ECL 2 CERN, Geneva
1. March 2007

Vitreous enamel

A highly effective material compound

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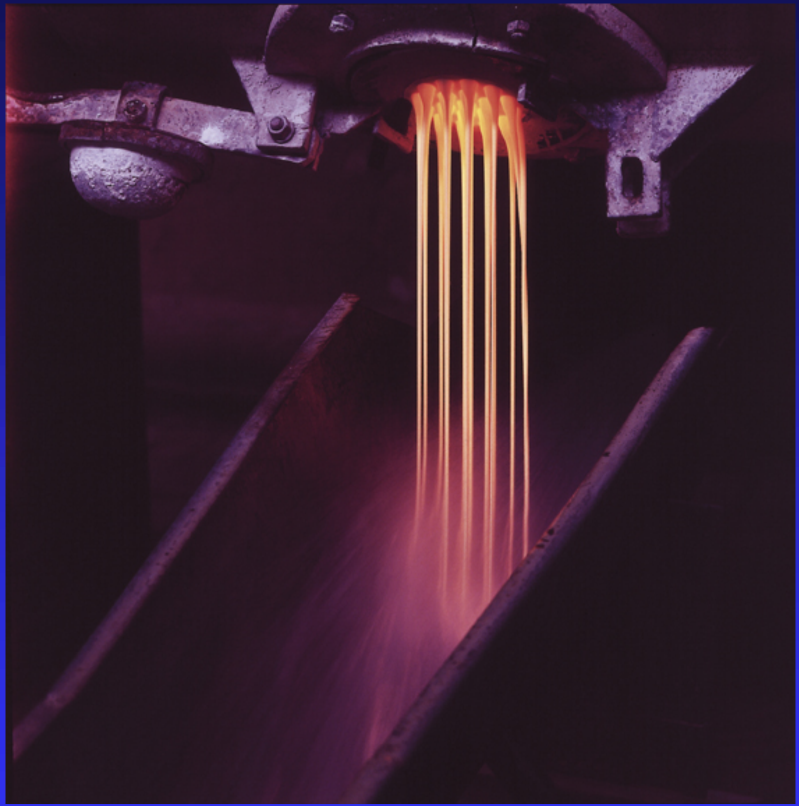
Properties of enamel

- **Vitreous Enamel – What is it?**
  - **Special inorganic glass with a thermal expansion rate precisely adapted to it‘s substrate. It‘s a bulk solid quenched from the melt – exhibiting a glass transition temperature. - Difference to amorphous materials deposited by sputtering or evaporation.**



- **General Properties**
- **Electrical Properties**
- **Adherence**

General properties (choice)

- Very high heat resistance
- Good adherence of the material compound
- Excellent mechanical stability
- Very good adherence of seals
- No electrostatic charging
- Very low interaction with organic material
- Perfect cleanability
- Perfect aging properties

Electrical properties

- **Most of the glasses are electrical insulators.**
- **Existence of semiconducting glasses is known since about forty years. – Electron conductivity**
- **Good progress in understanding the mechanisms of ion and electron transport in glasses.**
- **Specific electrical resistance of insulating enamels at room temperature: approx. $>10^{12}\ \Omega$ cm.**
- **At 400°C it decreases to approx. $10^{5}\ \Omega$ cm.**
- **Of course the isolating properties depend of the thickness of the enamel layer, this is especially important for the dielectric strength.**

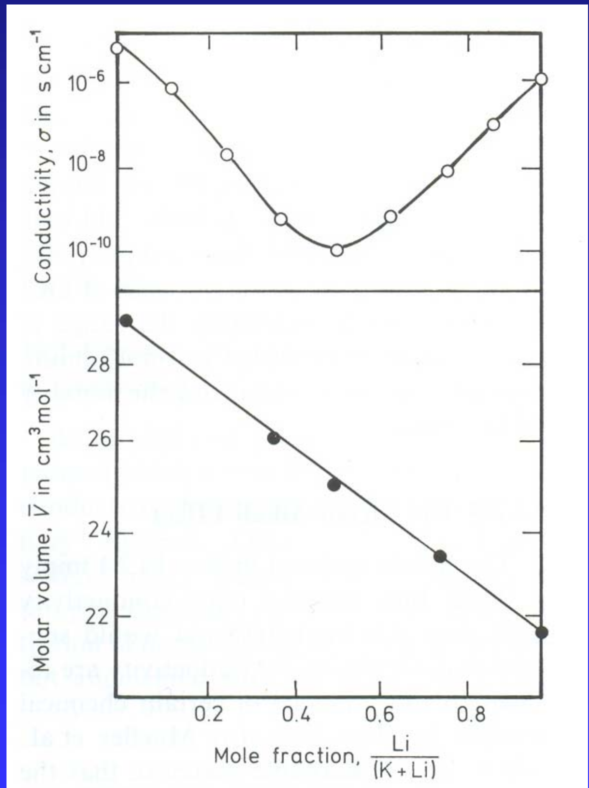
Effect of composition elements

The Nernst-Einstein equation is giving a good description for the electrical conductivity: The diffusion rate is determining mainly the effect.

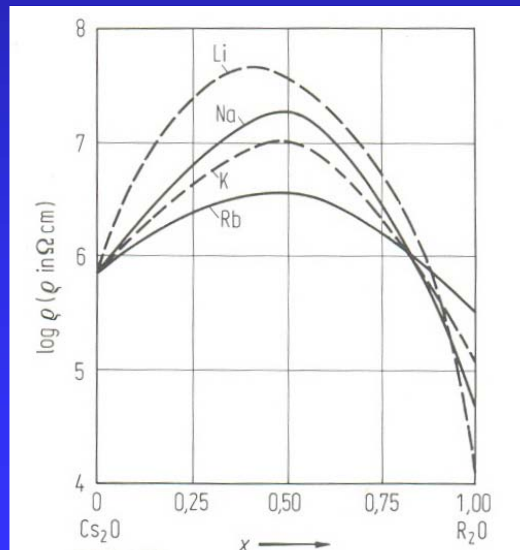
- **Charge transport is mostly done by cations.**
- **Alkali metal ions have the highest diffusion rates.**
- **A glass free of network modifiers is having a low conductivity.**
- **BaO, SrO, PbO, CaO and SiO_2 decrease cond.**
  - **Effect of polarisation and blocking of channels**
- **Na_2O, Li_2O, K_2O, Rb_2O, Cs_2O, increase cond.**
- **Mixed alkali effect.**

Mixed alkali effect

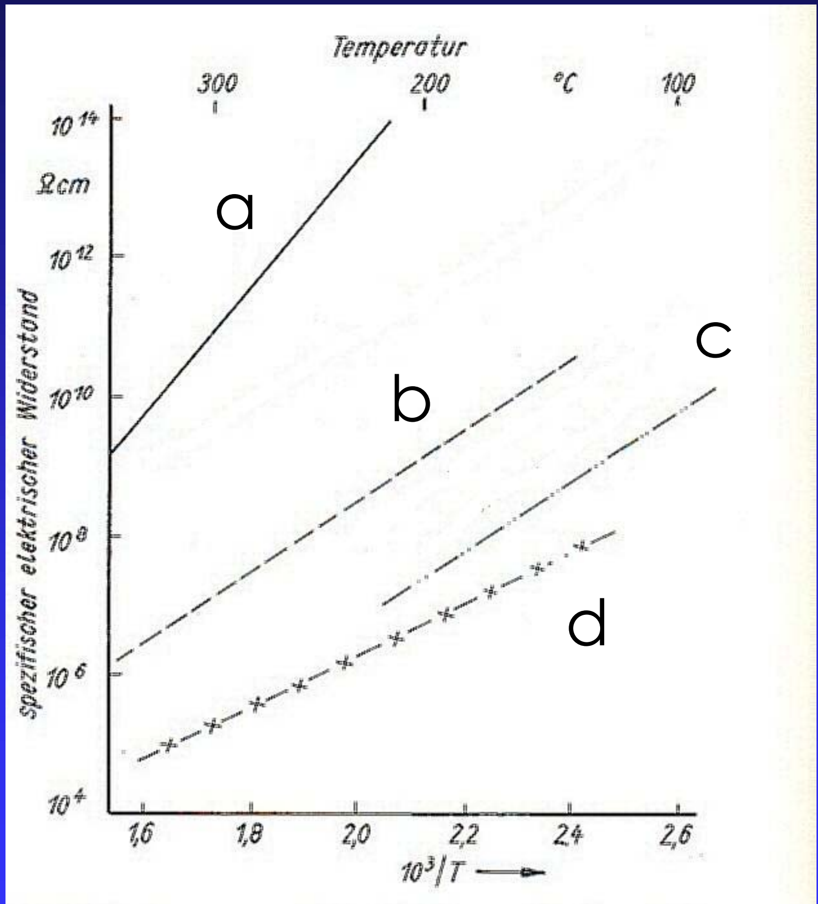
System
(Li_2O/K_2O)* $2SiO_2$
at 150°C



Substitution of Cs_2O in the glass
0,15 $(Cs, M)_2O$ * 0,85 SiO_2
by different alkali oxides
leads to a maximum
for the electric resistance
at approx. x= 0,5



Effect of temperature



Temperature dependence of the specific electric resistance of different enamels:

a) **PbO containing free of alkali**

b) **Conventional white line enamel**

c) **Alkali containing enamel**

d) **Antimony enamel**

Different conductivities

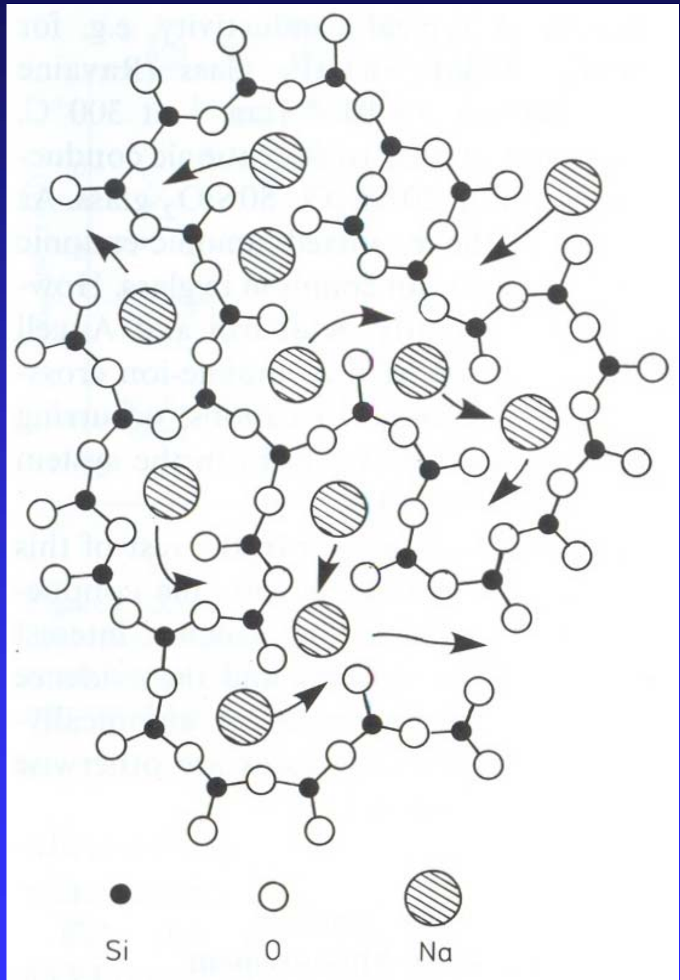
Intrinsic conductivity: - Bulk effect

Extrinsic conductivity: - Vibration of the network – opening of channels – temperature effect – typical Arrhenius plots.

Surface conductivity:

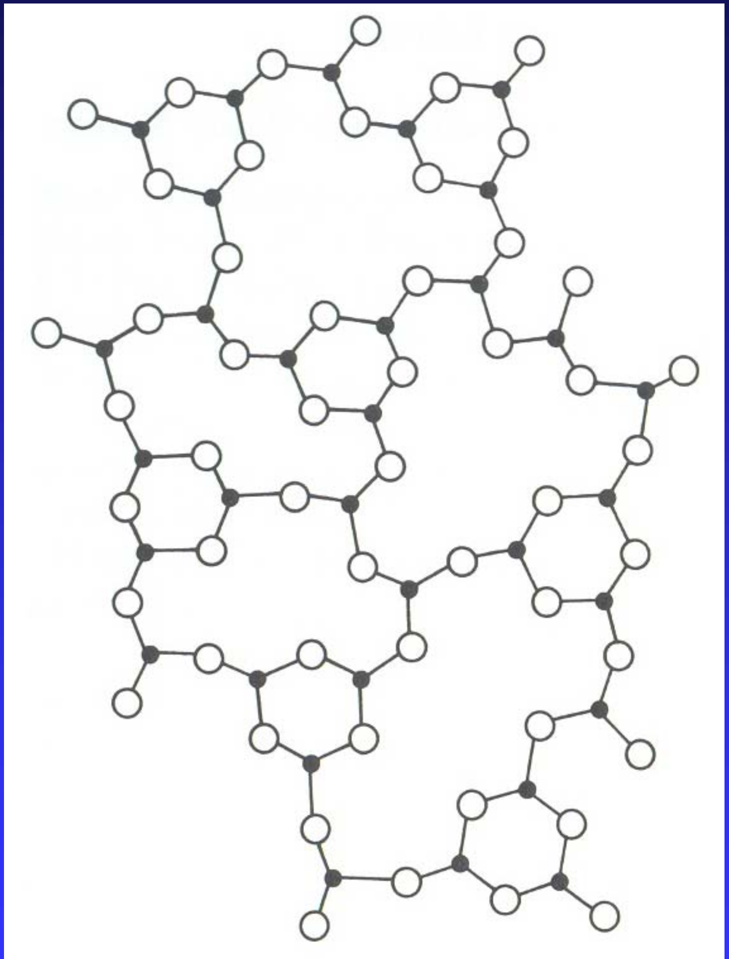
- effect of water adsorption – formation of hydroxyl ions – disappears under vacuum conditions
- effect of alkali enrichment on the surface.

Mechanistic model



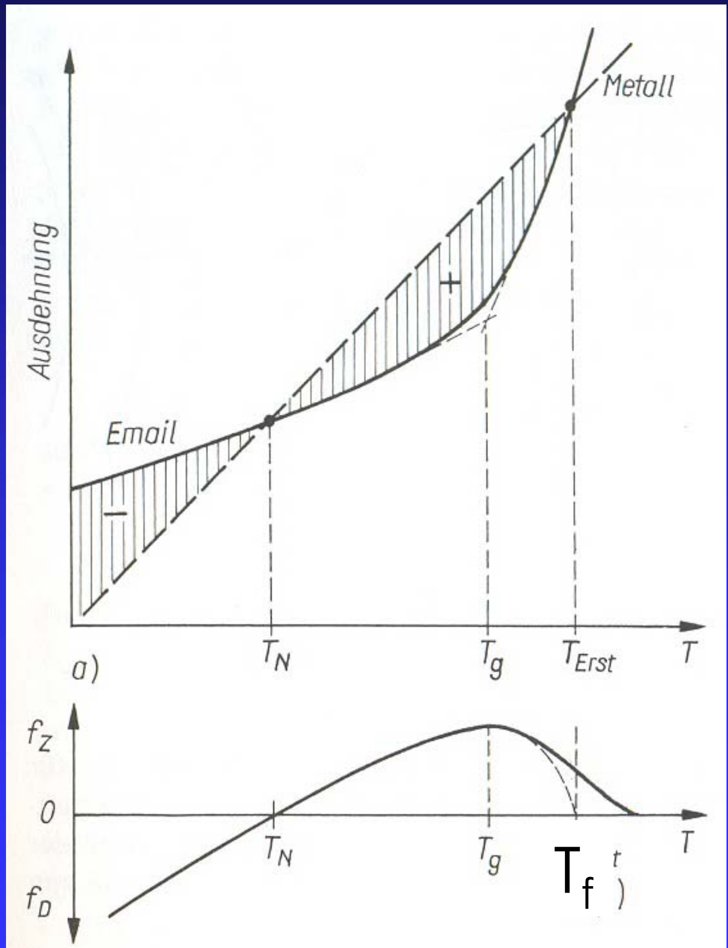
Schematic 2-dimensional representation of the Warren-Biscoe structure of alkali silicate glasses, showing the possibilities of localized and extended cationic motion within an anionic framework

Structure model



Schematic 2-dimensional representation of the Krogh-Moe structure of boric oxide glass with $(B_3O_6)^{3-}$ boroxol groups

Thermal expansion



Development of tensions in the system metal/ enamel during cooling:

+ tensile stress

- compressive stress

T_f = Point of fusion

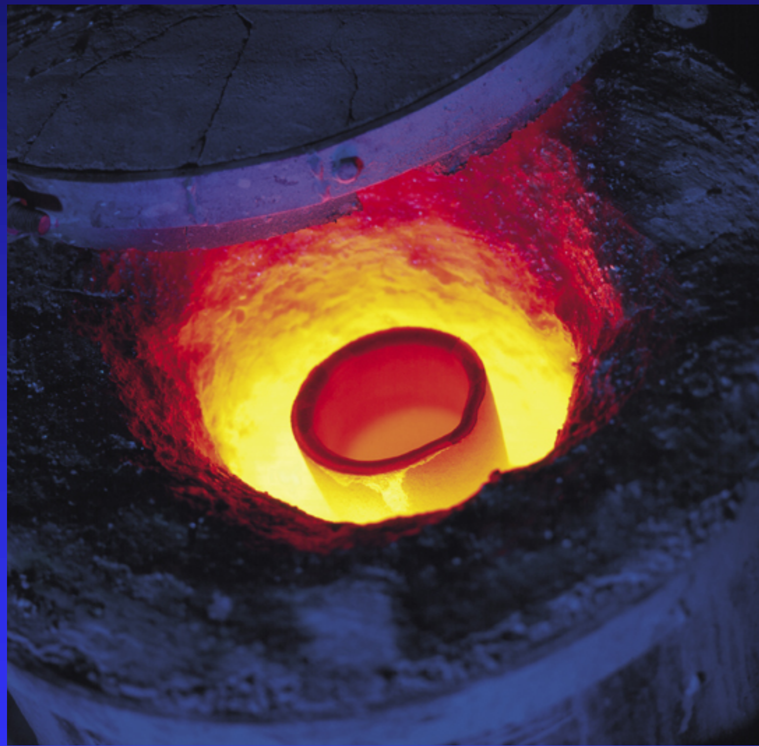
T_g = Transformation temp.

T_N = Point of neutral stress

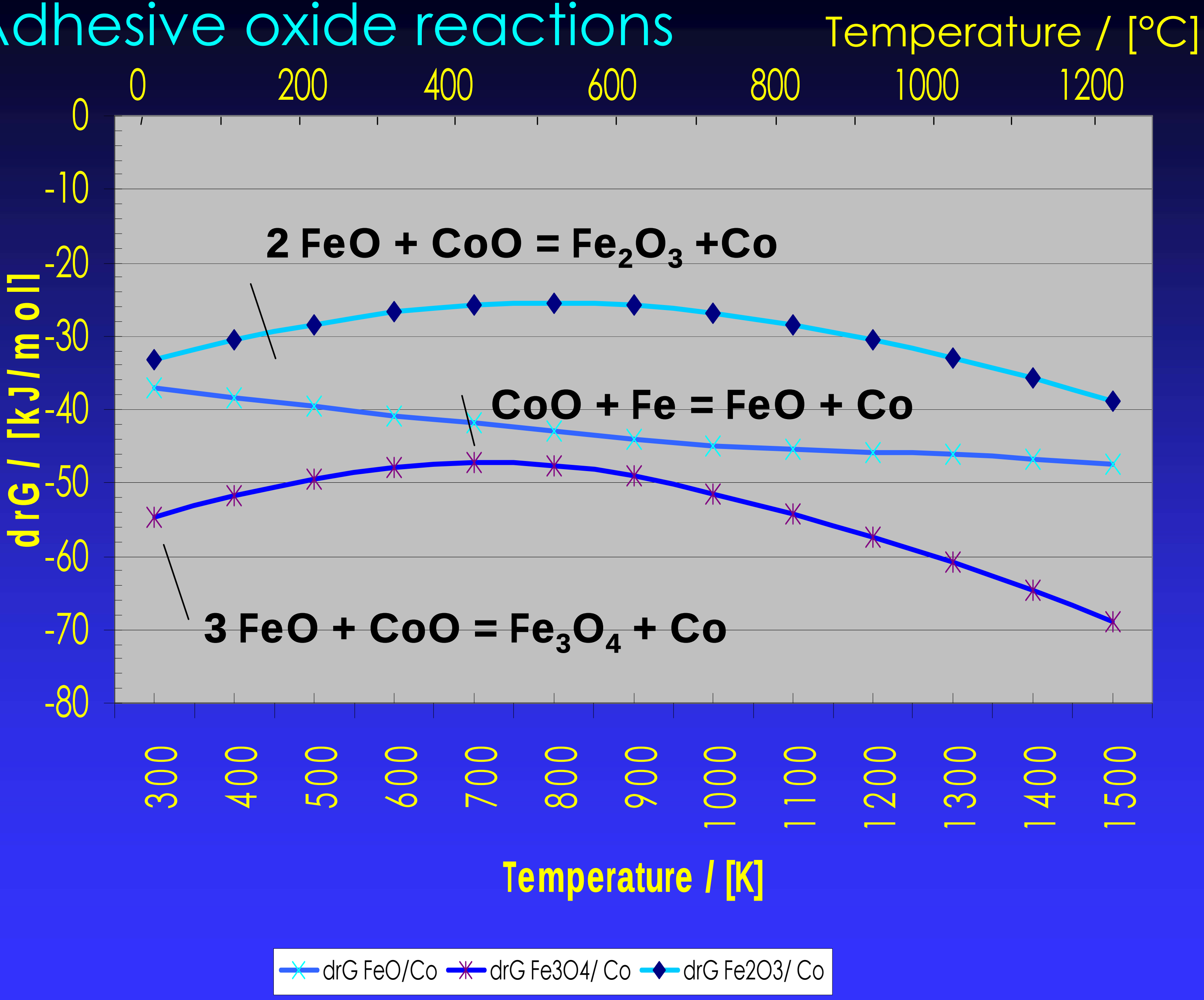
Adherence on iron substrates

Mechanical interlocking of the materials

- **Roughness of the iron surface**
- **Electrolytic corrosion**
  - **Reduction of adhesive oxides by Wustite**



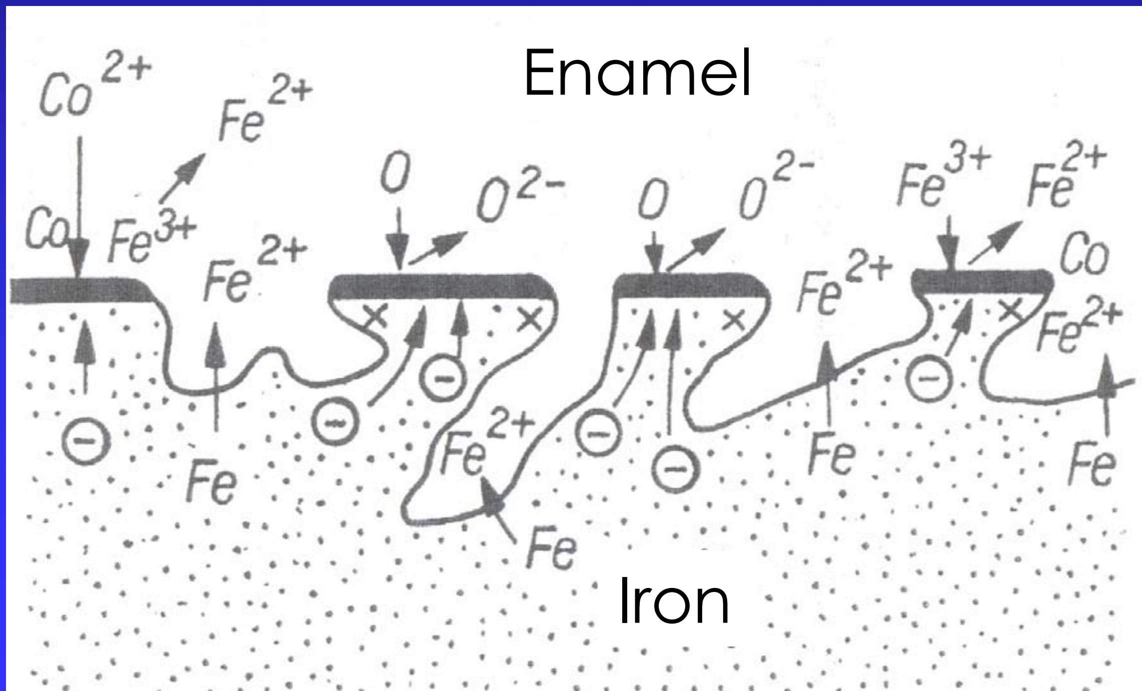
Adhesive oxide reactions



Galvanic corrosion of metal by the enamel

Schematic depiction of the galvanic process during enamelling of iron

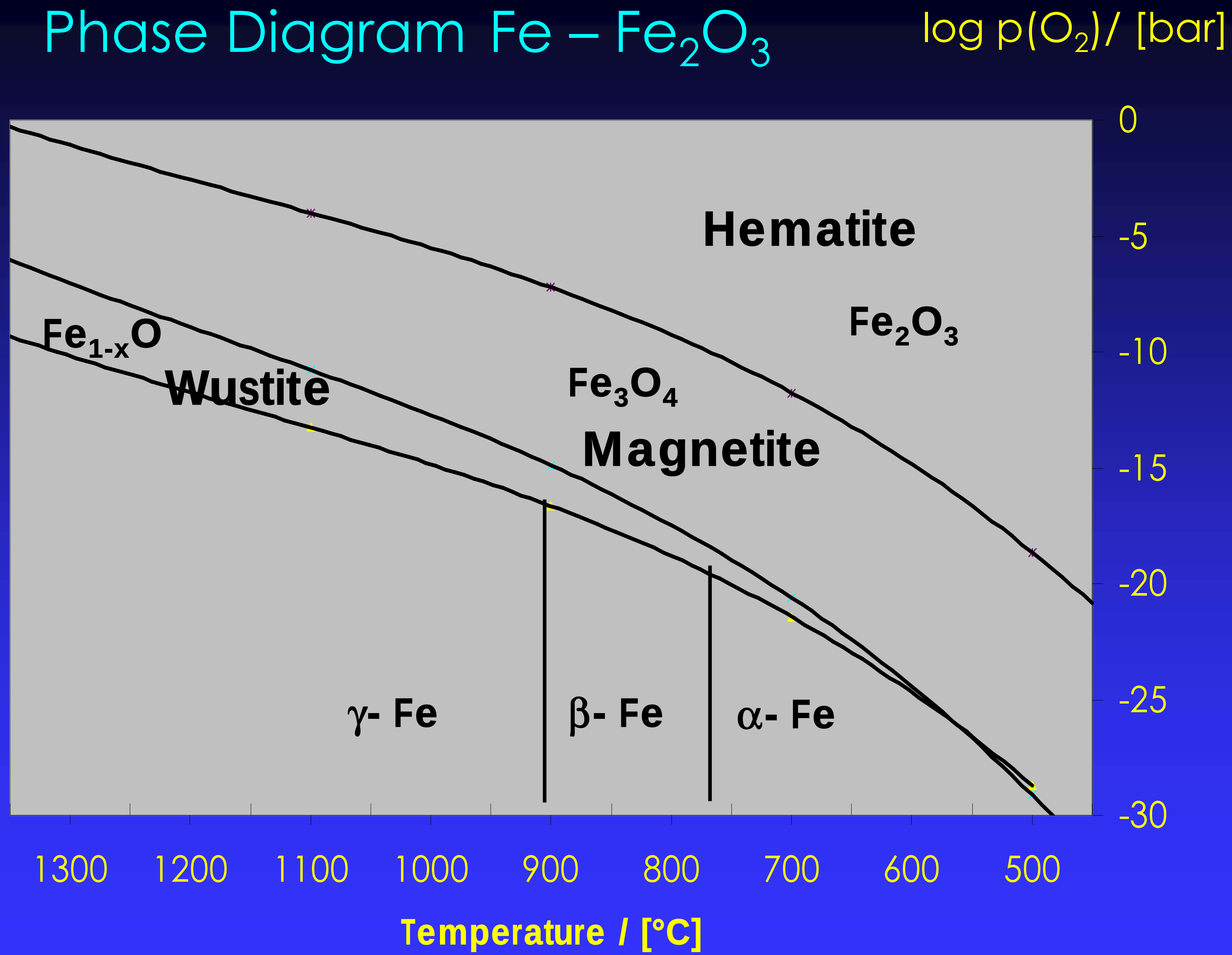
(Dietzel 1934)



Adherence on iron substrates

- **Good adhesive iron oxide layer**
  - **The main phases should be Magnetite**
    - **Hematite decreases the adherence**
  - **Kinetics of the oxidation (linear or parabolic)**
  - **Thickness of the intermediate layer**

Phase Diagram Fe – Fe_2O_3



Development of new enamels

- **Viscosity and surface tension corresponding to working conditions**
- **Dilatation corresponding to the substrate**
- **Adherence: ground coat and direct on**
- **Surface hardness, elasticity**
- **Surface to the needs: smooth, glossy or matt**
- **Colour and opacity, crystallisation**
- **Electrical parameters**
- **Chemical resistance: acid, alkaline, water a.s.o.**
- **Slurry parameters: rheology**


Thank you
for your attention

Impedance spectra of enamel