Surface Tension of Ternary FeNiCr alloys

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Motivation:

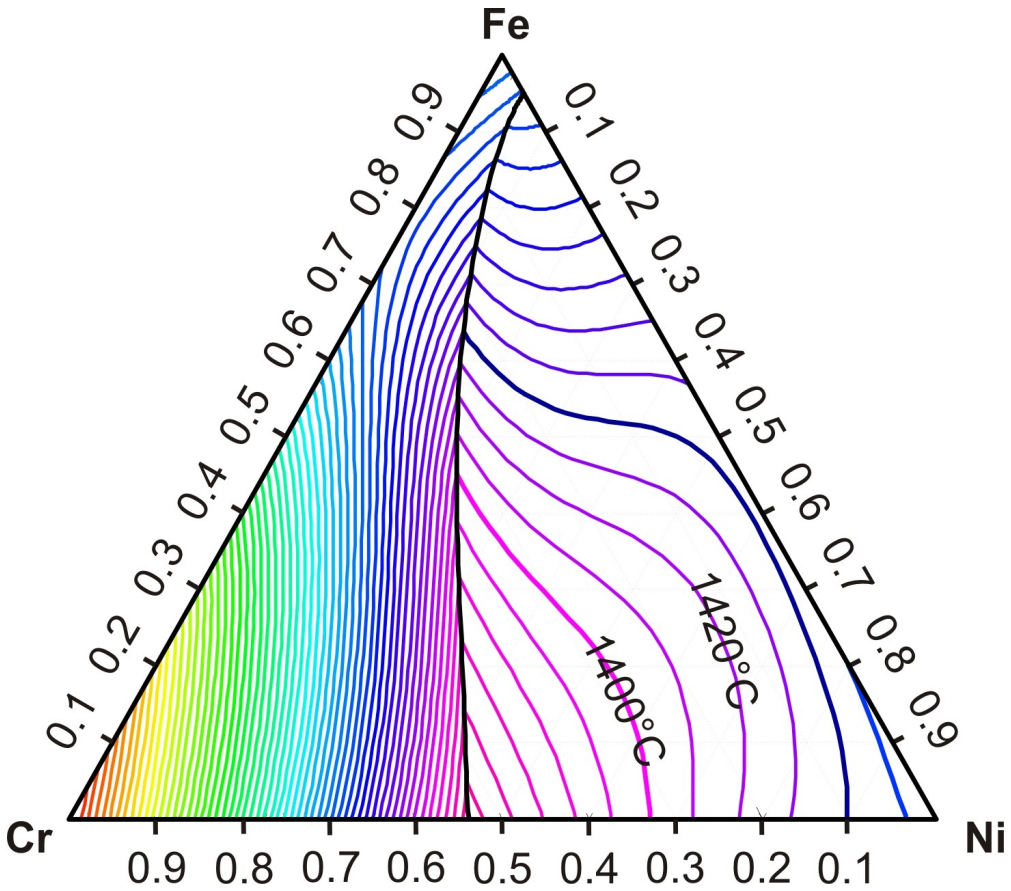
Thermophysical properties: density, surface tension, viscosity

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

photo: www. stahlonline.de

Model system FeNiCr:

Calculated melting temperatures:



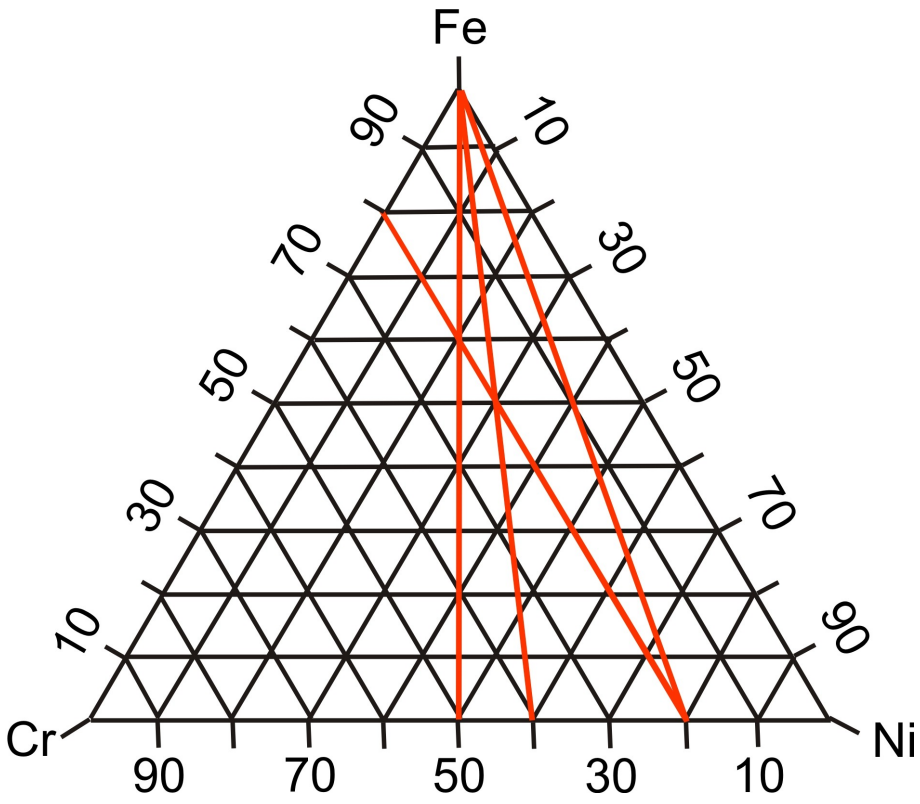
Cr rich side (left):

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

⇒ focus on the Cr-poor side (right)

Model system FeNiCr:

Very many steels based on ternary FeNiCr-system

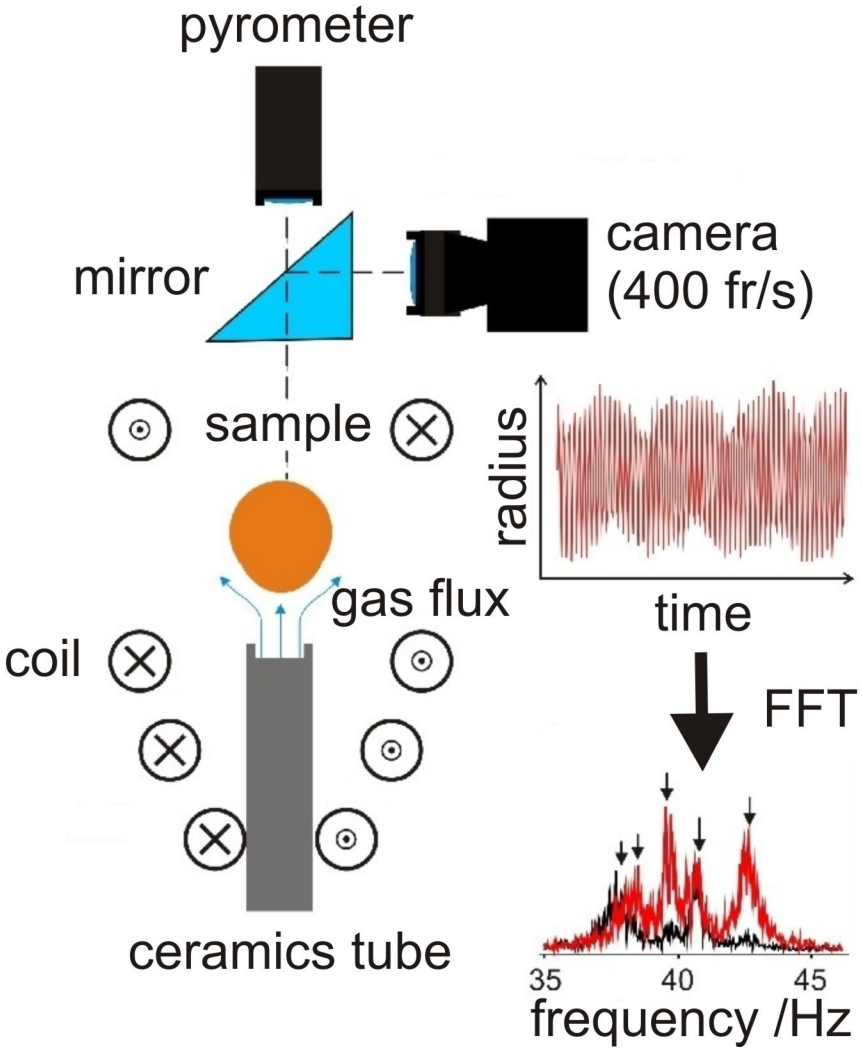


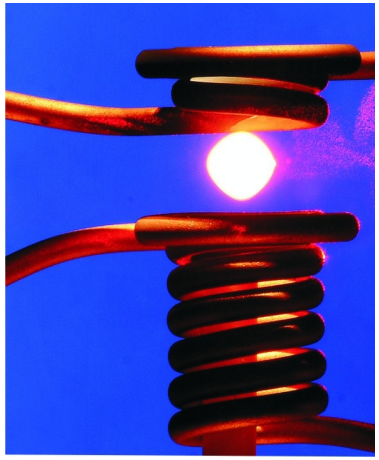
Four cuts through phase diagram:

1. $Fe_xNi_{0.8-x}Cr_{0.2}$
2. $Fe \rightarrow Cr_{50}Ni_{50}$
3. $Fe \rightarrow Cr_{40}Ni_{60}$
4. $Fe \rightarrow Cr_{20}Ni_{80}$

Aim:
Development of a database containing surface tension data

Electromagnetic Levitation - Oscillating Drop





levitated liquid drop

Oscillating Drop

oscillating spherical force-free liquid drop[1]:

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

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

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

Rayleigh formula

under ground-based experimental conditions: drop is not force-free !

ω_R Rayleigh frequency

γ surface tension

R radius of the liquid sample

ρ density of liquid sample (temperature dependent)

[1]Lord Rayleigh , Proc. Roy. Soc. **29** (1873) 71

Oscillating Drop

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

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

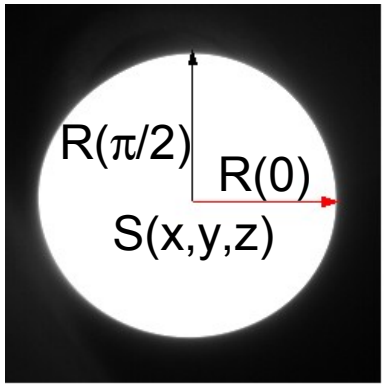
Rayleigh frequency ω_R splits up into 5 not degenerated frequencies:

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

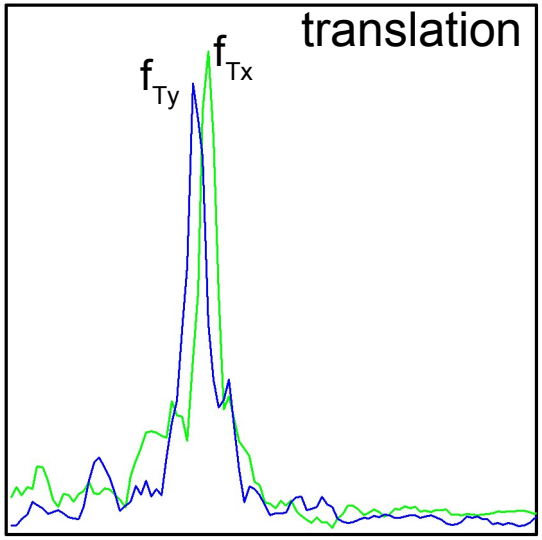
$\overline{\omega_\tau^2} = \frac{1}{3}\left(\omega_{\tau x}^2 + \omega_{\tau y}^2 + \omega_{\tau z}^2\right)$ mean square translation frequency

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

Oscillating Drop

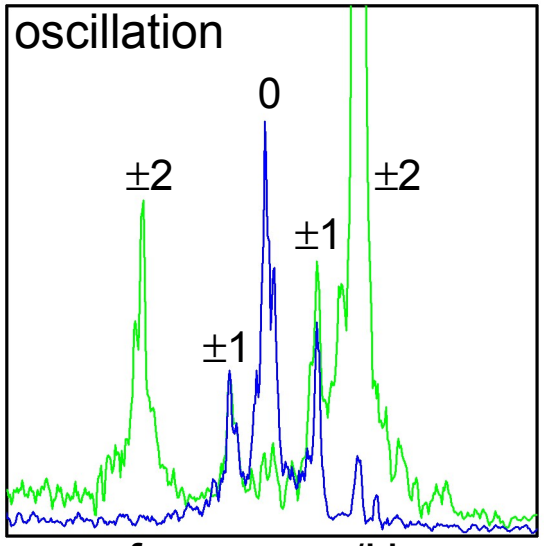


fft {R(0)}, fft{R(π/2},
fft {A}



frequency /Hz

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

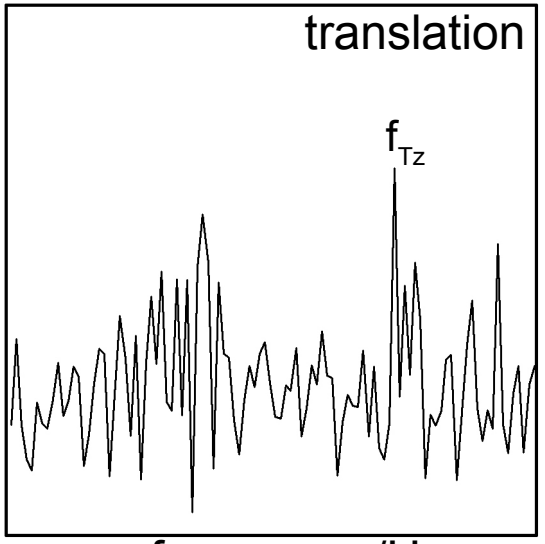


frequency /Hz

selection rules:

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

+ visible, - not visible



frequency /Hz

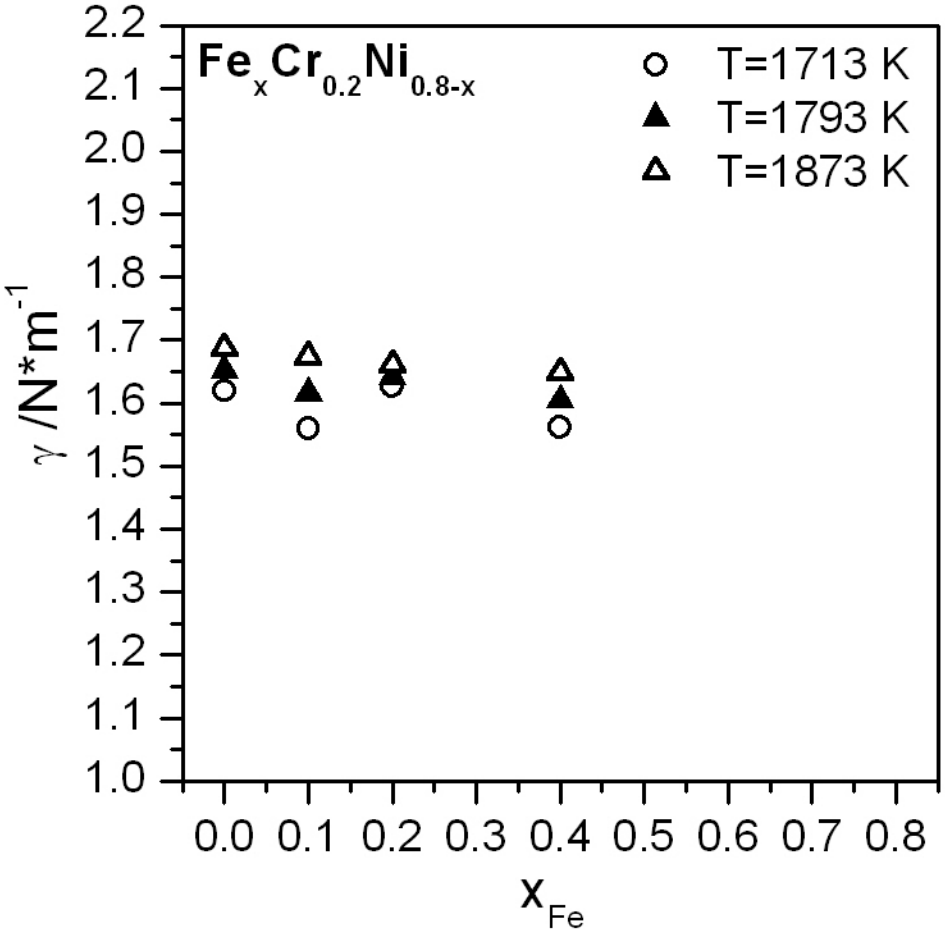
Electromagnetic Levitation - Oscillating Drop

From electromagnetic levitation, temperature dependence of surface tension is obtained:

$\Rightarrow$ usually linear:

$$\gamma = \gamma_L + \gamma_T \cdot (T - T_L)$$

For constant T the dependence of surface tension on concentration can be derived



Surface Tension – Theoretical background

Surface tension calculation method based on Butler´s equation[3]

for binary solution of A and B:

$$\gamma = \gamma_A + \frac{RT}{A_A}\ln\frac{(1-c_B^s)}{(1-c_B^b)} + \frac{1}{A_A}G_A^{E,s} - \frac{1}{A_A}G_A^{E,b}$$

$$= \gamma_B + \frac{RT}{A_B}\ln\frac{c_B^s}{c_B^b} + \frac{1}{A_B}G_b^{E,s} - \frac{1}{A_B}G_B^{E,b}$$

γ_A, γ_B surface tensions of components A, B with molar free surface A_A and A_B

$G_A^{E,b}$, $G_B^{E,b}$, $G_A^{E,s}$, $G_B^{E,s}$ partial excess Gibbs energies of A and B in the bulk (b) and in the surface (s)

$c_A^b, c_A^s, c_B^b, c_B^s$ concentrations of A, B in the bulk (b) and the surface (s)

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

Surface Tension – The Butler equation

Butler´s equation is difficult to handle for multi-component systems

Generalisation:

equilibrium

$$\mu_i^b = \mu_i^s$$

$$\mu_i^b = \mu_i^{0,b} + RT \ln a_i^b$$

$$\mu_i^{0,b} = \mu_i^0$$

$$\mu_i^s = \mu_i^{0,s} + RT \ln a_i^s - A_i \gamma$$

$$\mu_i^{0,s} = \mu_i^0 + \gamma_i A_i$$

$$\mu_i^s = \mu_i^0 + \gamma_i A_i + RT \ln a_i^s - A_i \gamma$$

$\mu_i^{0,b}$, $\mu_i^{0,s}$ = chemical standard potential of *i* in bulk (b) and surface (s)

μ_i^0 = chemical standard potential of *i*

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

Surface Tension – Calculation

Generalized Gibbs Energy Constraint Method[4]

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	$\pi_l = \gamma \cdot A_0$ surface energy for unit area

Gibbs free energy: $G = \sum_i \mu_i^b n_i^b + \sum_i \mu_i^s n_i^s + \gamma \sum_i A_i n_i^s$

with chemical potentials:

$$G = \sum_i n_i^b (\mu_i^0 + RT \ln a_i^b) + \sum_i n_i^s (\mu_i^{0,s} + RT \ln a_i^s)$$

G calculated from bulk and surface phase constraint

Surface Tension – Calculation

Prerequisite data for calculation:

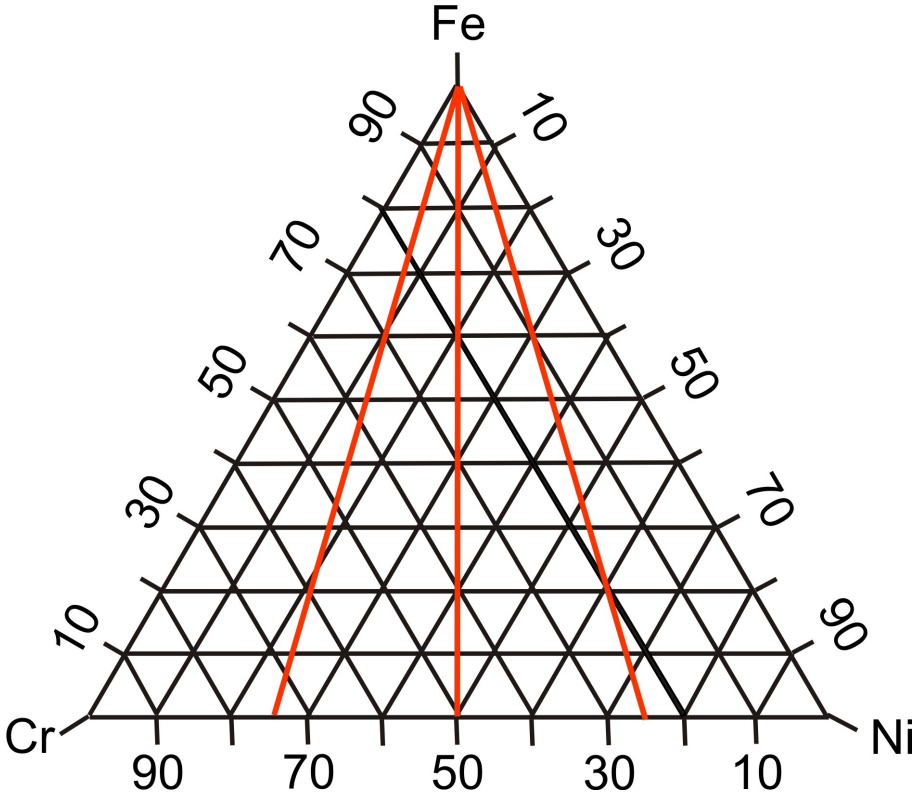
- *Chemical potentials* μ of the pure liquid components, i.e. the G-values $\Rightarrow$ equilibrium calculations
- *Excess Gibbs energies* of the liquids (L-terms of Redlich-Kister formalism or other models)
- Temperature dependent *density values* of the pure liquid components $\Rightarrow$ molar surface 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 $G^{ex,s} = \beta G^{ex,b}$

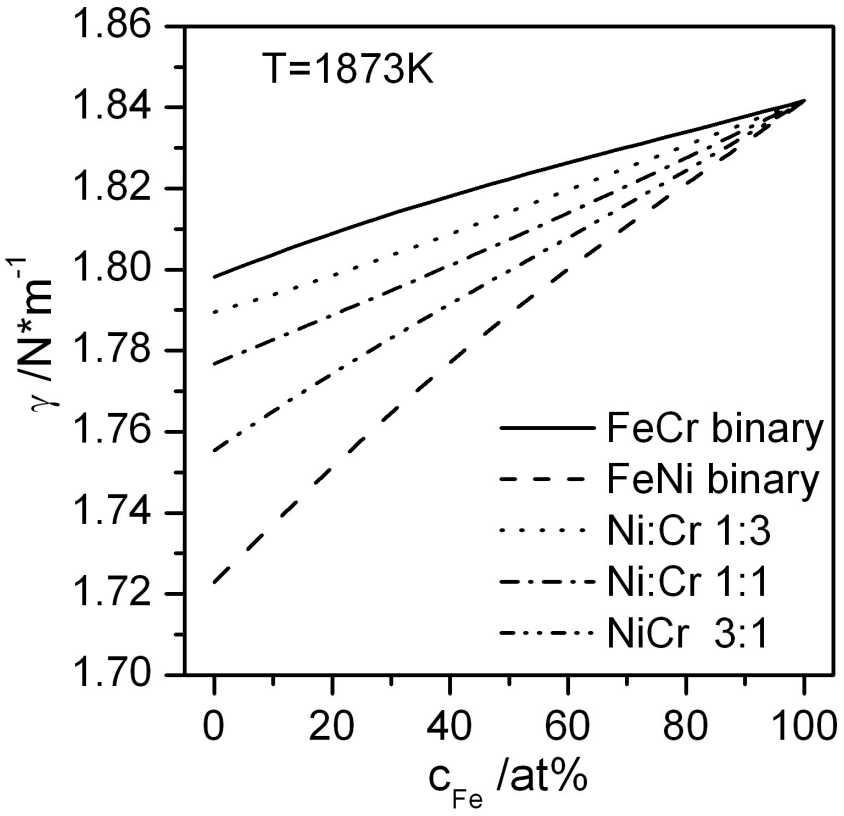
Surface Tension – Calculation

1. Stoichiometric matrix of multicomponent system containing all relevant information, e.g. molar surface area
2. Calculation of surface tension $\gamma_i(T)$
3. Calculation of $A_i\gamma_i$
4. Determination of excess Gibbs energies of surface components from bulk data (β)
5. Determination of surface bulk equilibrium

→ surface tension either as ratio of additional Lagrangian multiplier and scaling factor or as ratio of difference in chemical potential and molecular surface area

Surface Tension – Calculation





Summary:

- Motivation
- Model system FeNiCr
- Electromagnetic levitation
- oscillating drop technique
- Surface Tension

Theoretical background

- The Butler equation

Calculation

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Thanks for your attention !

photo: www. stahlonline.de