Accelerated vacuum decarburisation of molten steel by combination of oxygen and metal oxides

D. Rzehak, 12.07.2012

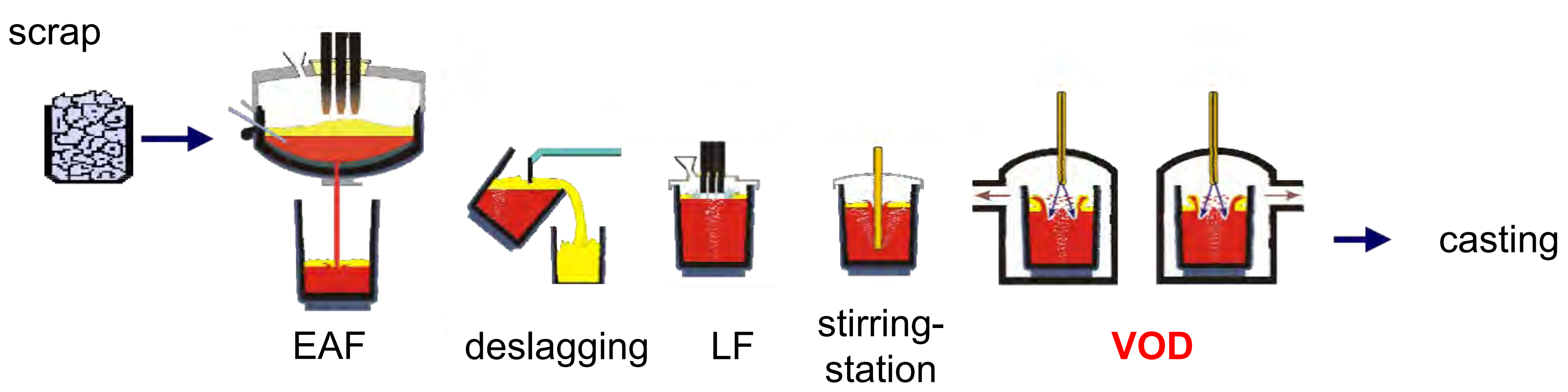
DEUTSCHE EDELSTAHLWERKE

Providing special steel solutions

Content:

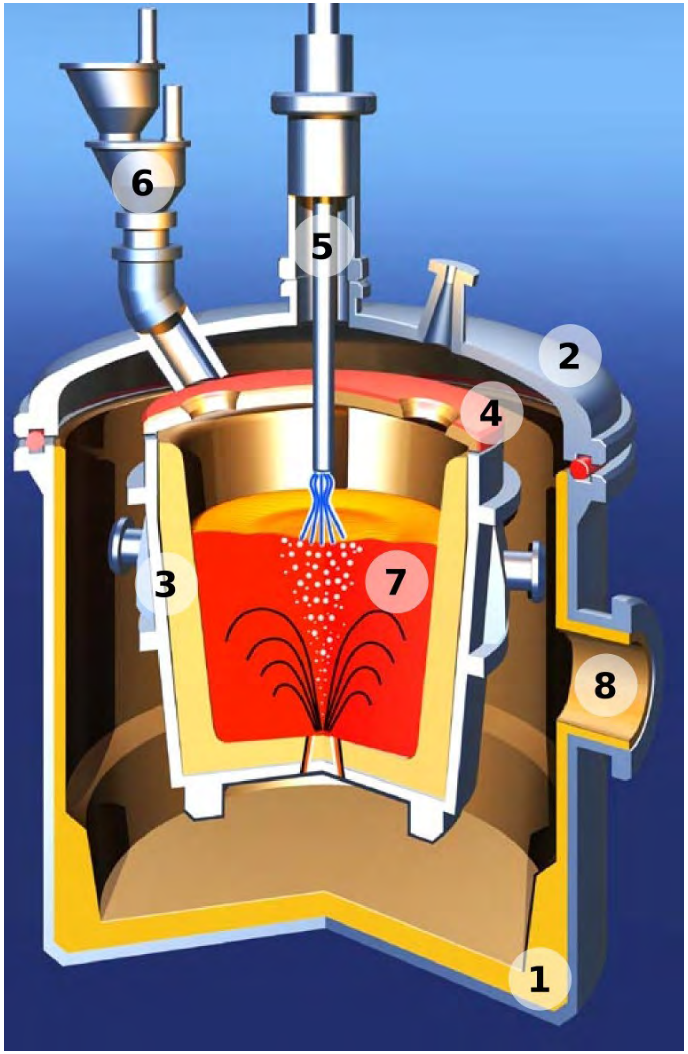
- The vacuum oxygen decarburization (VOD) process
- Thermodynamic principle of the VOD
- Tank model
- Laboratory trials
- Industrial trials
- Conclusions

VOD in the steelmaking process



Source: Deutsche Edelstahlwerke GmbH
http://www.dew-stahl.com/produkte/produktion/rohstahlproduktion/

VOD – Tank degasser



(1)Tank

(2)Lid with seal

(3)Ladle

(4)Splashing protection panel

(5)Top lance

(6)Alloying system

(7)Steel melt

(8)Vaccum connection

Source: SMS Mevac GmbH
http://www.sms-mevac.com/media/Mevac_SecMet_D_sp.pdf

VOD – Tank degasser: process characteristics

- turbulent and exothermic reaction of oxygen and carbon rich steel melt
- good stirring of the melt necessary
- supersonic top lance and porous plug cause splashing of melt and slag
- long treatment time of up to 1-2 hours
- huge dust load in the offgas
- …

injection of metall-oxide-powder →

- increase the oxygen density in the gas jet
- particles can act as a nucleating agents for CO-bubbles
- recycling of process dust
- cooling effect, due to endothermic reduction
- amount of solved oxygen may decrease, less negative effect of blocking the boundary layer
- …

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Thermodynamic principle of the VOD: Cr-C-O-Equilibrium

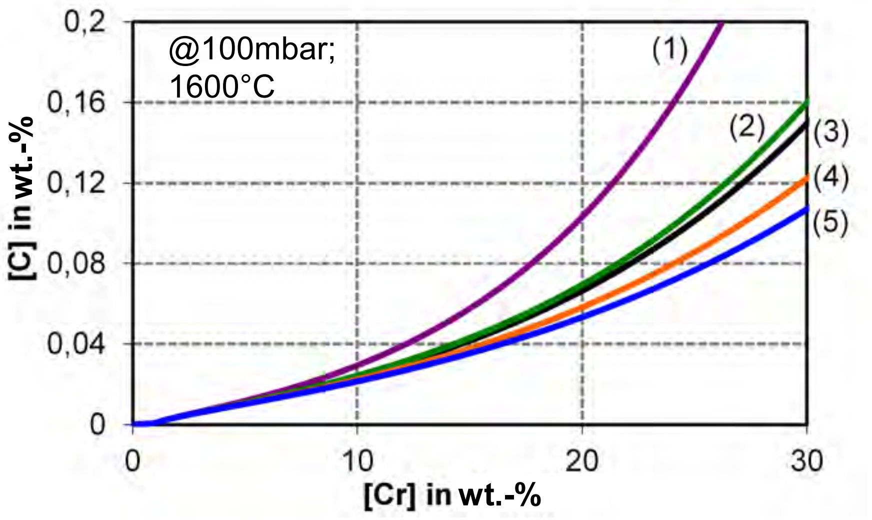
$$[C]+[O]\Leftrightarrow\{CO\}$$
$$2[Cr]+3[O]\Leftrightarrow(Cr_2O_3)$$

$$K_{CO}=\frac{p_{\{CO\}}}{a_{[C]}\cdot a_{[O]}}$$
$$K_{Cr_2O_3}=\frac{a_{(Cr_2O_3)}}{a_{[Cr]}^2\cdot a_{[O]}^3}$$

$$a_C=f_C\cdot[\%C]$$
$$f_C=\prod^i f_C^{Y_i}=f_C^C\cdot f_C^O\cdot f_C^{Cr}$$
$$\log f_C^{Y_i}=e_C^{Y_i}\cdot[\%Y_i]$$

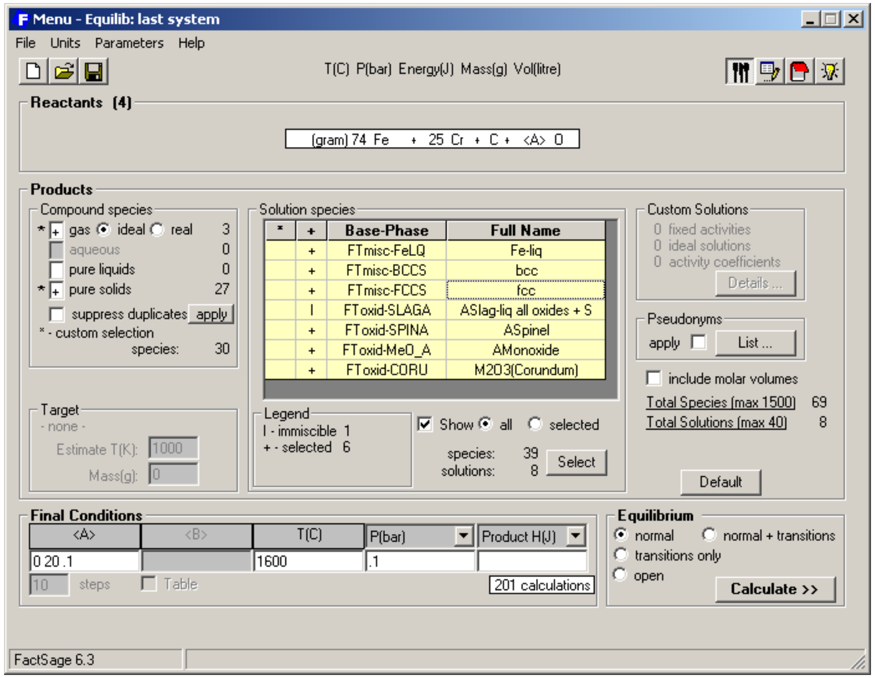
Assumption $a_{(Cr2O3)}=1$

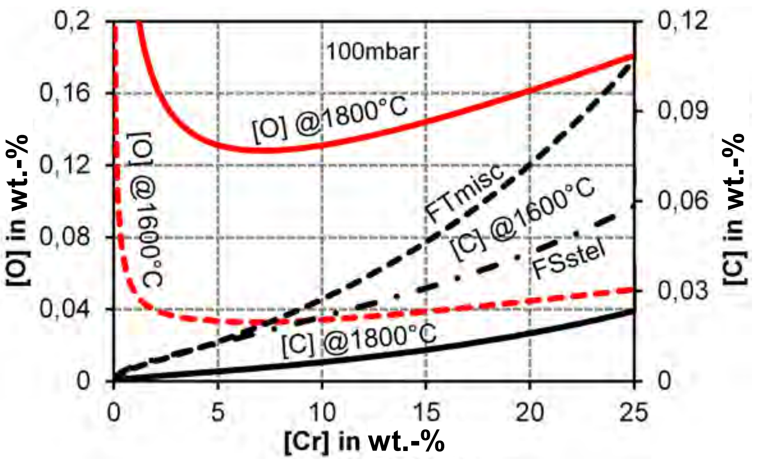
effect of different interaction coefficients:

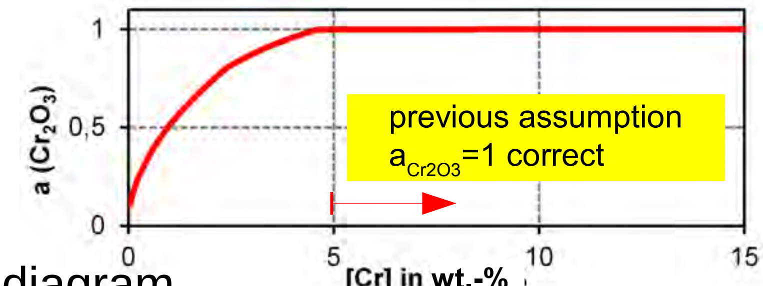


#	e_C^{Cr}	Publisher	Year
(1)	-0,033	Goto	1963
(2)	-0,024	Schenck, Steinmetz	1968
(3)	-0,023	Nakamura	1970
(4)	-0,02	Chipman	1955
(5)	-0,018	Schmidt, Etterich, Bauer, Fleischer	1968

Thermodynamic principle of the VOD: Cr-C-O with FactSage





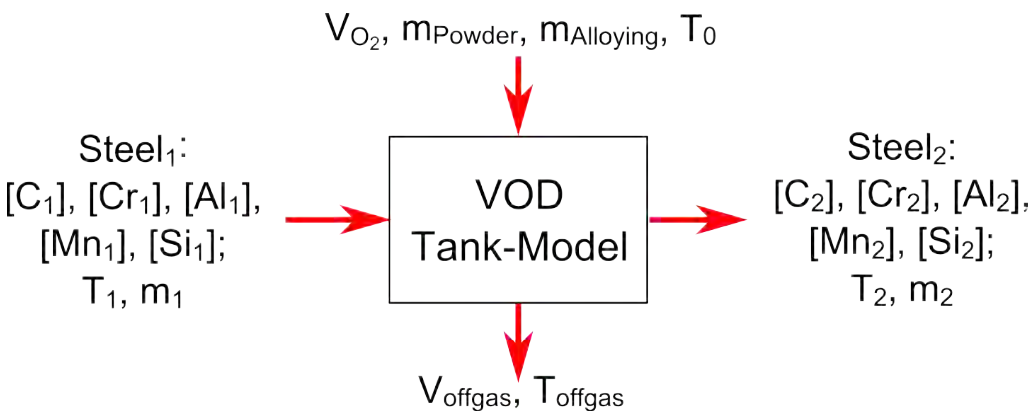


- Variable oxygen input gives the “Vacher-Hamilton”-diagram
- Different [C]-content with “FTmisc” and “FSstel”
  - “FTmisc (…) optimized for iron-rich solutions only (and is not for calculations involving stainless steels)”
  - “FTmisc (…) will give good calculations of deoxidation equilibria for strong deoxidants when used with FToxid-SLAG “

FTmisc seems to correlate better with published values!

Content:

VOD Tank-Model: structure



Heat-balance:

$$\Delta Q_{melt} = Q_{powder} + Q_{O_2} + Q_{material-additions} + Q_{loss}$$

Mass-balance:

$$n_{O_{gas}} + n_{O_{powder}} = \Delta n_C + n_{O_{gas} \rightarrow Me_x O_y} + n_{O_{gas} \rightarrow NV}$$

VOD Tank-Model: Heat-balance

Heat-balance:

$$\Delta Q_{melt} = Q_{powder} + Q_{O_2} + Q_{material-additions} + Q_{loss}$$

Calculation of each energy item contains:

- Enthalpy of heating (including phase transformation)
- Enthalpy of reaction (including solving into liquid melt)

} Calculated with FactSage

↓

Temperature dependent polynomial functions

↓

Database for VOD tank-model

For example Q_{powder}:

$$Q_{powder} = Q_{powder-heating} + Q_{powder-reduction}$$

$$Q_{powder-heating} = n_{powder} \cdot \Delta H^0_{powder}$$

$$Q_{powder-reduction} = n_{powder} \cdot \sum \Delta H_i^{reduction} \cdot x_i$$

Reduction of metall-oxide-powder:

$$(FeO) + [C] \Leftrightarrow [Fe] + \{CO\} + \Delta H^{reduction}_{FeO}$$

$$(Fe_2O_3) + 3[C] \Leftrightarrow 2[Fe] + 3\{CO\} + \Delta H^{reduction}_{Fe_2O_3}$$

$$(Cr_2O_3) + 3[C] \Leftrightarrow 2[Cr] + 3\{CO\} + \Delta H^{reduction}_{Cr_2O_3}$$

VOD Tank-Model: start-values

Chemical analysis of the metall-oxide-powder:

FeO	Fe_2O_3	Cr_2O_3	Fe_{met}	SiO_2	CaO
in wt-%					
20,58	46,33	3,43	22,24	4,58	2,84

Boundary conditions for the VOD calculation:

m_{steel}	T_1	m_{powder}	$m_{material\text{-}addition}$
in kg	in °C	in kg	in kg
85000	1600	0-1500	0

$[C]_1$	$[Cr]_1$	$[Si]_1$	$[Al]_1$	$[Mn]_1$
in wt.-%				
0,7	18	0,04	0,07	1,2

VOD Tank-Model: process-point-calculation

e.g. setpoint: $[C]_2$=0,01

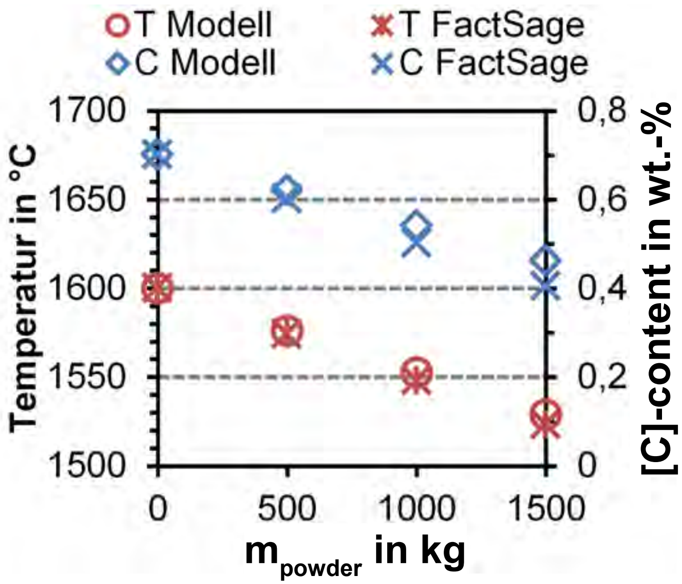
Changes in melt temperature T_2 during combined blowing:

setpoint	calculated	
m_{powder}	V_{O2}	T_2
in kg	in Nm³	in °C
0	1051	1732
500	959	1694
1000	868	1657
1500	776	1619

cooling effect: 38°C
- reduced exothermic C-burning, less V_{O2}
- endothermic powder reaction

VOD Tank-Model: evaluation with FactSage

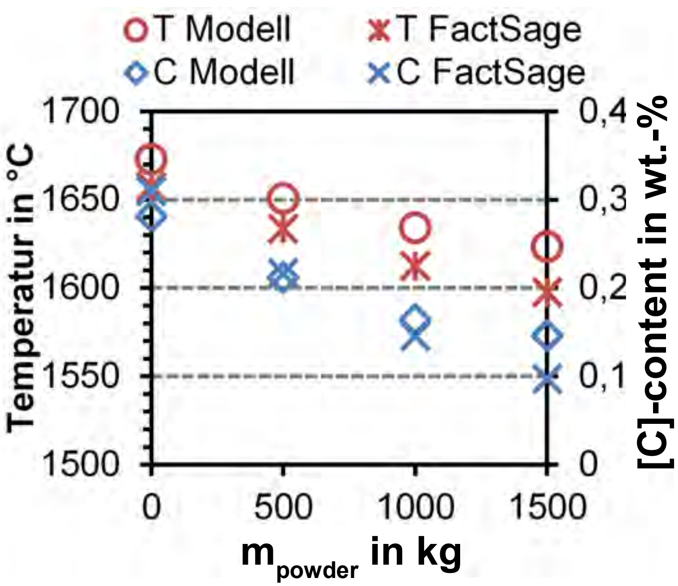
- only powder blowing
- slight deviation in carbon content, possible reason:
  no dilution effect by the powder in tank-model



m_powder in kg	0	500.00	1000.00	1500.00
T in °C	1600	1573.99	1548.39	1522.99
PHASE: Gas	VOL %	VOL %	VOL %	VOL %
CO_FactPS	-	100.00	100.00	100.00
CO2_FactPS	-	0.00	0.00	0.00
total in m³	**-**	**1,06E+06**	**2,08E+06**	**3,08E+06**
PHASE: Fe-liq	WEIGTH %	WEIGTH %	WEIGTH %	WEIGTH %
Al_FTmisc	0,070	0.07	0.07	0.07
C_FTmisc	0,700	0.60	0.50	0.40
CaO_FTmisc	-	0.00	0.00	0.00
Cr_FTmisc	18,000	17.95	17.90	17.86
Fe_FTmisc	79,990	80.13	80.27	80.41
Mn_FTmisc	1,200	1.20	1.19	1.19
Si_FTmisc	0,040	0.05	0.06	0.08
total in kg	**8,50E+04**	**8,53E+04**	**8,56E+04**	**8,59E+04**
PHASE: Monoxide#1	WEIGTH %	WEIGTH %	WEIGTH %	WEIGTH %
Al2O3_FToxid	-	0.12	0.27	0.64
CaO_FToxid	-	99.87	99.72	99.34
Cr2O3_FToxid	-	0.00	0.00	0.00
FeO_FToxid	-	0.00	0.00	0.00
MnO_FToxid	-	0.01	0.02	0.03
total in kg	**-**	**13,242**	**27,854**	**42,486**

VOD Tank-Model: evaluation with FactSage

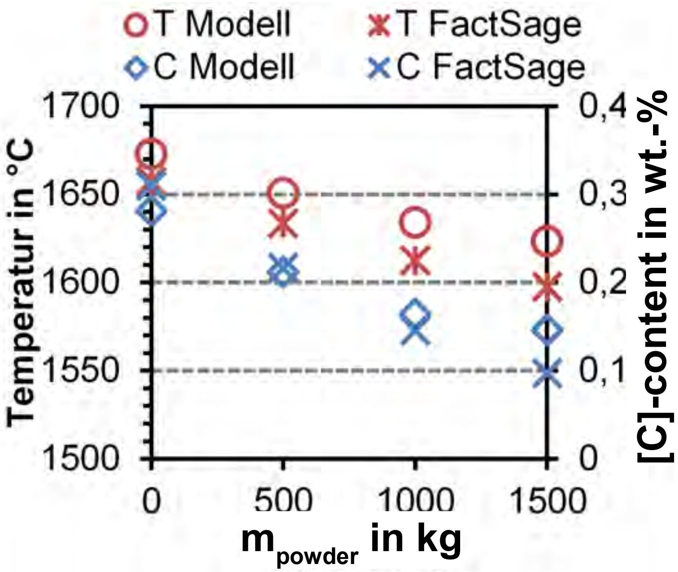
- combined blowing
- V_{O2}= const. = 349 Nm³
- reasons for ΔC:
  - no dilution effect by the powder in tank-model



m_powder in kg	0.00	500.00	1000.00	1500.00
T in °C	1657	1633	1612	1597
PHASE: Gas	VOL %	VOL %	VOL %	VOL %
CO_FactPS	99,911	99,853	99,750	99,597
CO2_FactPS	0,089	0,147	0,250	0,403
total in m³	**4,46E+04**	**5,42E+04**	**6,15E+04**	**6,62E+04**
PHASE: Fe-liq	WEIGTH %	WEIGTH %	WEIGTH %	WEIGTH %
Al_FTmisc	0,007	0,002	0,001	0,000
C_FTmisc	0,309	0,216	0,145	0,098
Cr_FTmisc	18,054	17,991	17,908	17,809
Cr2O_FTmisc	0,018	0,029	0,048	0,074
CrO_FTmisc	0,013	0,020	0,032	0,048
Fe_FTmisc	80,351	80,485	80,634	80,810
Mn_FTmisc	1,205	1,201	1,178	1,118
O_FTmisc	0,001	0,002	0,003	0,005
Si_FTmisc	0,040	0,053	0,051	0,036
total in kg	**8,46E+04**	**8,49E+04**	**8,52E+04**	**8,54E+04**

VOD Tank-Model: evaluation with FactSage

- combined blowing
- V_{O2}= const. = 349 Nm³
- reasons for ΔT:
  - precipitation of phase like: liquid slag



m_{powder} in kg	0.00	500.00	1000.00	1500.00
T in °C	1657	1633	1612	1597
PHASE: Ca(Al,Fe)4O7	WEIGTH %	WEIGTH %	WEIGTH %	WEIGTH %
Ca1Al4O7_FToxid	-	100,00	-	-
total in kg	**-**	**29,577**	**-**	**-**
PHASE: Ca(Al,Fe)12O19	WEIGTH %	WEIGTH %	WEIGTH %	WEIGTH %
Ca1Al12O19_FToxid	-	100,00	-	-
total in kg	**-**	**92,802**	**-**	**-**
PHASE: Slag-liq#1	WEIGTH %	WEIGTH %	WEIGTH %	WEIGTH %
Al2O3_FToxid	-	-	48,470	31,132
CaO_FToxid	-	-	16,716	11,847
Cr2O3_FToxid	-	-	0,816	1,240
CrO_FToxid	-	-	6,248	10,446
FeO_FToxid	-	-	0,718	1,273
MnO_FToxid	-	-	11,852	22,875
SiO2_FToxid	-	-	15,169	21,171
total in kg	**-**	**-**	**169,830**	**359,550**
PHASE: M2O3(Corundum)#1	WEIGTH %	WEIGTH %	WEIGTH %	WEIGTH %
Al2O3_FToxid	98,616	-	90,581	-
Cr2O3_FToxid	1,384	-	9,418	-
total in kg	**101,660**	**-**	**31,491**	**-**

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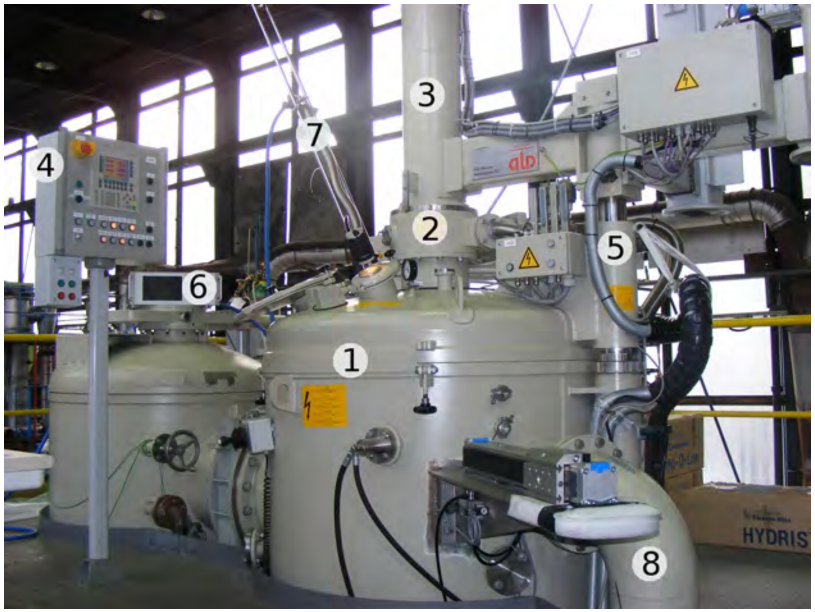
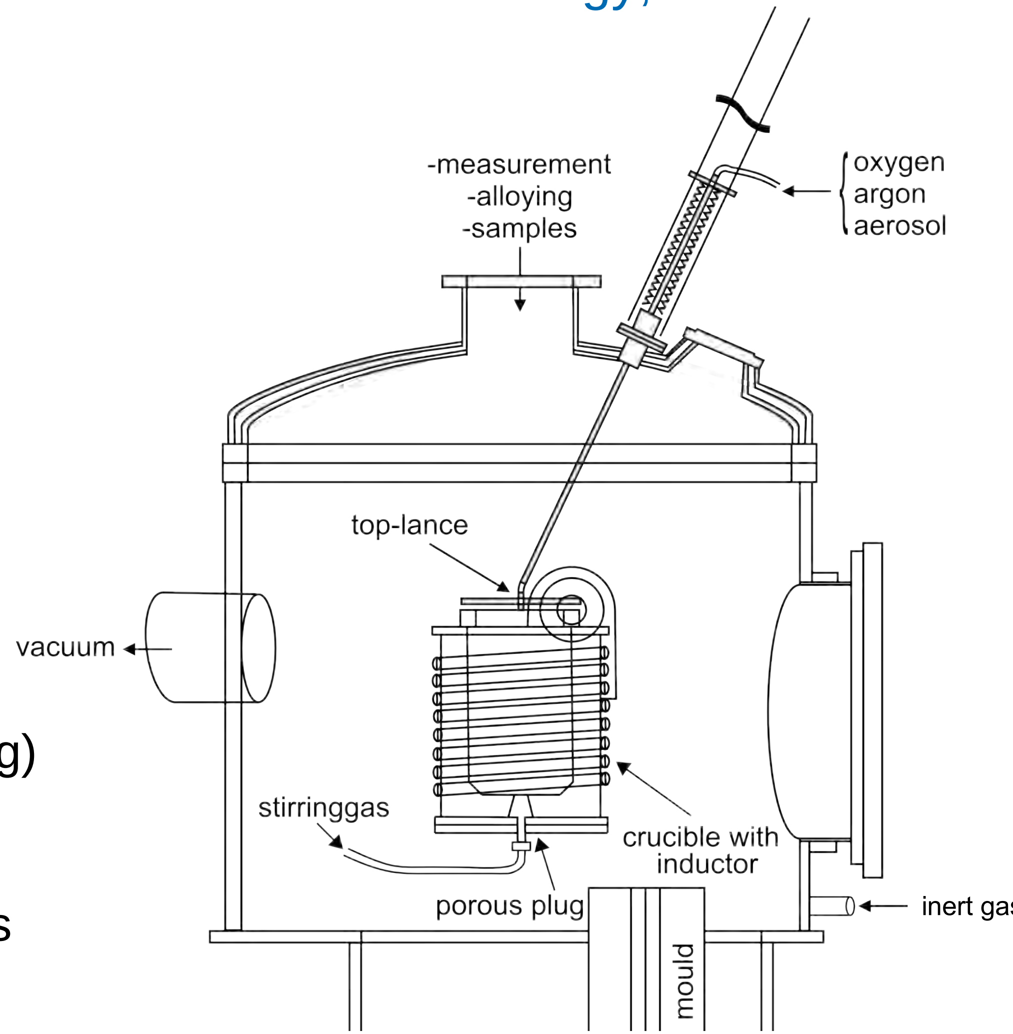
Laboratory trials at the Department of Ferrous Metallurgy, RWTH Aachen



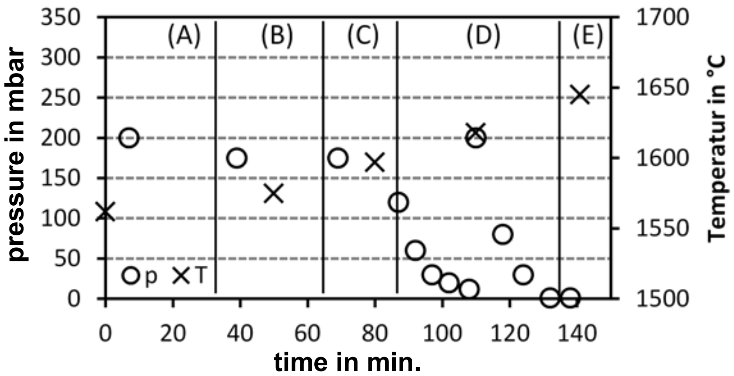


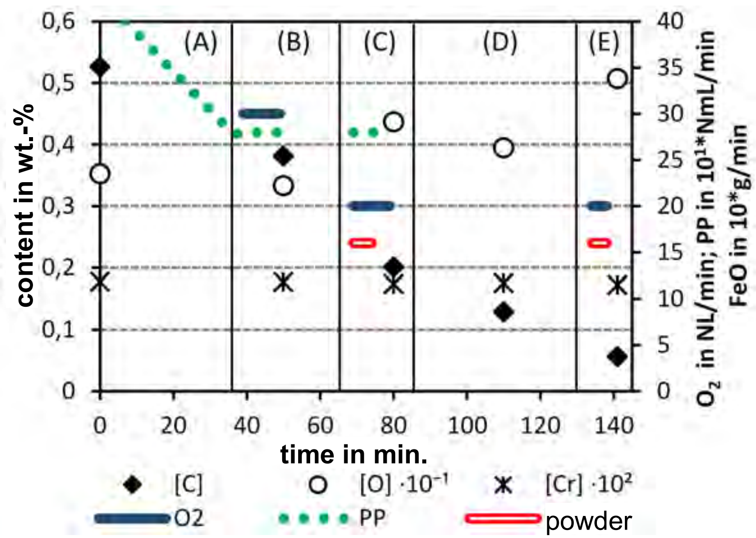
(1)Tank with closed lid
(2)Valve (measuring, sampling, alloying)
(3)Manipulator
(4)Operation panel
(5)Turning unit for up to 4 manipulators
(6)Celox measurement system
(7)Top lance
(8)Vacuum connection

Laboratory trials at Department of Ferrous Metallurgy, RWTH Aachen

- investigation of the accelerated decarburization with combined blowing
- geometry and process parameter similar to industry
- VOD treatment divided into short blowing periods of 10min.
- sample, oxygen-activity, temperature

$[C]_1$	$[Cr]_1$	$[Si]_1$	$[Al]_1$	$[Mn]_1$
in wt.-%				
0,5	18	0,08	0,02	0,01



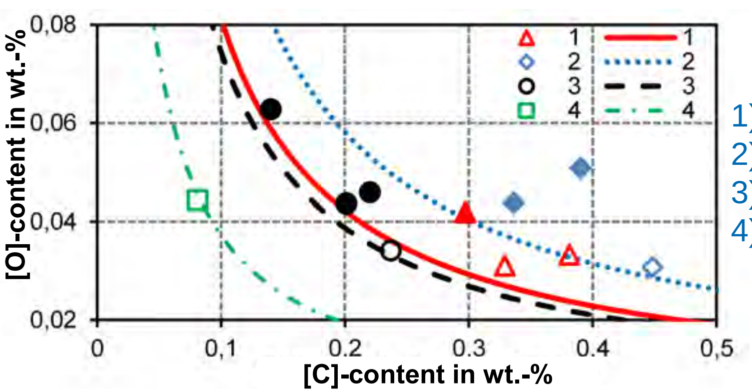


Laboratory trials at Department of Ferrous Metallurgy, RWTH Aachen

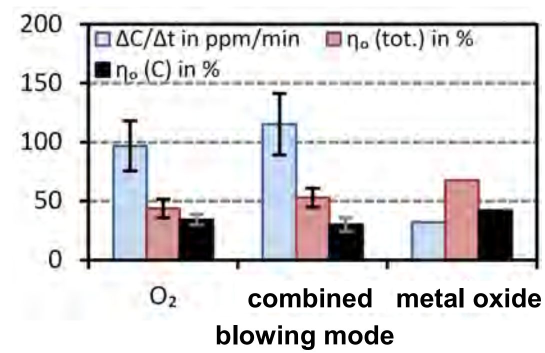
Results:

- simulation of VOD-process in vacuum induction furnace is possible
- thermodynamic equilibrium is nearly reached during blowing
  → porous plug and top lance are sufficient
- single powder blowing is not reliable, freeze of the top lance nozzle
- low oxygen efficiency, η_O(C):
  - O_2-blowing: 34%
  - combined blowing: 30%

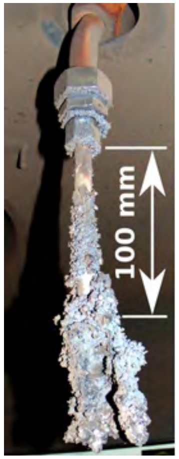
  } e.g. industrial oxygen efficiency: 60%
- combined blowing accelerates the decarburization of about 20%
  - but the oxygen amount is increased by 70%!
  - Cr-burning↑ and decarburization efficiency ↓

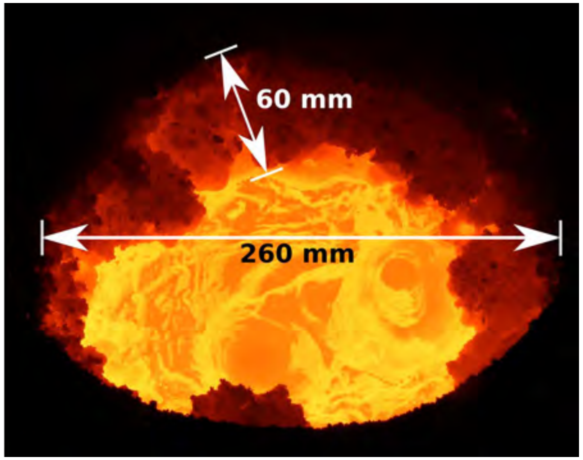


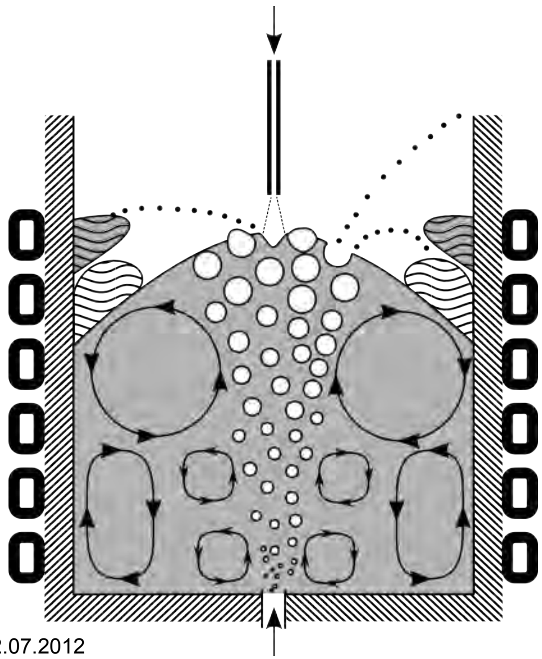
1) 1550°C, 200mbar
2) 1600°C, 300mbar
3) 1600°C, 200mbar
4) 1600°C, 100mbar



Laboratory trials at Department of Ferrous Metallurgy, RWTH Aachen

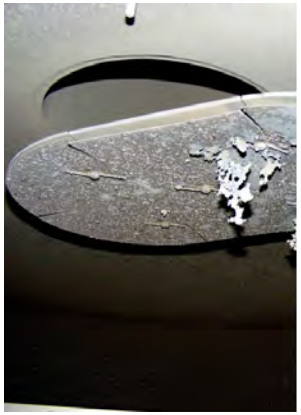


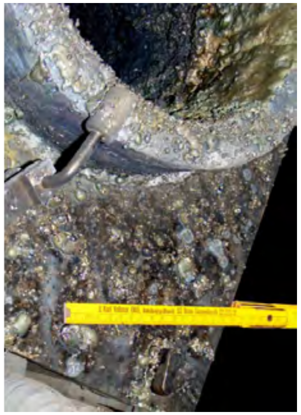




reason for low oxygen and powder efficiency:

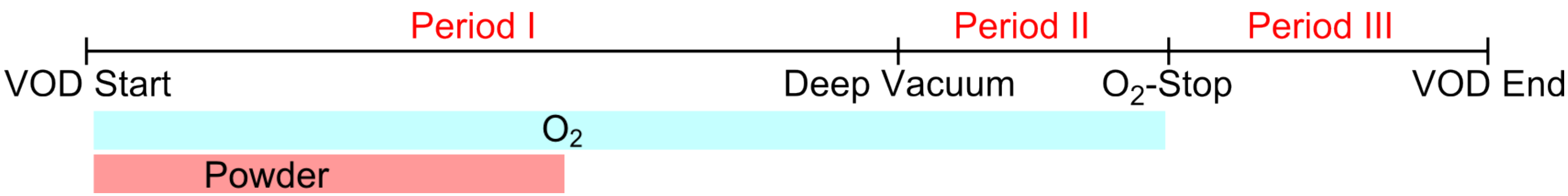
- slag is freezing at the crucible
  - → heavy and solid “slag-ring” was formed during the VOD-trials
  - → water cooled inductor causes an cold crucible directly above the steel melt
  - → no contact between steel and “slag-ring” due to induction forced parabolic melt surface
  - → unknown loss of oxygen



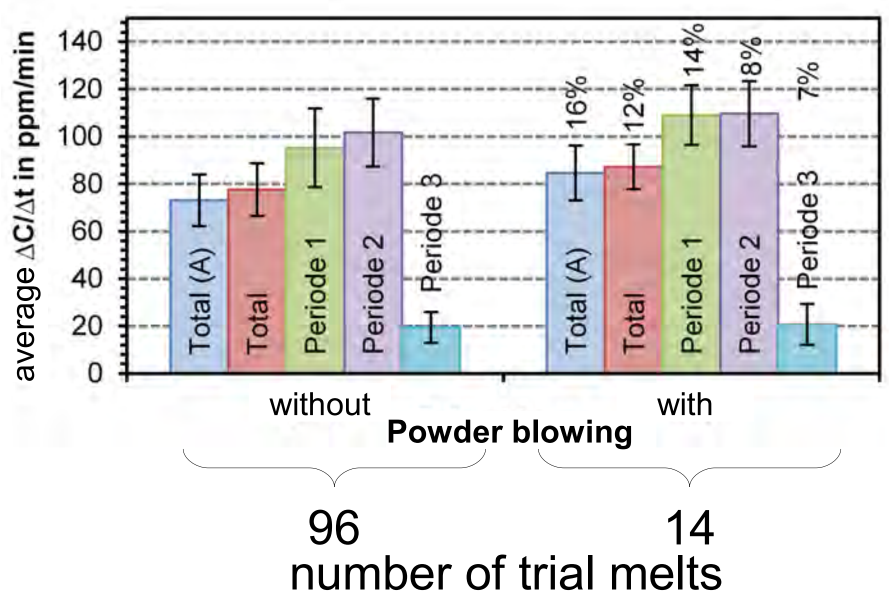


Content:

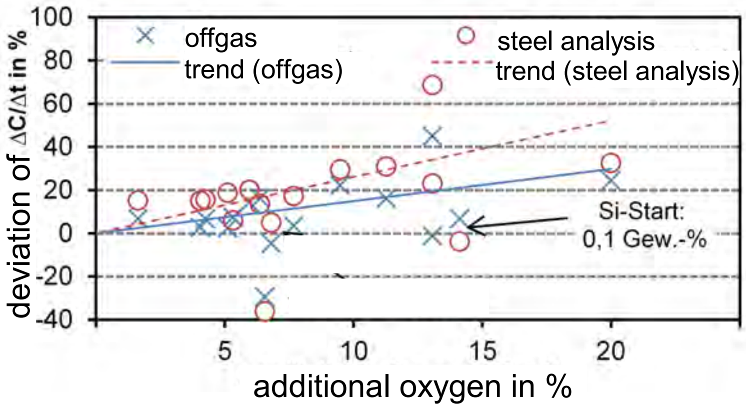
Industrial trials at ACRONI, Slowenia



- 85t steel melt
- oxygen flow rate: 800Nm³/h
- up to three argon plugs
- powder injection through a second lance, transport gas: Argon
- steel analysis not possible during treatment
- process control via offgas analysis

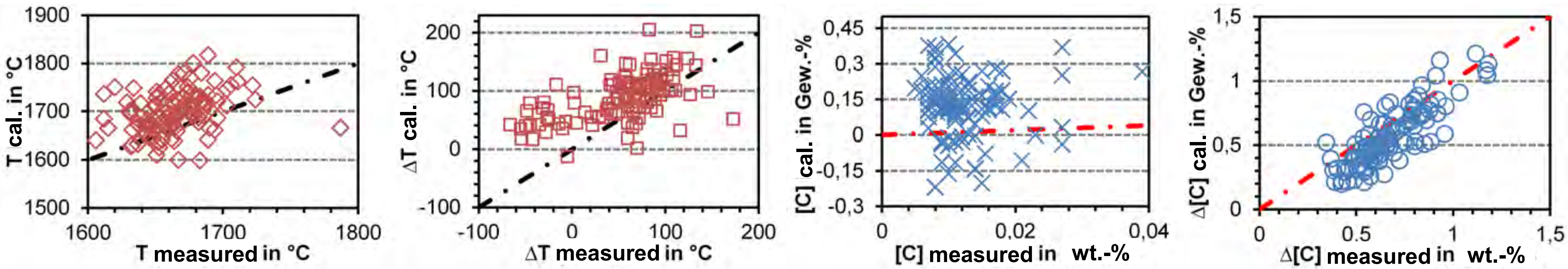


Industrial trials at ACRONI, Slowenia



- combined blowing accelerates the decarburization during the entire VOD-treatment
- increase of decarburization > additional oxygen

VOD Tank-Model: evaluation with industrial trials



- calculated absolute temperature shows a positive deviation, similar to that in FactSage
  - → also a constant T-loss during treatment time is calculated
- scattering in temperature caused typical industrial fluctuations e.g. different status of the ladles
- absolute carbon content does not correlate
  - → reason: no measured steel weight before VOD
  - → estimated steel weight produces failures in heat and mass balance

Content:

Conclusions

- the mass and heat balance of combined blowing VOD was simulated with basic thermodynamic assumptions
  - → scatter of the industrial process interferes the deviation from the model
  - → results of tank-model correspond with detailed thermodynamic calculation of FactSage
- combined blowing of oxygen and metal oxide powder increases the decarburization rate of the VOD
- reaction rate and effectivity depends strongly on the behaviour of the slag
  - → slag is oversaturated with oxygen
  - → slag must emulsify into the steel
- the accelerating effect of CO-bubble nucleation at powder particles is not clearly identified in laboratory and industrial trials
- powder blowing has no negative effect

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Ph. D. thesis will be published in 2013 at:
http://www.bth.rwth-aachen.de/

Thank you for your attention