"Materials, Metallurgy and Interdisciplinary Co-working"

VŠB TU Ostrava - RWTH Aachen University

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Metallurgical Treatment of New Steel Grades

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Chair for Metallurgy of Iron and Steel

RWTH Aachen University

Speaker: Alexander Lob

Content

- High Manganese Steels in the System Fe-Mn-C
- Critical Elements for Fe-Mn-C Steel
- Dephosphorization of high Manganese Steels
- Solubility of Gases in the System Fe-Mn-C
- Experiments on Phosphorus, Nitrogen and Hydrogen
- Results of the first Experiments

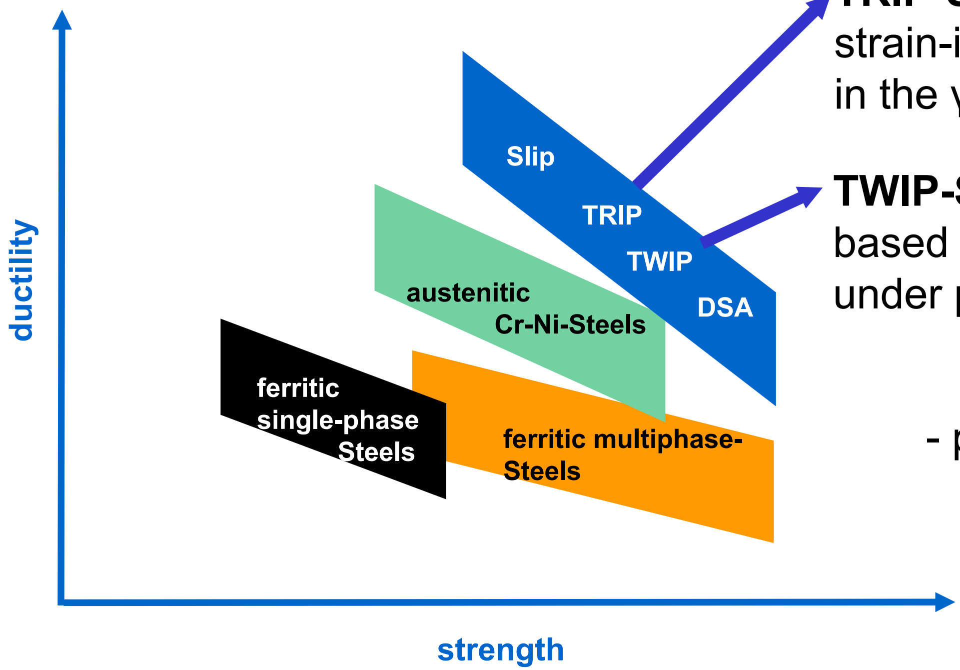
Steels of Interest in the frame of SFB 761

Elements	**Fe**	**Mn**	**C**	Al	S	P	Si	Ni	Cr
Content [wt%]	**75.0**	**23.5**	**0.3**	0.1	0.008	0.002	0.05	0.0259	0.024

Chemical composition TRIP-Steel for SFB 761

Elements	**Fe**	**Mn**	**C**	Al	S	P	Si	Ni	Cr
Content [wt%]	**75.0**	**23.5**	**0.6**	0.1	0.008	0.002	0.05	0.0259	0.024

Chemical composition TWIP-Steel for SFB 761



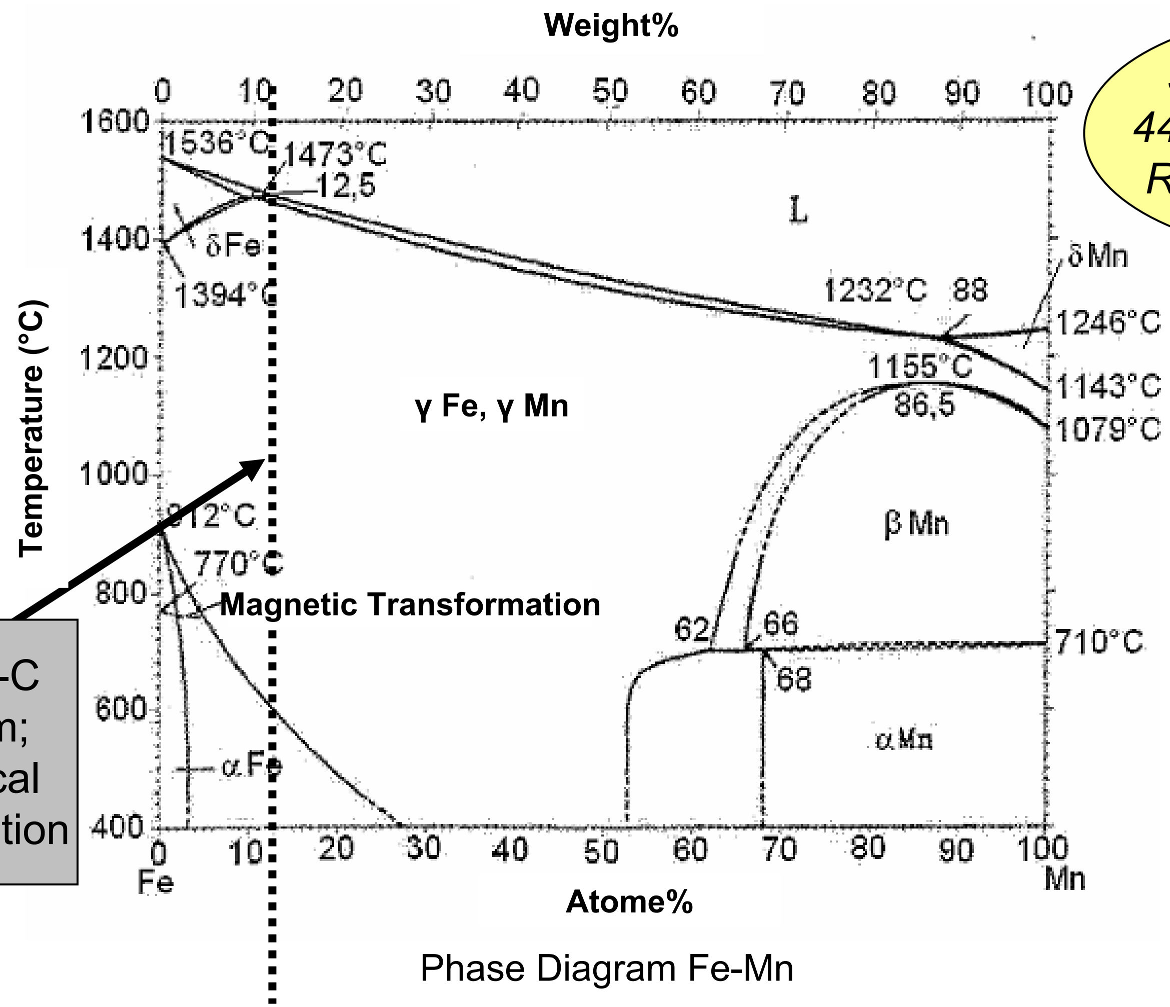
TRIP-Steel (*TRansformation Induced Plasticity*): strain-induced ε_{hcp}- and α_{bcc} - martensitic formation in the γ_{fcc} austenitic matrix under plastic deformation

TWIP-Steel (*Twinning Induced Plasticity*): based on the formation of mechanical twins under plastic deformation

- physical forming mechanism

steel system Fe-Mn-C: high strength combined with high ductility

Characteristics of the System Fe-Mn-C



Fe-Mn-C system; chemical composition

system Fe-Mn-C:
440°C ≤ fcc ≤1430°C
RT ≤ ε-hcp ≤ 440°C

Phase Diagram Fe-Mn

Hansen, M.; Anderko, K.: Constitution of binary alloys, McGraw-Hill Book Company, 2.Ed, New York Toronto (1958), pp. 664-668

Critical Elements for Fe-Mn-C Steel

1) <u>Phosphorus in steel-making process</u>

Effects: cracking and microsegregations during solidification, accumulation of Fe_3P

Sources: iron containing elements, coke, lime, alloying elements, scrap

Problem: chemical oxygen affinity for manganese is higher than that for phosphorus

2) <u>Nitrogen in steel-making process</u>

Effects: (+) formation of nitrides → increasing of strengths

(-) shrinkage holes and pores during solidification, aging (interstitial [N]) embitterment and texture forming while deep drawing

Sources: atmospheric humidity

Problem: high solubility in high-manganese austenitic steels

3) <u>Hydrogen in steel-making process</u>

Effects: casting break out danger, cracks, formation of CH_4

Sources: atmospheric humidity, hydrated lime, refractory, rusty scrap, deoxidiser

Problem: high solubility in high-manganese austenitic steels

[P], [N] and [H] in steel lead to poor mechanical properties

Phosphorus in the System Fe-Mn-C

dephosphorization: low temperatures and high contents of oxygen
highly exothermic reaction, reversible at temperatures above 1580 ºC

$$2P + \frac{5}{2}O_2 \rightarrow P_2O_5$$

place for dephosphorization:
converter = high temperatures and high contents of oxygen

$$2[P] + 5[O] + 3(FeO) \leftrightarrow (3FeO \cdot P_2O_5) \quad \xrightarrow{\text{eq.const.}} \quad K = \frac{a_{3FeO \cdot P_2O_5}}{a_p^{\,2}\, a_{FeO}^{\,3}\, a_O^{\,5}}$$

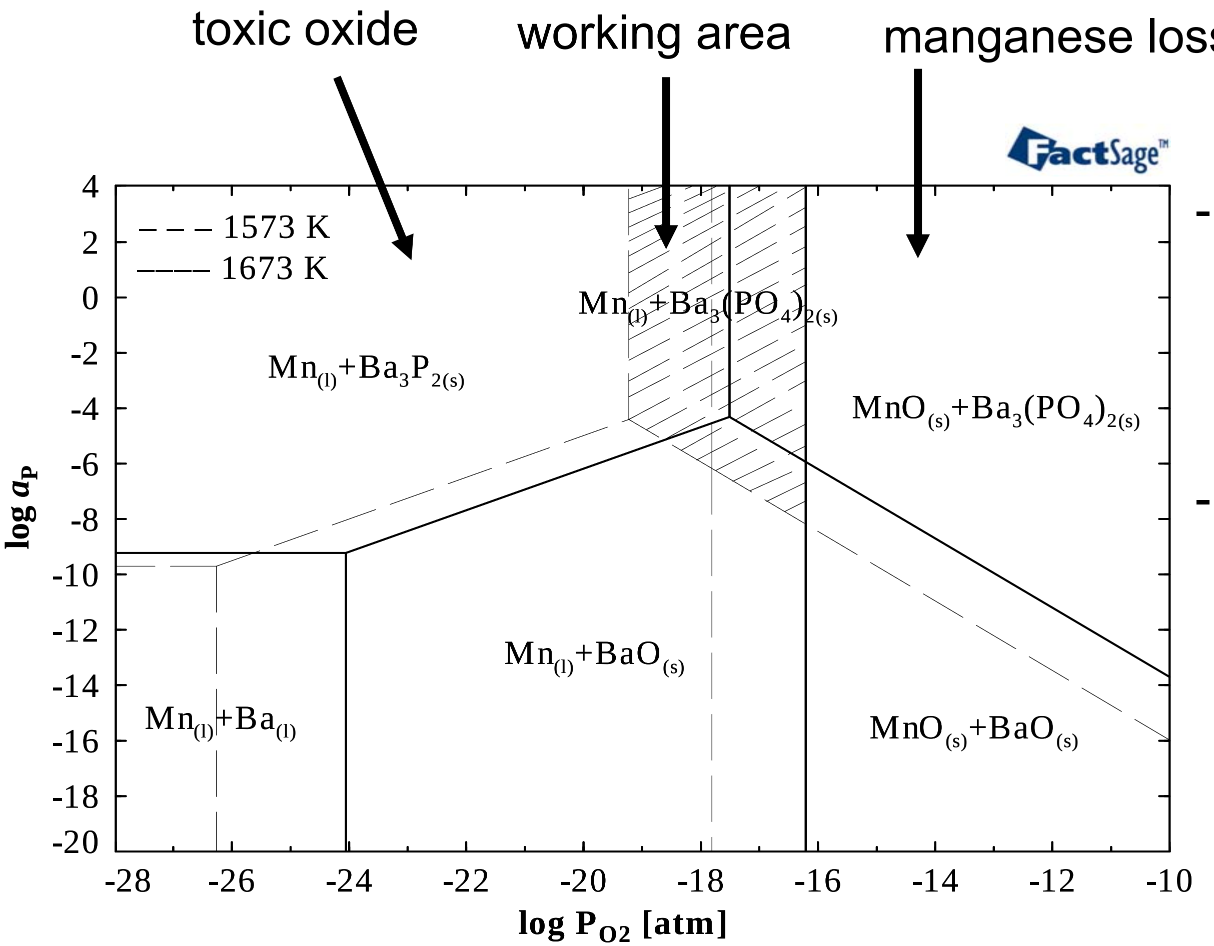
using lime without loosing FeO

$$(3FeO \cdot P_2O_5) + 4(CaO) \leftrightarrow (4CaO \cdot P_2O_5) + 3(FeO)$$

manganese losses while dephosphorization

Problem of conventional dephosphorization in high manganese steels = manganese losses while dephosphorization

Selective Oxidation

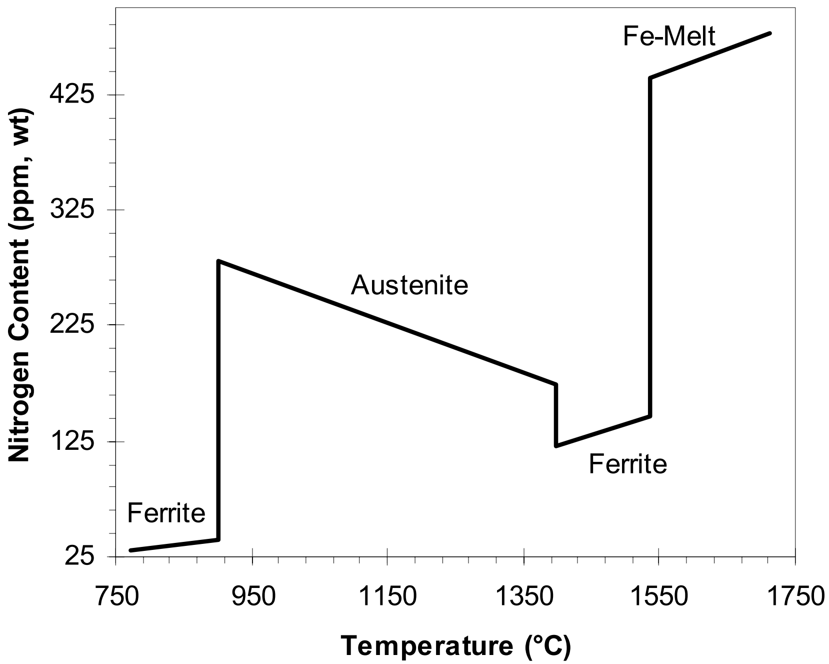


Ba-P-O and Mn-O Predominance area diagram

- a slag saturated in BaO is able to oxidate and stabilize the phosphorus in the slag avoiding massive oxidation of manganese
- working area ($Mn + Ba_3(PO_4)_2$) increases with the reduction of temperature of the steel/slag system

dephosphorization with BaO without loosing manganese

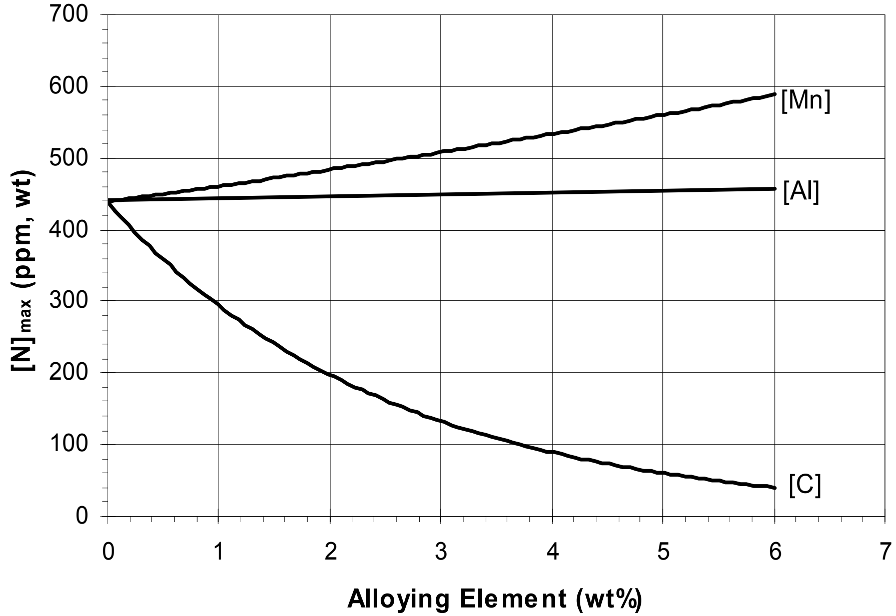
Nitrogen in the System Fe-Mn-C



Solubility of nitrogen in pure iron at

p_{N2} = 1013 mbar

high [N]-content in the austenite and with increasing manganese contents

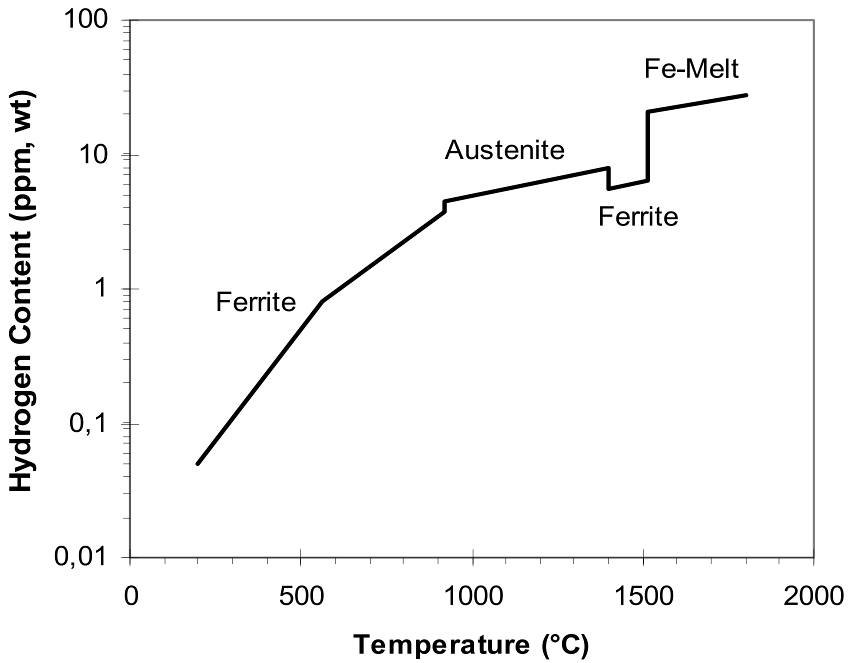


Solubility of nitrogen in binary iron alloys [Mn, C, Al] at 1592°C

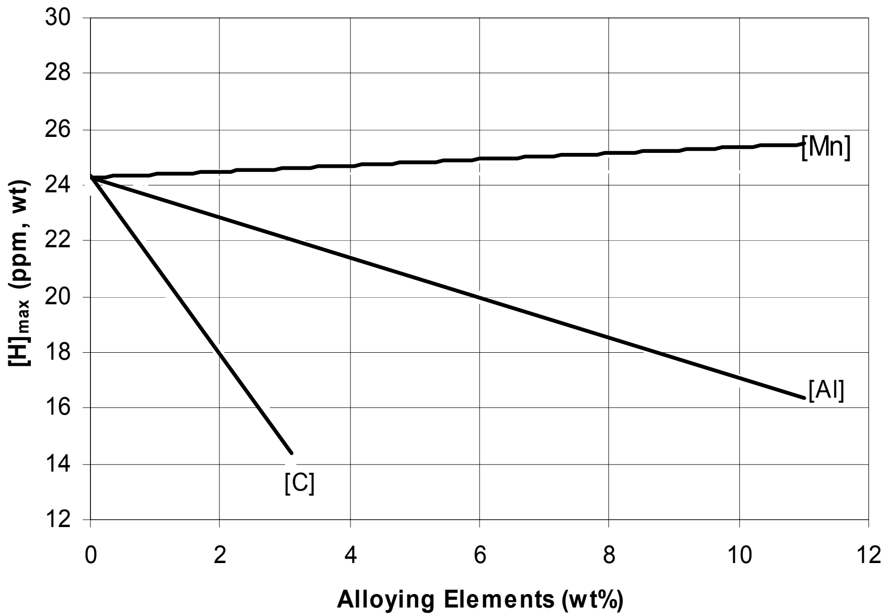
Weinstein, E.; Elliot, J. F.: Trans. Met. Soc., AIME 227 (1963), pp. 382-393

Hydrogen in the System Fe-Mn-C

increasing [H] in the austenite and with increasing manganese contents



Solubility of hydrogen in pure iron



Solubility of hydrogen in binary iron alloys [Mn, C, Al]

Weinstein, E.; Elliot, J. F.: Trans. Met. Soc., AIME 227 (1963), pp. 382-393

Solubility of Gases

Nitrogen

$$\frac{1}{2}\{N_2\} \rightarrow [N]$$

$$K_N = \frac{a_N}{\sqrt{p_{N_2}}}$$

$$a_N = f_N [\% N]$$

$$[\% N] = \frac{K}{f} \sqrt{p_N}$$

Hydrogen

$$\frac{1}{2}\{H_2\} \rightarrow [H]$$

$$K_H = \frac{a_H}{\sqrt{p_{H_2}}}$$

$$a_H = f_H [\% H]$$

$$[\% H] = \frac{K}{f} \sqrt{p_H}$$

the content of solved gases depends on:
- chemical composition
- temperature
- pressure

K = equilibrium constant
a = activity
f = activity coefficient

Gmelin, L.; Durrer, R.; Trenkler, H.; Krieger, W.: Gmelin-Durrer Metallurgie des Eisens. Weinheim: Verlag Chemie, (1978) (5a/b)

Solubility of Gases

Temperature dependence

K = equilibrium constant
T = temperature (K)

$$\lg K = \frac{A}{T} + B$$

Constants	[N]	Ref.	[H]	Ref.
A	-285	/9/	-1900	/1/
B	-1.21	/9/	0.9201	/2/

Stone, R. P.; Plessers, J.; Turkdogan, E. T.: Die Genauigkeit der Bestimmung des Wasserstoffgehaltes in flüssigem Stahl mit dem Hydris-System. Stahl und Eisen 110 (1990), 11, pp. 65 – 71

Dependence on chemical composition

Nitrogen

$$\lg f_N = e_N^N [wt\%N] + e_N^{Mn} [wt\%Mn]$$

with:

e_N^{Mn} = -0.028

e_N^N = 0

Hydrogen

$$\lg f_H = \sum e_H^j [\% j]$$

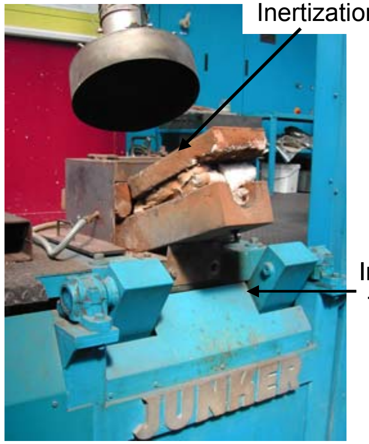
Alloy element j	Interaction parameter e^j_H
Al	0.011
C	0.060
Cr	-0.002
Mn	-0.001
Ni	-0.002
P	0.015
S	0.008
Si	0.023

Frohberg, M. G.: Thermodynamik für Werkstoffingenieure und Metallurgen. Leipzig: Deutscher Verlag für Grundstoffindustrie (1994)

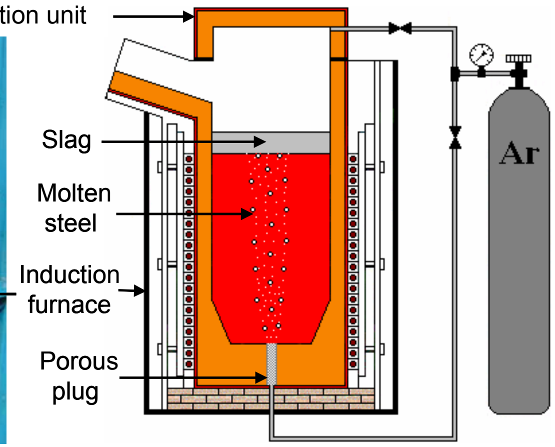
Experiments

on Nitrogen

- melting of Fe and C
- stepwise charging of manganese flakes
- sampling for analysing the chemical composition of the melt
- sampling for analysing the nitrogen content
- measurement of temperature



Induction-Furnace at IEHK
(50kg medium frequency)



Schematic furnace with principle of gas flooding

on Phosphorus

- controlled Ar stirring condition to guarantee temperature and composition homogenization
- gas and inductive flow to increase the metal/slag area

Experiments on Hydrogen

online hydrogen measurement with Hydris®

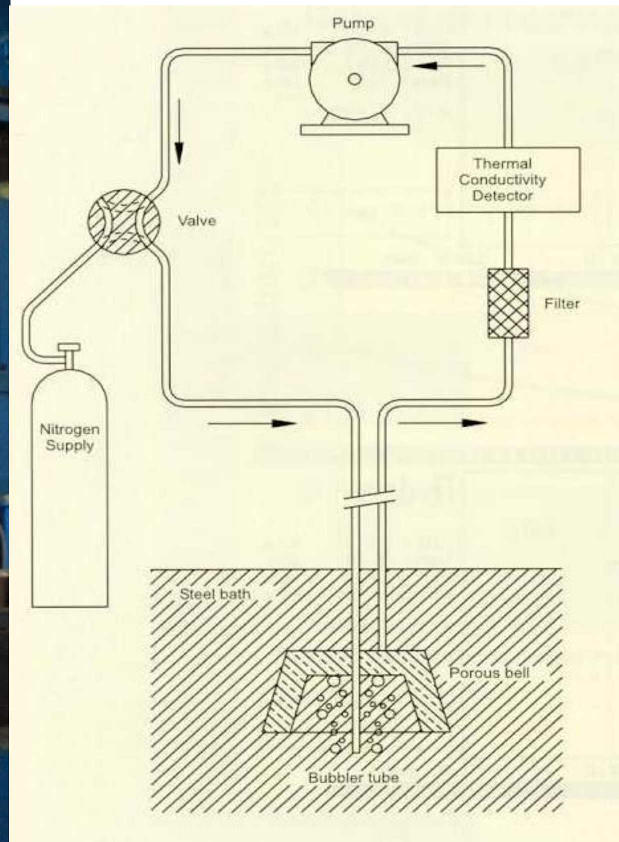
exhaust duct

Hydris®-lance

Hydris®-probe

refractory

hood for inerting (protection against the atmospheric humidity)



Functional principle of Hydris®

Experiments on Hydrogen

Steps for pin tube sample taking

rapid treatment of every step with Pin Tubes

1) sample extraction from the melt

1

2) quenching the sample into cold water

2

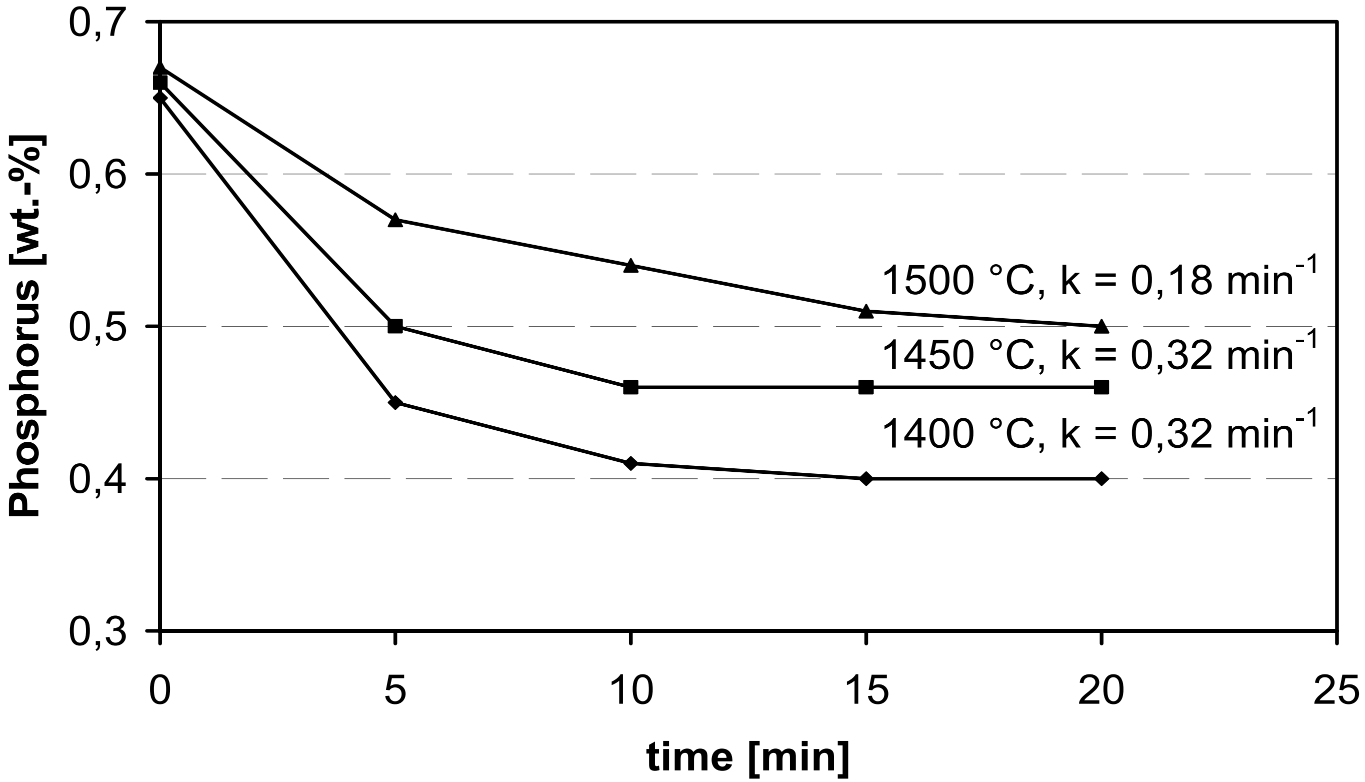
3) removing the fused quartz from the solidified sample

4

4) leaving the solidified sample into liquid nitrogen

Analysing →

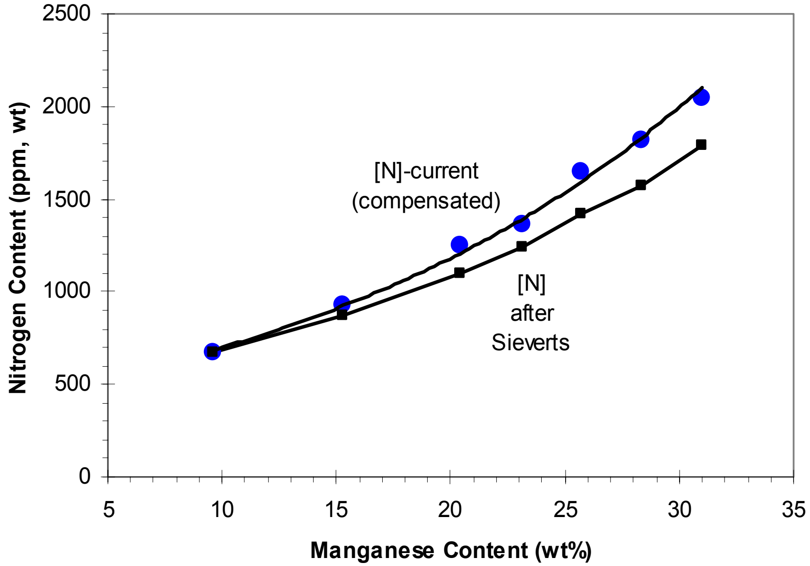
Results of Phosphorus Experiments



Dephosphorization treatment with BaO-Basis slag

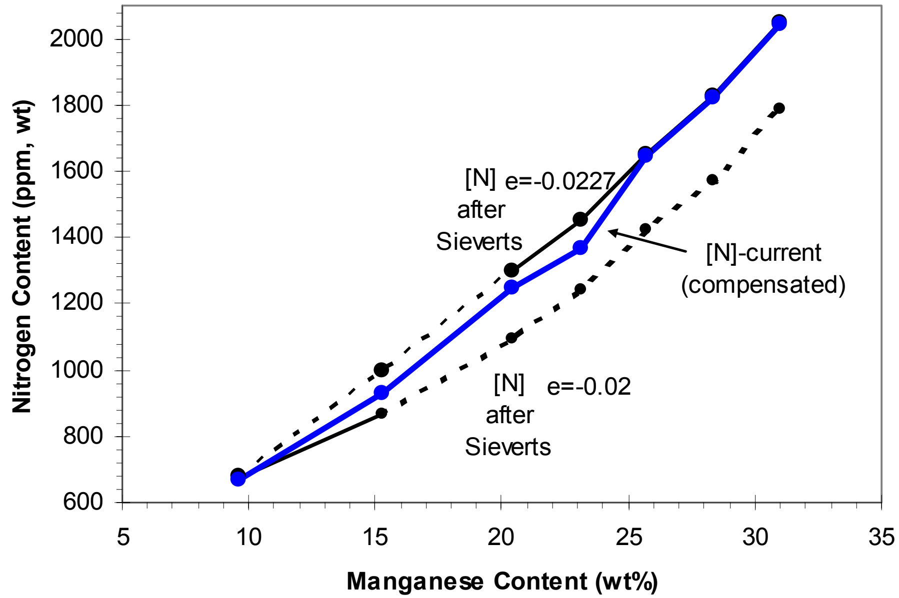
dephosphorization is favoured at low temperatures

Results of Nitrogen Experiments



Comparison of measured nitrogen solubility values with calculated after Sieverts (= 1013 mbar)

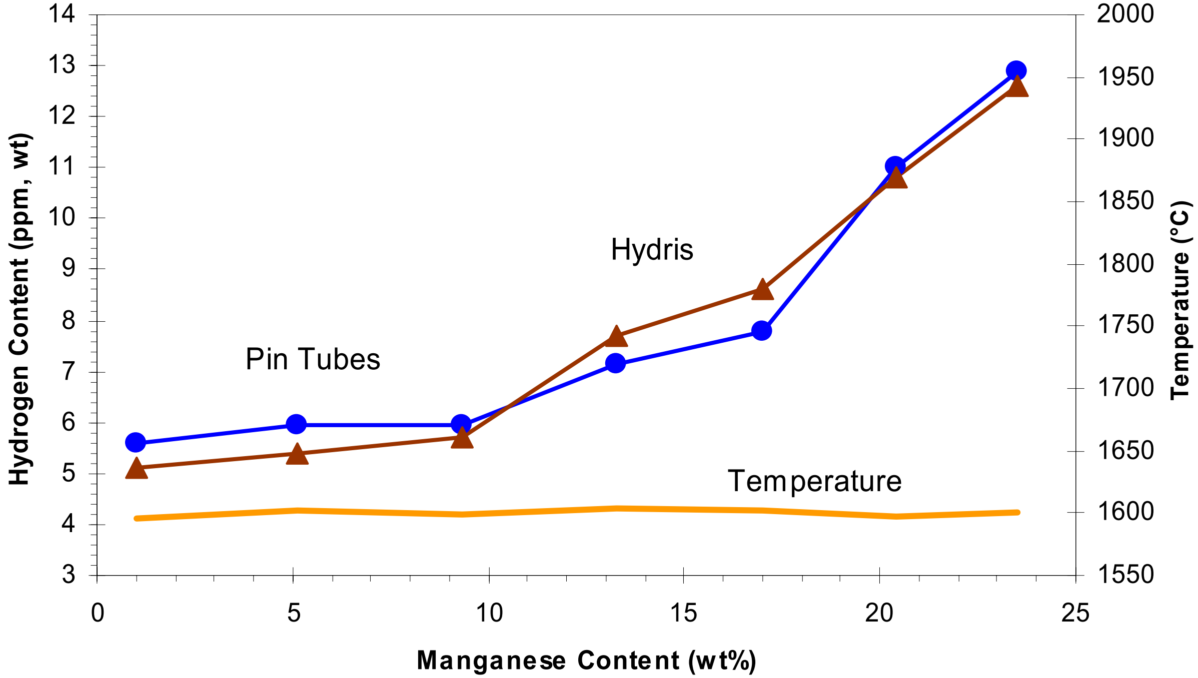
calculation of a new interaction parameter for nitrogen for high manganese contents



Measured nitrogen values with calculated values after Sieverts for e_N^{Mn} = -0.02 and e_N^{Mn} = -0.0227 (= 1013 mbar)

increasing nitrogen content with increasing manganese contents

Results of Hydrogen Experiments



Comparison between Hydris® - and Pin Tubes measurement for increasing manganese contents

increasing hydrogen content with increasing manganese contents

both measurement techniques give conformable results

Conclusions

System Fe-Mn-C:
- high strength combined with high ductility
- austenitic structure

Critical Elements:
- phosphorus has a low oxygen affinity
- high gas solubility (N, H) in austenitic systems

Examinations:
- dephosphorization with a new slag BaO
- solubility examinations with nitrogen and hydrogen for increasing manganese contents

Results:
- effective dephosphorization with BaO slag, especially for low temperatures
- increasing nitrogen and hydrogen contents for increasing manganese contents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Attention