# General Galvanizing
## - Contribution to steel reactivity -
## - Steel chemistry and expected coatings-

**Nordic Galvanizers**
**23 & 24 April 2019**
**Lund**

Roger Pankert

# Content

- **Observations about different steels and reactivity**
  - **Influence of carbon content**
  - **Influence of steel poisons: P, S**
  - **Influence of alloying elements: Si, Al, Mn**
  - **Explanation attempts**

- **Steel composition**
  - **Microstructures**
  - **Coating architecture**
  - **View on non reactive steels**

# Zn-Fe reaction during Galvanizing

## Fe is steel

- Alloying elements
  - Si, P, S
  - Al
  - Ti, Mn, Mo, …
- Production history
  - hot or cold rolled
  - Microstructure & dislocations
  - Hydrogen
  - Roughness

## Zn is not just Zn

- Alloying elements
  - Pb, Bi, Sn, ..
  - Al, (Mg), …
  - Ni, …..
- Impurities
  - Cu, Cd, ….

- Uneven coatings
- Surface defects
- Abnormalities

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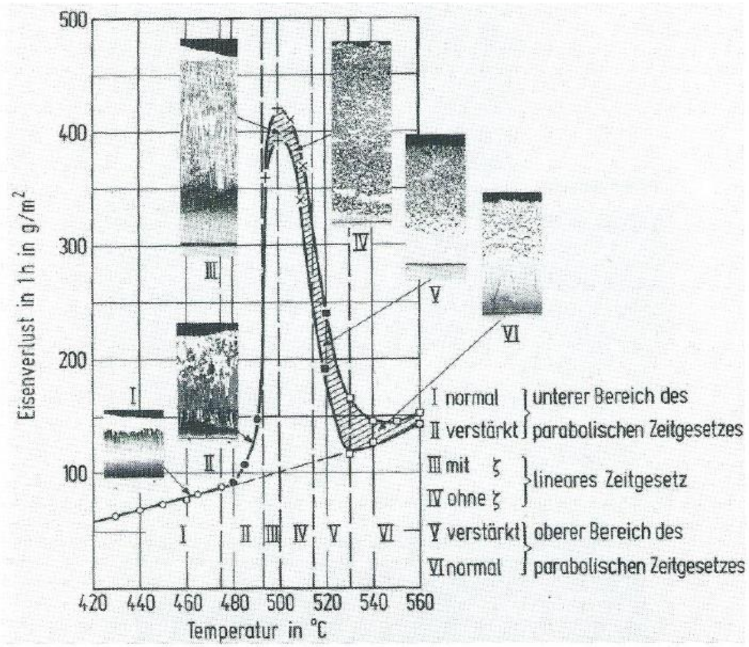
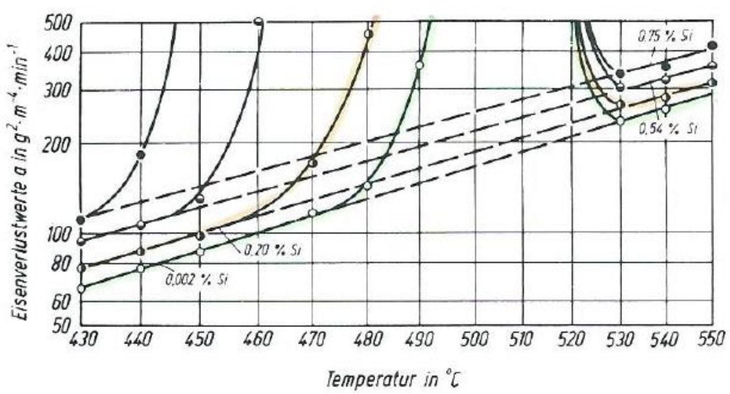
# Fe dissolution in liquid Zinc




- **Dissolved Fe creates intermetallic phases**
  - **δ-phase: 12% Fe**
  - **ζ-phase: 7%Fe**
- **ζ forms first and transforms later into δ**
- **10 g dissolved Fe/m2 can:**
  - **promote 20 µm ζ-phase layer**
  - **promote 11 µm δ-phase layer**

**The Fe-loss for a 0,2% Si containing steel is only 15% higher than for a 0,02% SI containing steel!**

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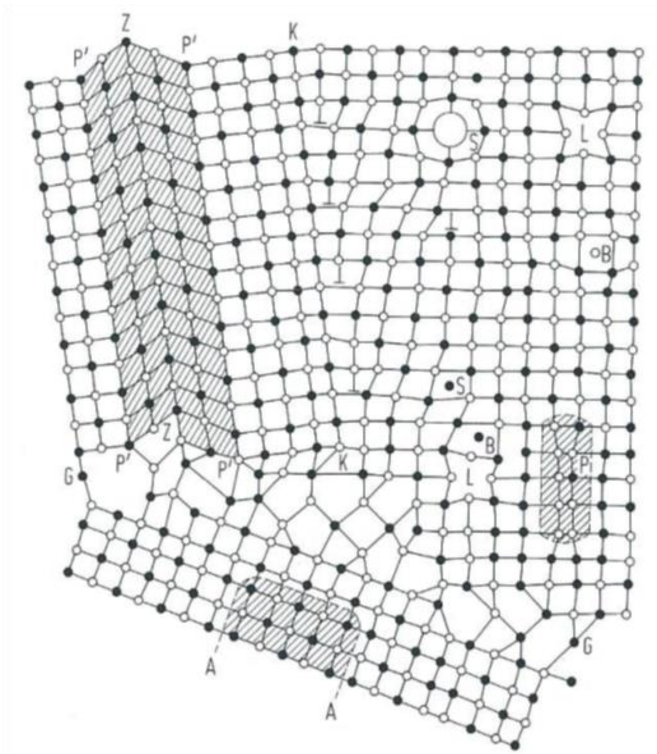
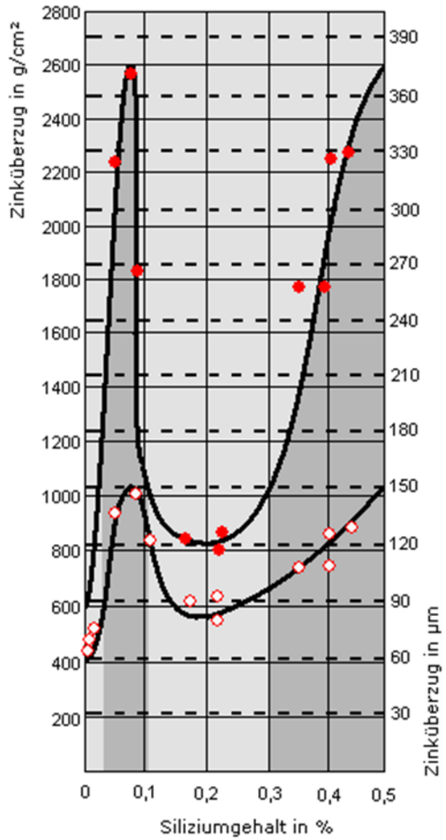
# Fe dissolution in liquid Zinc




- L: vacancy
- B: interstitial atom
- S: foreign atom
- A: anti-phase-boundary
- Z. twinboundary
- P: coherent phase-boundary
- ⊥: dislocation

**Fe ”attack” strongest where lattice is destroyed!**

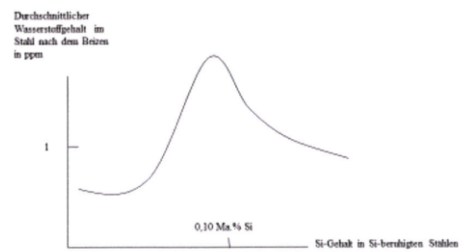
# Attempts to explain reactivity of Si in steel by hydrogen theory (IKS Germany)



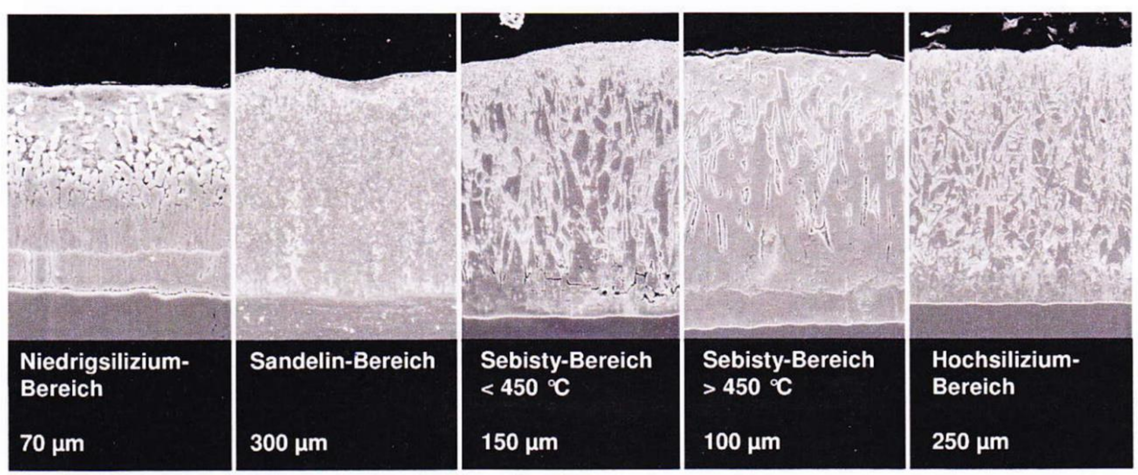

● Tauchzeit 3 Min.
○ Tauchzeit 3 Min.

Temperatur des Zinkbades 460°C

Durchschnittlicher Wasserstoffgehalt in Si-beruhigten Stählen nach dem Beizen und vor dem Verzinken




**Typische Strukturen bei Verzinkungstemperaturen zwischen 435 °C – 490 °C**

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# Shematic compositions of coatings

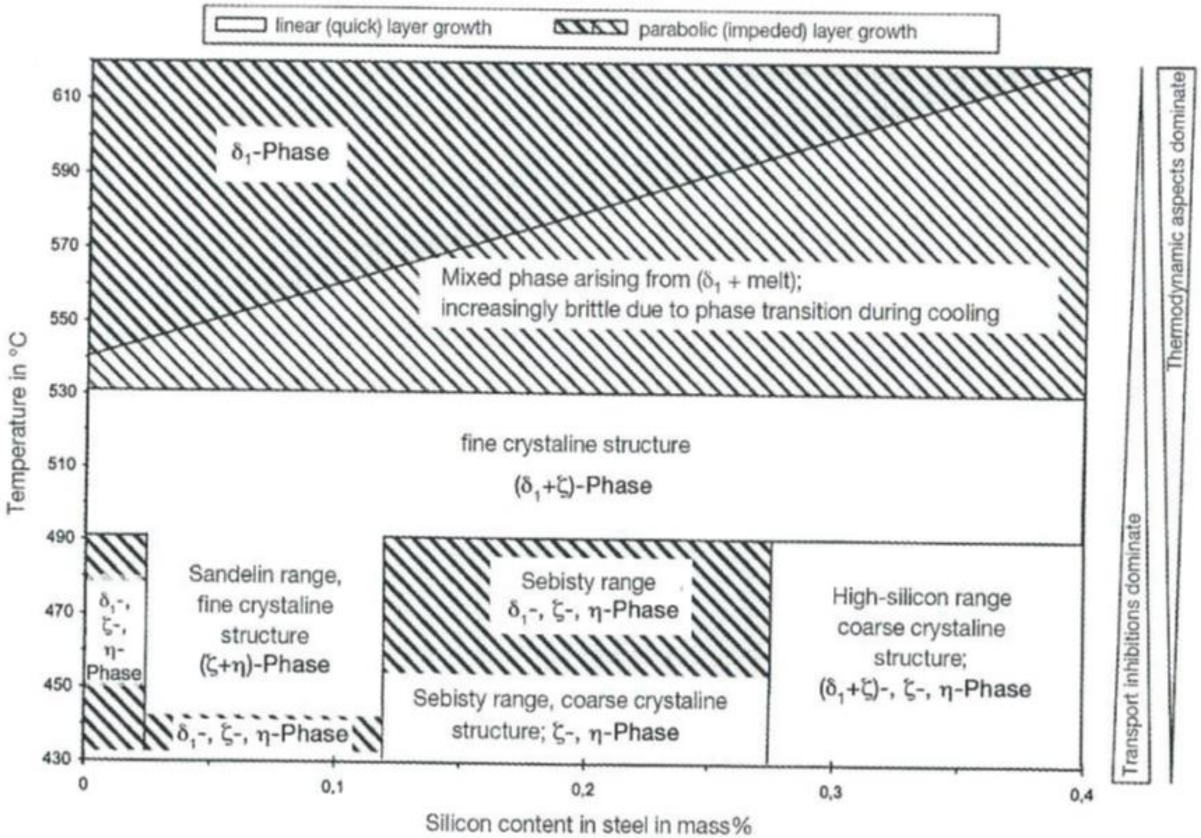


Fig. 40: General survey of the crystalline structure in hot-dip batch galvanizing for low-phosphorus structural steel in conventional zinc melt (galvanizing time > 5 minutes)

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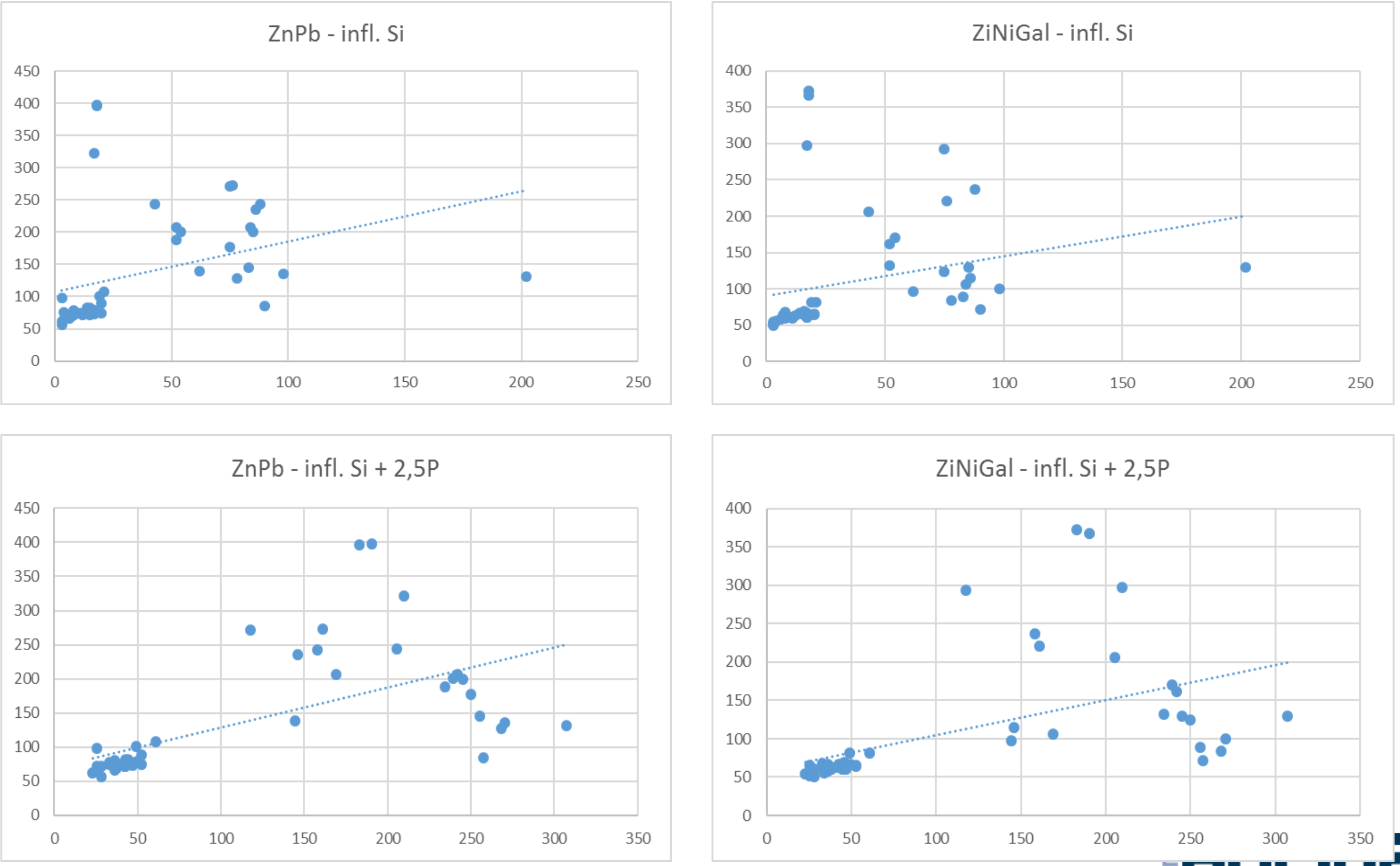
# ….. but there must be something more to be considered ….

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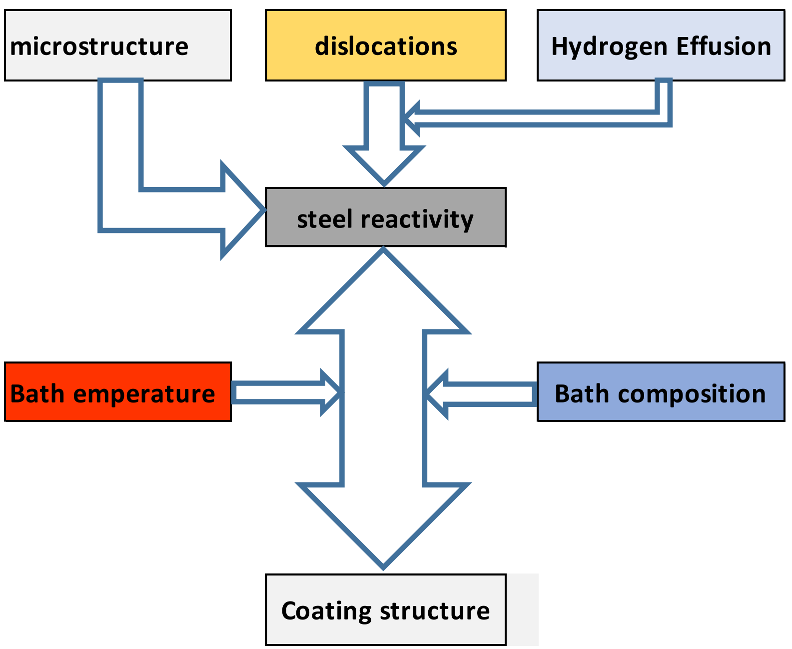
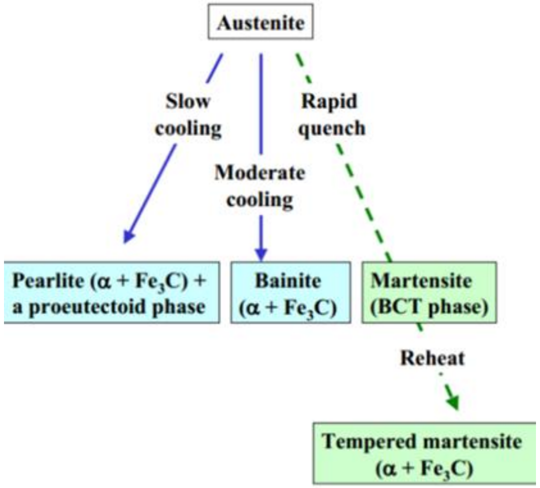
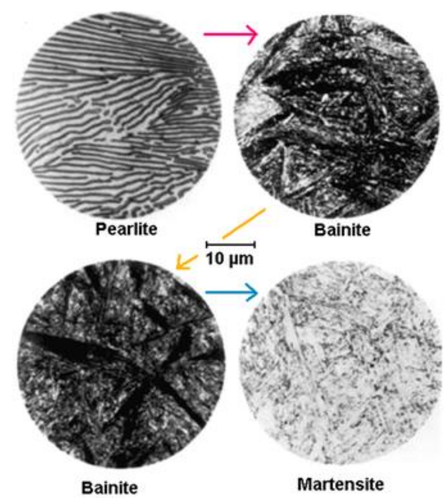
# Microstructure steel

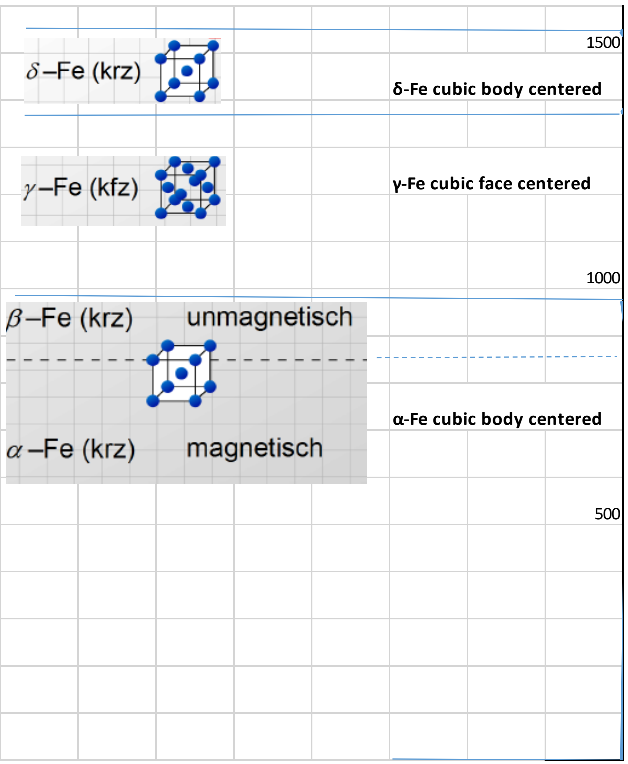
- Depends on steel chemistry
- Depends on cooling parameters

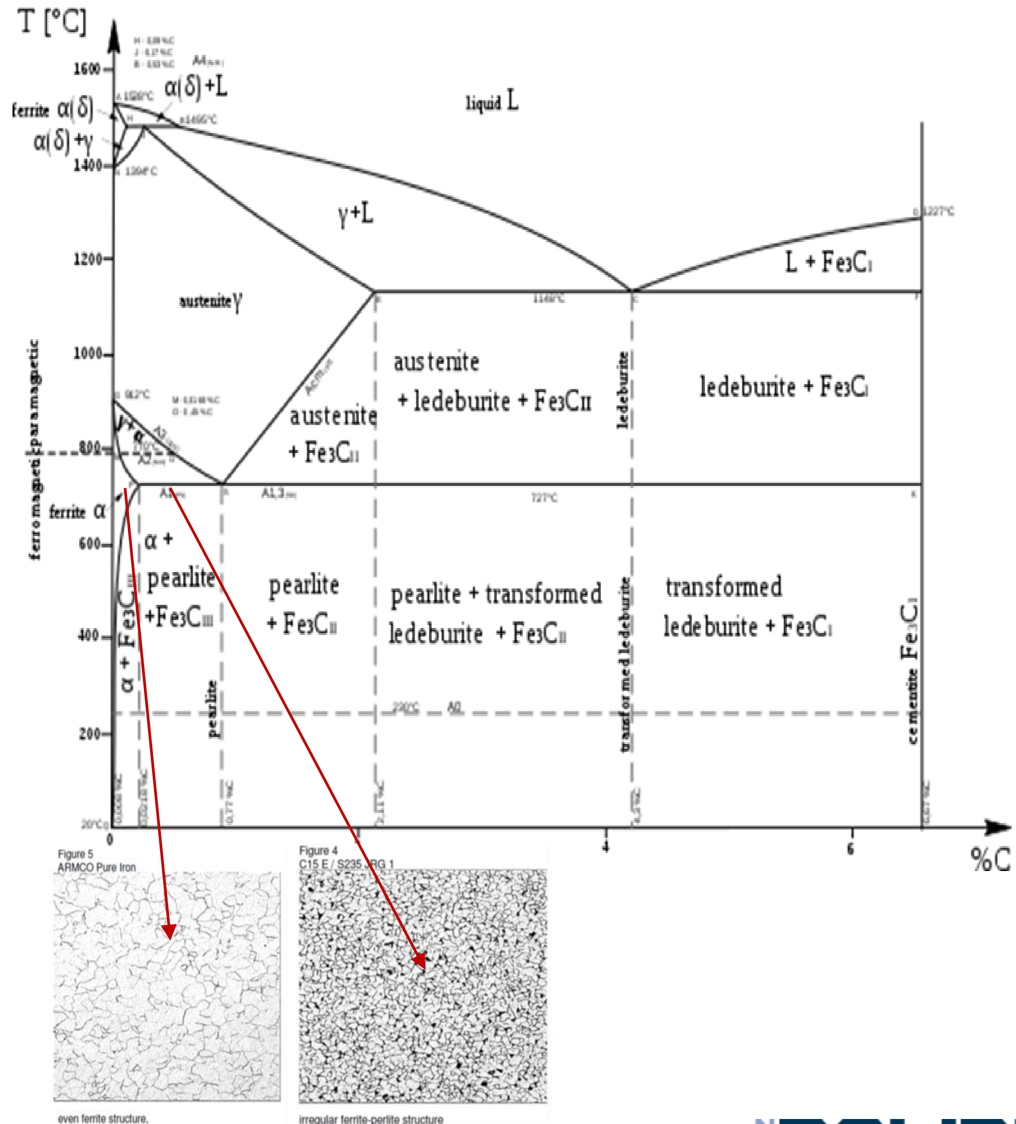


# Iron and Fe-C phase diagram (Infl. of Carbon)

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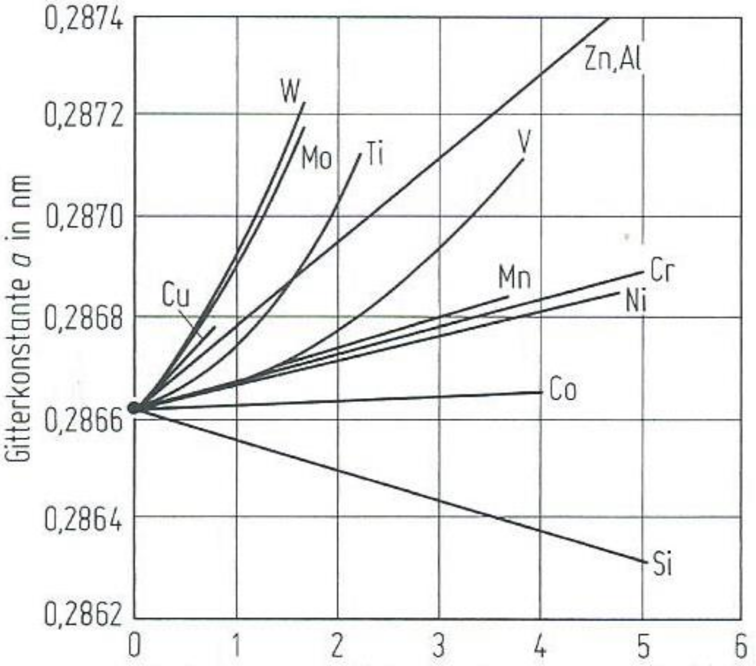
# Influence of Carbon

- Amount of Carbon is the most significant element for microstructure (Ferrite, Perlite, …)
- Diffusion of C responsible for growth of crystals
- Diffusion speed lowest at eutectoid concentration
- 0,025% solubility at 727 ¤C
- At eutectoid composition around 12% $Fe_3C$ (in Perlite) plus Ferrite

- The higher the Carbon, the more crystals, the more attack surface by the liquid Zn
- Reactivity increases (slightly)

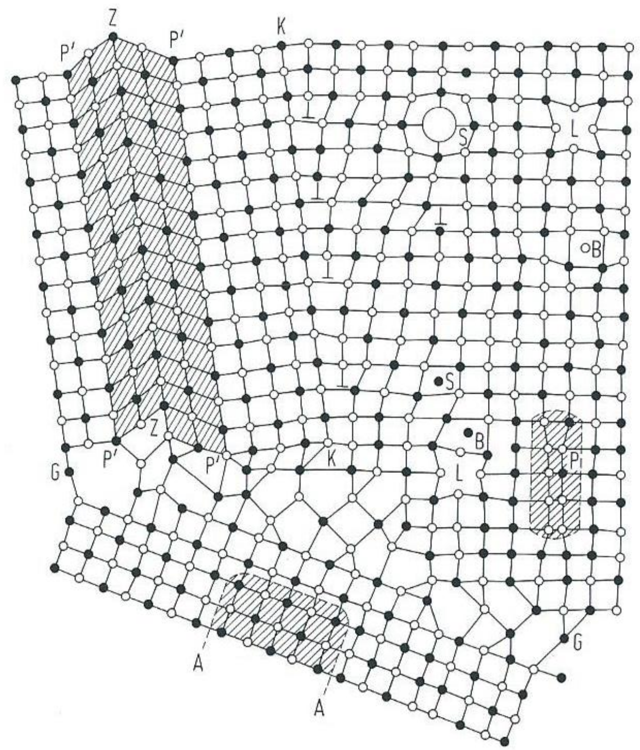
**Diffusion and ”equilibrium” of alloying elements depends on ”space”**



# Reactivity of steel

- **Coating thickness depends on dissolved Fe**
- **Dissolved Fe increases with.**
  - **Surface of grain boundaries**
  - **Amount of distortions**

- **Coating thickness depends on**
  - **amount Fe captured in δ-layer**
  - **Amount Fe captured in ζ-layer**




Z: twin-boundary
S: foreign atom
L: vacancy
B: interstitial solution
⊢: dislocation

Etc …

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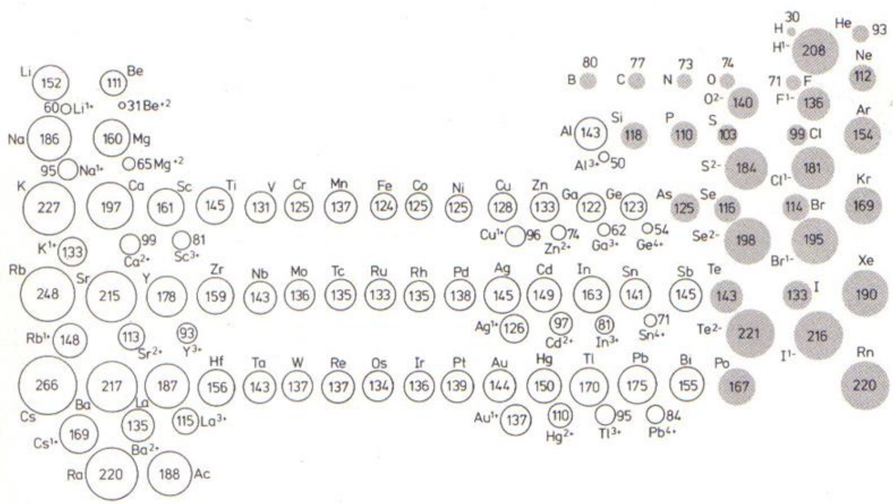
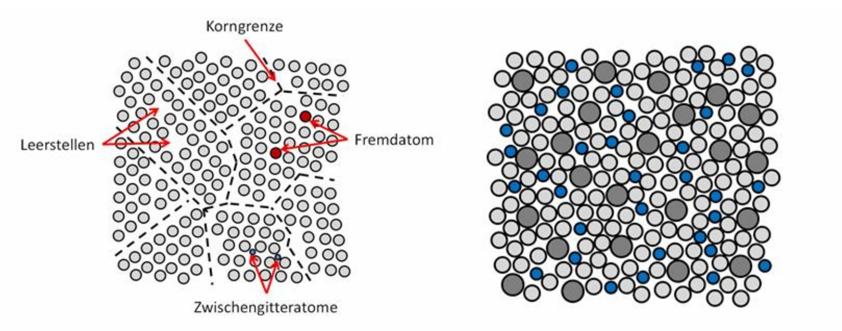
# Inluence of atomic radius on steel lattice






Polykristallines Metall　　Amorphes Metall

- **Elements << Fe go to interstitial places**
  - **Dislocations**
  - **Hardening and reduced elongation**
  - **Twin formation**
- **Elements close Fe take Fe-places in lattice**
- **Elements > Fe take Fe places in lattice and increase lattice constant**
  - **Improved ductility**
  - **Better diffusion (stabilisation)**

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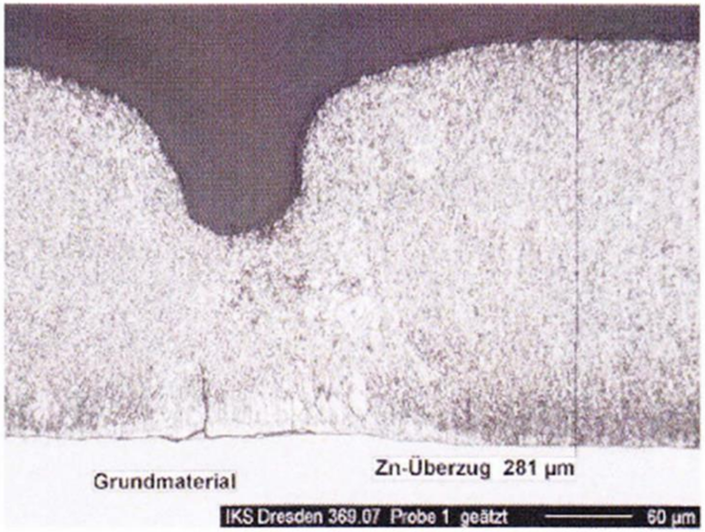
# Steel poisons

## Phosphorus

- huge segregations
- Low diffusion speed
- From on 0,01% P => brittleness




## Sulfur

- Huge segregations
- Solubility in ferrite: 0,02%
- (negative effect can be suppressed by Mn)

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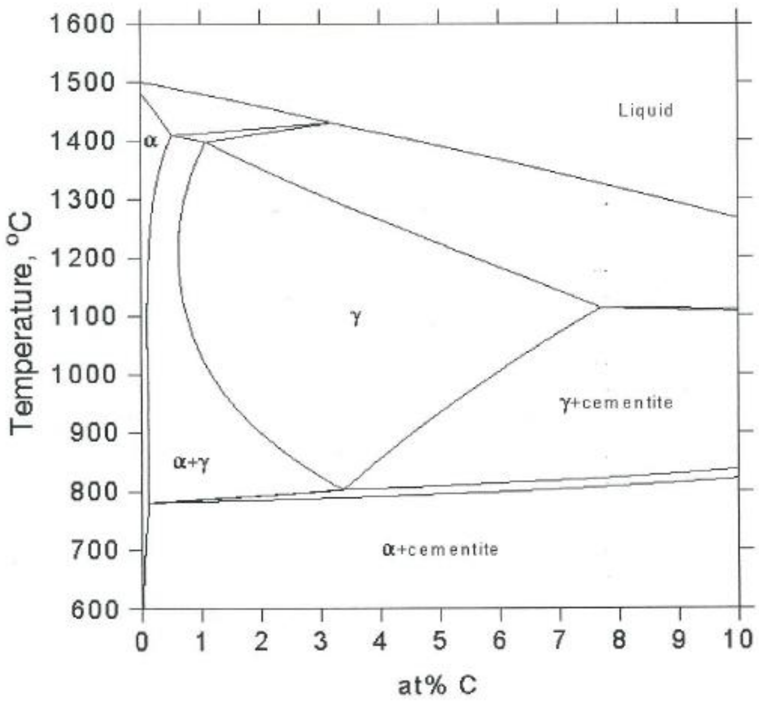
# Influence of Silicon

- **Si has low solubility in Fe**
- **Lowers solubility of c in Ferrit**
  - **Smaller Ferrite particles**
    - **More grain boundaries**
    - **More dislocations**
- **Destabilisation of Cementite ($Fe_3C$)**
  - **Weaker grain-boundaries**




- **Below solubility limit therefore no or small influence on reactivity**
- **Above solubility level**
  - **$Fe_3C$ less stable**

- **Precipitation of FeSi-particles**
  - **Tetragonal**
    - Interstitial solutions with vacancies

# Influence of Aluminium

**Stabilizes ferrite**

**Low additiond (favours small crystals)**

**Larger additions: larger ferrite crystals**

- Reduced amount of grain boundary
- Increased ductility
  - **Less dislocations**

**Increased diffusion speed of Carbon**

- Carbon agglomeration on grain boundaries
  - **Reduced wettability**

## Infl. Al in Zn-melt

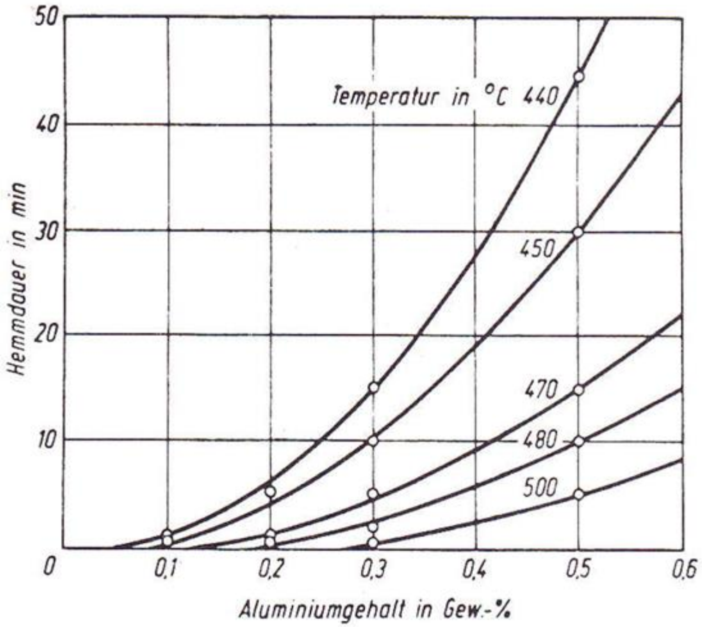
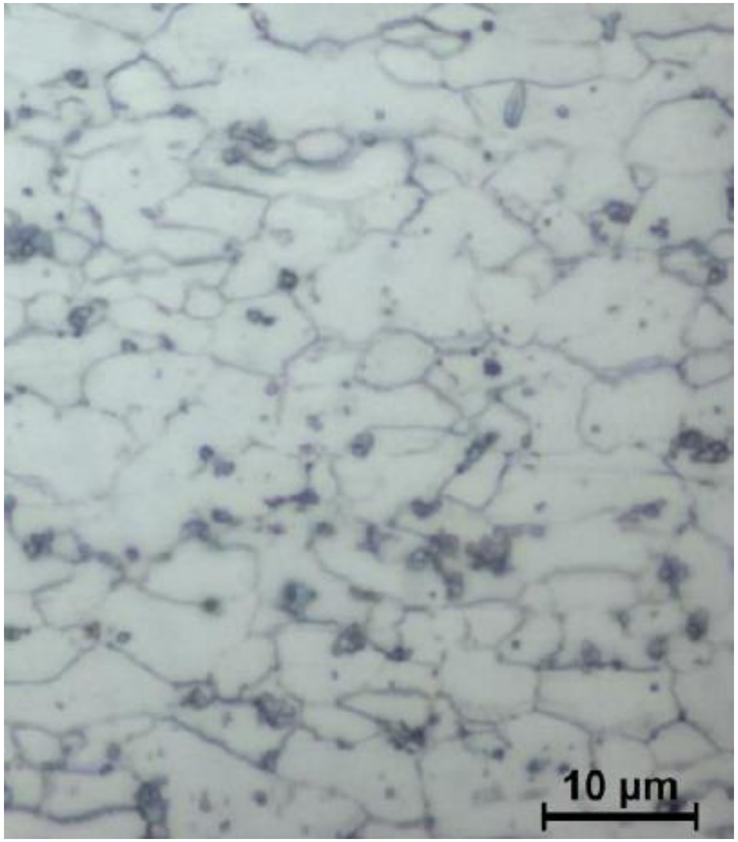



Abb. 13: Abhängigkeit der Hemmdauer vom Aluminium

# Influence of Manganese

- Huge solubility in ferrite (10%9
- Capts S and Si
  - Mno-MnS
  - 2MnO-SiO2
- Promotes large grains
- Promotes C-diffusion
- Improves ductility of the steel

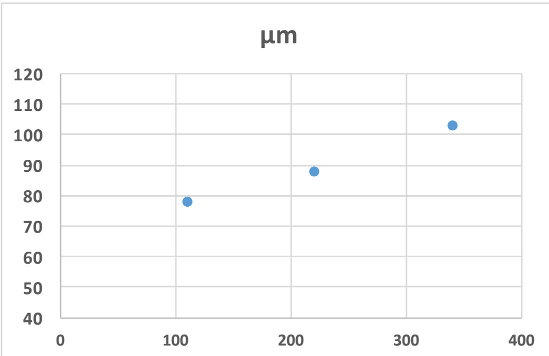



0,064C-0,019Si-0,008P-0,043Al-1,447Mn

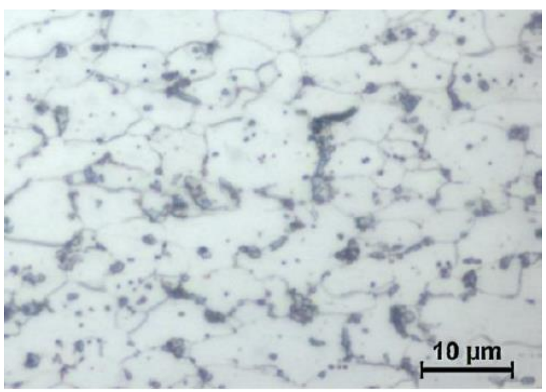
# Tests on Al-killed steels (traditional Zinc)

A (cold rolled SMS)

| C | Si | P | Al | Mn | S |
|---|---|---|---|---|---|
| 0,05 | 0,02 | 0,014 | 0,044 | 0,45 | 0,005 |

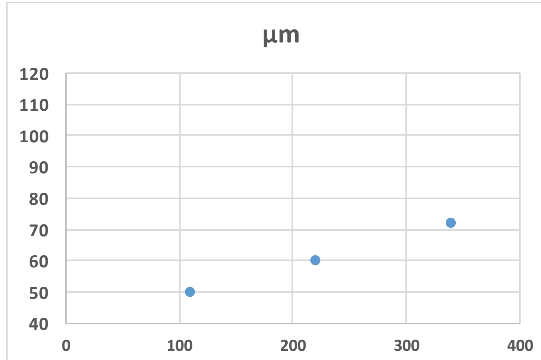



| 340 s | δ | ζ | Fe/m2 | Fe in δ (%) | tot |
|---|---|---|---|---|---|
| avg 4 meas | 16,48 | 43,87 | 36,35 | 39,2 | 103,5 |

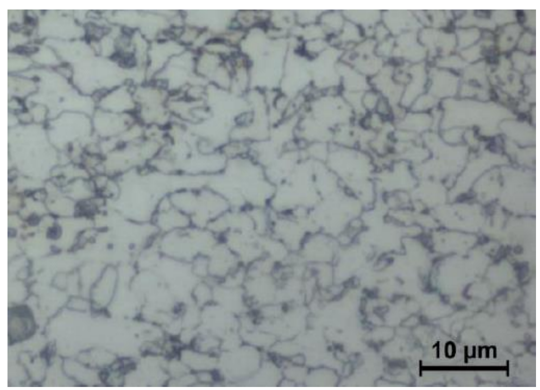



B (hot rolled TKS)

| C | Si | P | Al | Mn | S |
|---|---|---|---|---|---|
| 0,044 | 0,015 | 0,01 | 0,032 | 0,498 | 0,005 |

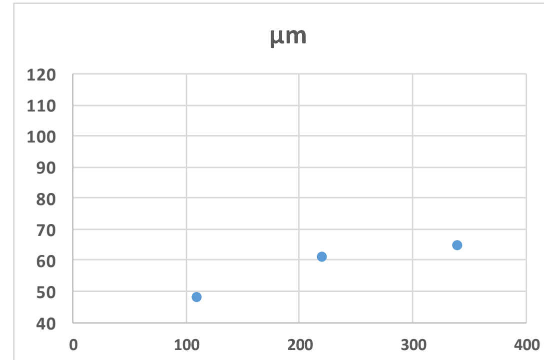



| 340 s | δ | ζ | Fe/m2 | Fe in δ (%) | tot |
|---|---|---|---|---|---|
| | 17,96 | 24,75 | 27,99 | 55,4 | 83 |

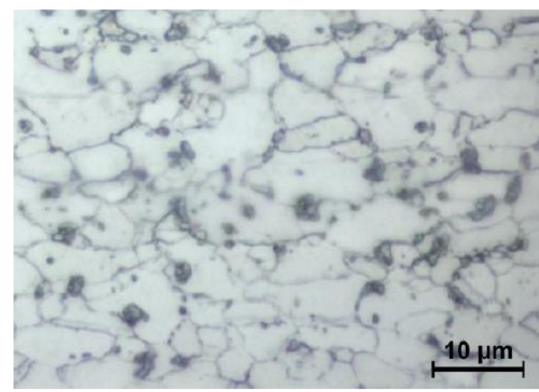



C (cold rolled TKS)

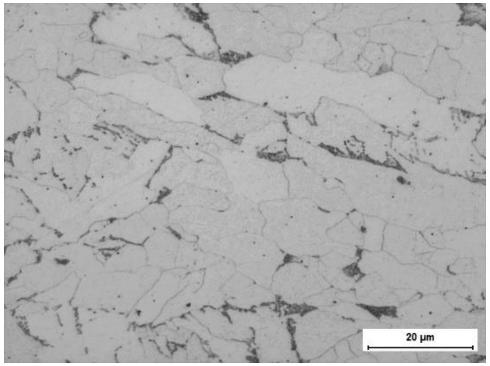
| C | Si | P | Al | Mn | S |
|---|---|---|---|---|---|
| 0,064 | 0,019 | 0,008 | 0,043 | 1,447 | 0,003 |

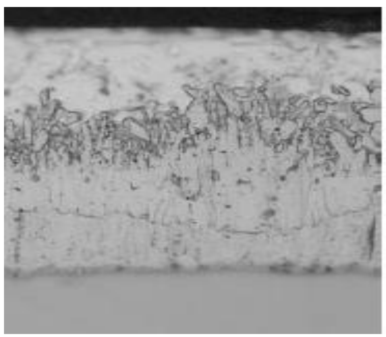


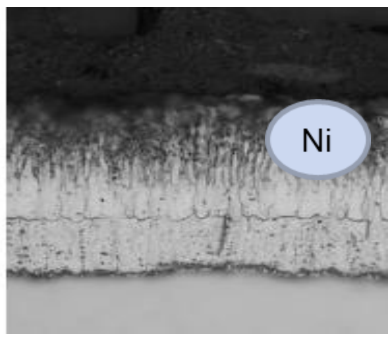

| 340 s | δ | ζ | Fe/m2 | Fe in δ (%) | tot |
|---|---|---|---|---|---|
| | 16,31 | 30,78 | 29,60 | 47,6 | 74,5 |



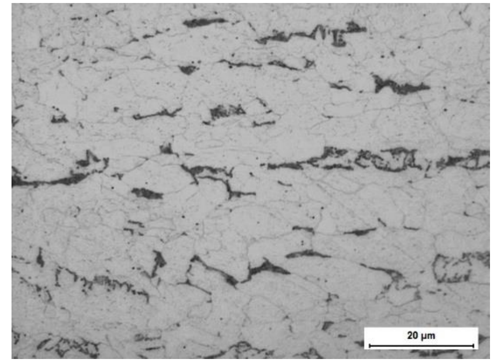
# Tests on Al-killed steels (Zn ⇔ ZnNi)

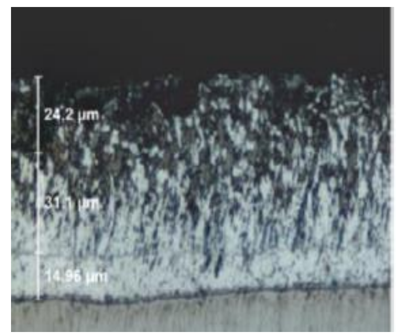


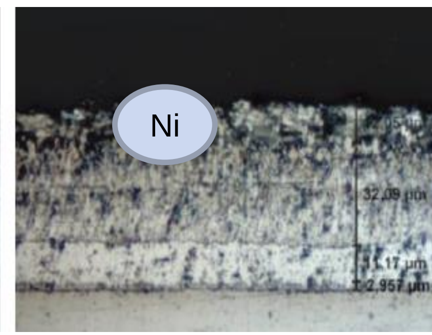






| C | Si | P | Al | Mn | S |
|---|---|---|---|---|---|
| 0,071 | 0,01 | 0,006 | 0,051 | 0,59 | 0,004 |
| | δ | ζ | Fe/m2 | Fe in δ (%) | tot |
| Pr 5 | 12 | 28 | 24,48 | 42,4 | 54,5 |
| pr 6 | 15 | 32,5 | 29,34 | 44,2 | 66 |




| C | Si | P | Al | Mn | S |
|---|---|---|---|---|---|
| 0,067 | 0,01 | 0,009 | 0,052 | 0,6 | 0,003 |
| | δ | ζ | Fe/m2 | Fe in δ (%) | tot |
| pr 7 | 10,5 | 32 | 25,20 | 36,0 | 62 |
| pr 8 | 13,2 | 16 | 19,47 | 58,6 | 51,2 |

Ni seems to promote δ-phase growth and therefore reduces coating thickness

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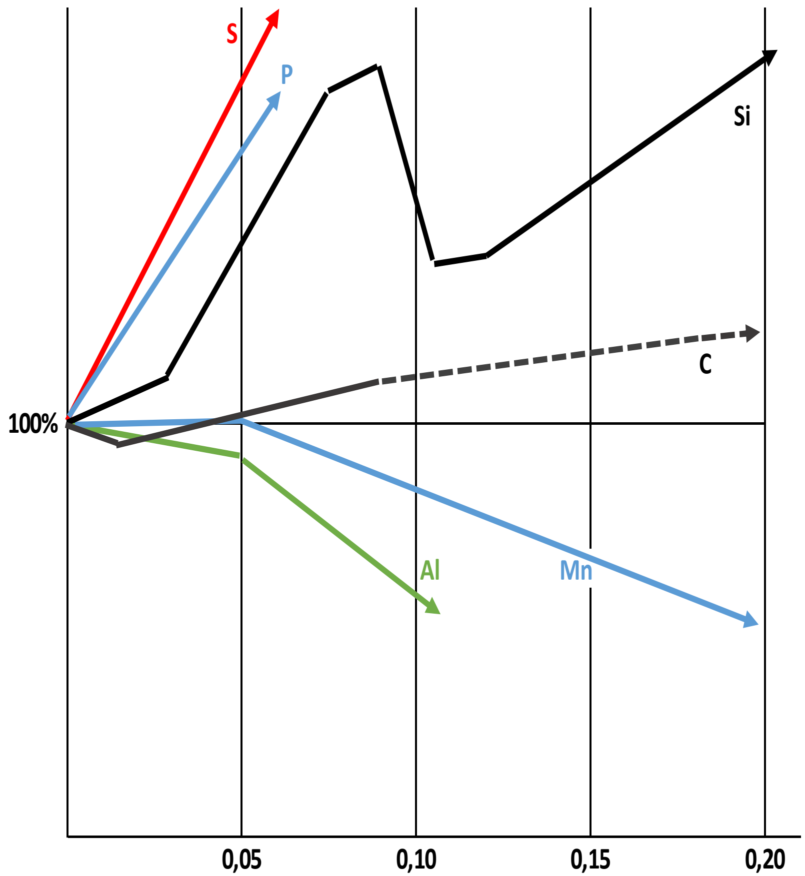
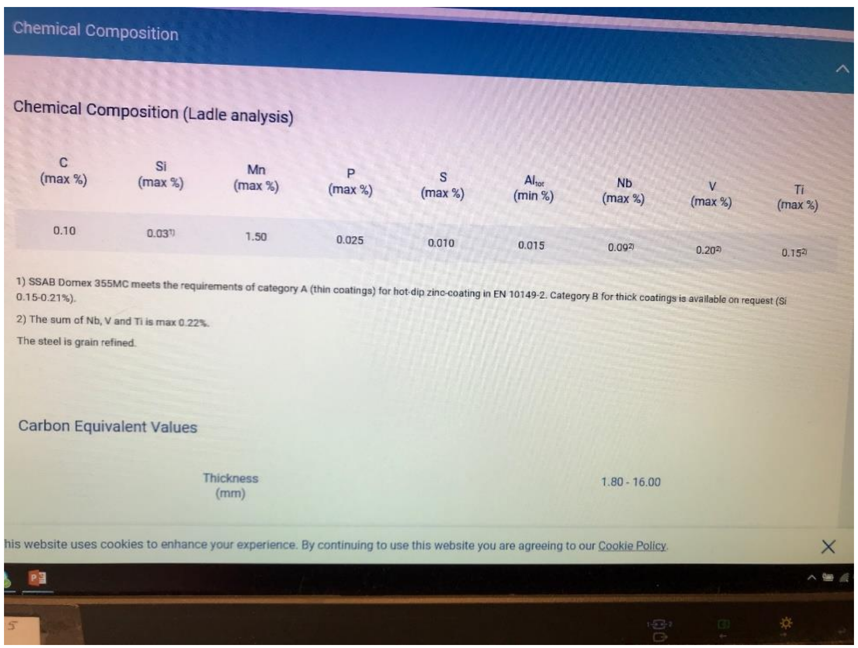
# Fe loss and steel reacticity schematic




## Revision ISO 14713-2

- A footnote to Table 1 (Coating characteristics related to steel chemistry) that recognises that steels containing <0.01% silicon that also have aluminium contents >0.035% might exhibit reduced levels of coating cohesion and lower reactivity that could result in a lower than expected coating thickness.

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# Conclusions

- S, P and Si increase Fe-loss
  - High Fe-amount per time-unit mostly promotes ζ-phase

- Al and Mn reduce Fe-loss
  - Fe-dissolved has time enough to react toward δ-phase

- Actually no bath composition available to ameliorate coating requirements on both (reactive and non-reactive) steel grades

**Thank you for your attention!**

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