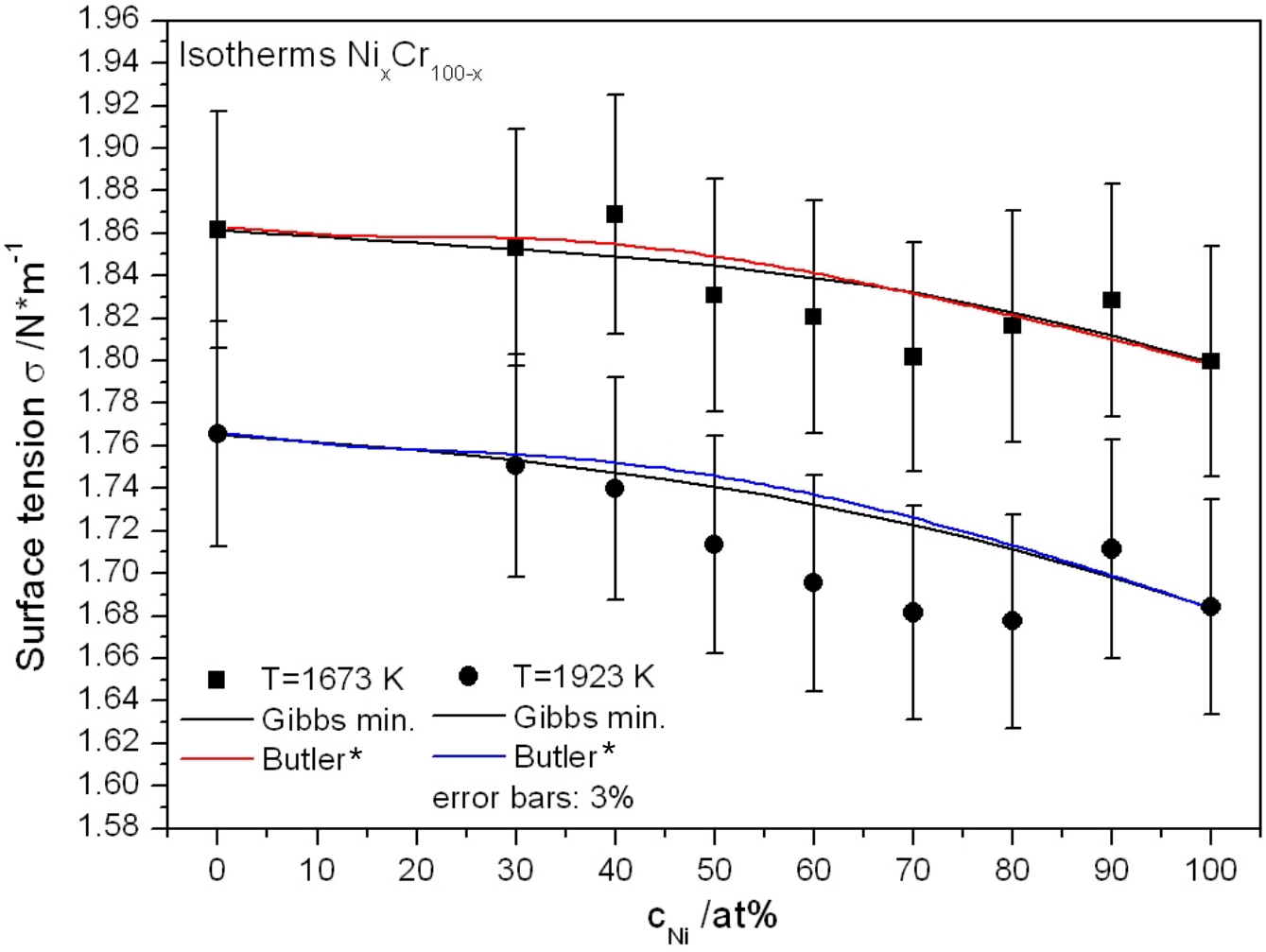
- Scaling factor β from bulk to liquid $\Rightarrow$ excess Gibbs energies of the surface liquid $G^{ex,s} = \beta\, G^{ex,b}$

Surface Tension – Constrained Gibbs Energy Minimisation

Results:

1. Calculation of surface tension $\sigma(T)$
2. Calculation of $A\ \sigma$
3. Determination of excess Gibbs energies of surface components from bulk data (β)
4. Determination of surface bulk equilibrium

Comparison: Theoretical and Experimental Results

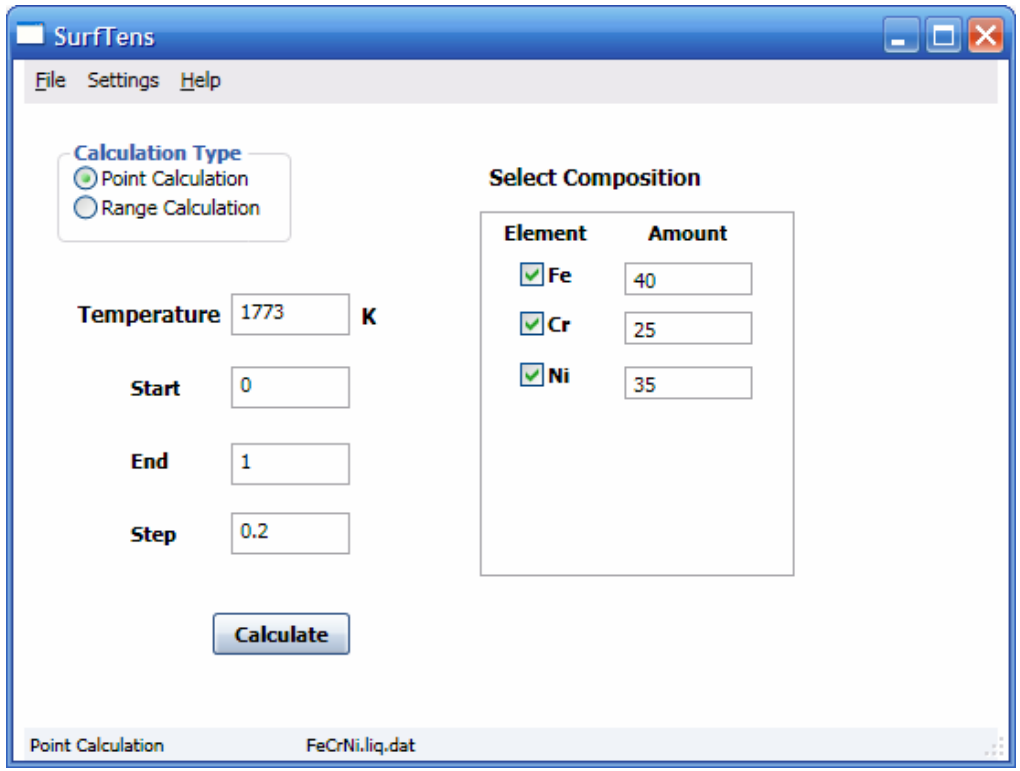


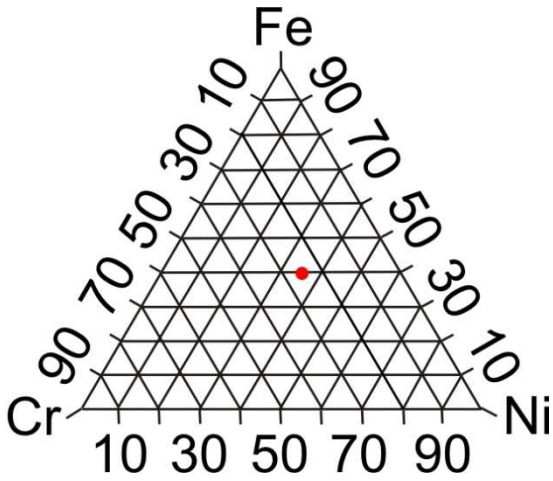
Surface tension as function of composition described well within experimental error of 3 %

* calculations by J. Brillo, DLR, Cologne

Software: Screenshots

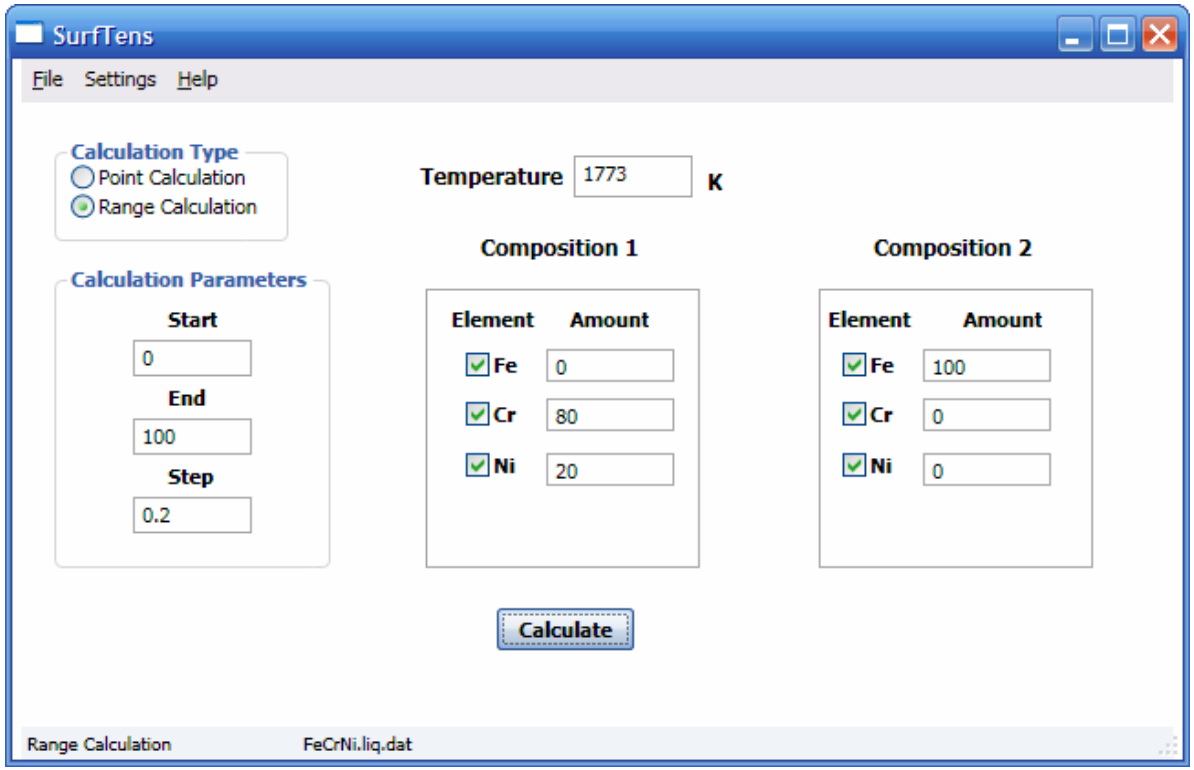
Calculation for a fixed composition ($Fe_{40}Cr_{25}Ni_{35}$)
for constant temperature (1773 K)

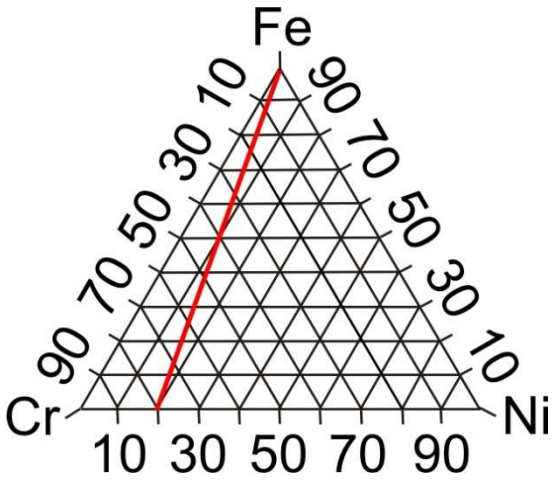




Software: Screenshots

Calculation for a composition range from $Cr_{80}Ni_{20}$ to Fe_{100} for constant temperature (1773 K)





Summary:

- Motivation
- FeNiCr Model system for steels
- Electromagnetic levitation
  Measurement of Surface Tension (oscillating drop method)
  Example: NiCr
- Calculation of Surface Tension
  The Butler equation
  Gibbs Energy Minimisation Method
- Comparison: Theoretical and Experimental Results

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Thanks for your attention !