# Decreased $CO_2$-Emissions by Adjusting CO-Concentration During Heat Treatment

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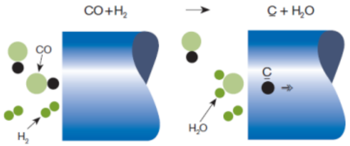
# Outline

- Carburizing/neutral hardening
- Control of furnace atmospheres
- Carbon mass transfer coefficient, β
- Dynamic control of CO
- DynaSty project
- Digital twin
- Optimization of heat treatments
- Industrial test
- Conclusions

# Carburizing / neutral hardening



- Carbon containing atmosphere (CO, $CO_2$, $CH_4$, $N_2$)
- To increase or maintain carbon content in part
- As much as 98% of furnace gases pass through without taking part and are burnt off as $CO_2$

From ”Steel and its Heat Treatment – a handbook”

# Control of furnace atmospheres

- Furnace atmosphere is usually controlled by an oxygen probe
- CO-content is often not measured but assumed to be ~20%
- CO content is usually set to 20% since that is what endogas generators used to produce
- Carbon potential can then be calculated and controlled
- If actual CO-content deviates from 20% →calculated Cp will be false

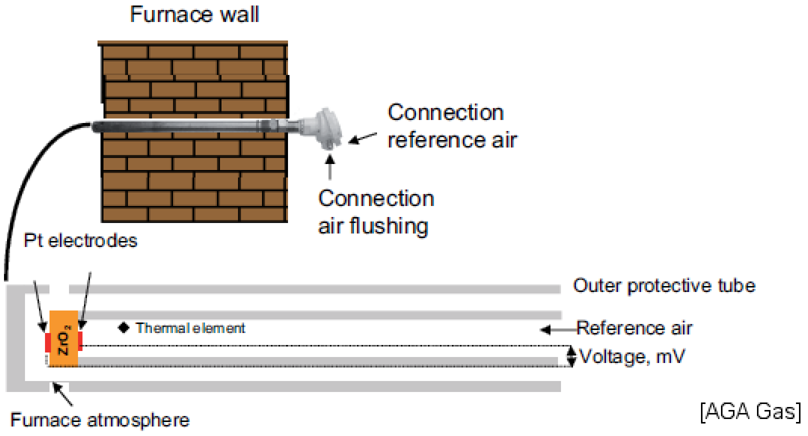


*Figure 15.10 Simplified illustration of an oxygen probe installed in a furnace wall with magnification of the section where platinum electrodes are mounted.*

From ”Steel and its Heat Treatment – a handbook”

# Furnace reactions

- Carburizing reactions

$$2CO \rightarrow C_{(\gamma-Fe)} + CO_2\,,$$

$$CH_4 \rightarrow C_{(\gamma-Fe)} + 2H_2\,,$$

$$CO + H_2 \leftrightarrow C_{(\gamma-Fe)} + H_2O\,.$$

- Reaction with propane
  - To reduce $CO_2$ and $H_2O$
  - Increase Cp

$$C_3H_8 + 3H_2O \text{ -> } 3CO + 7H_2$$

# Carbon potential, Cp

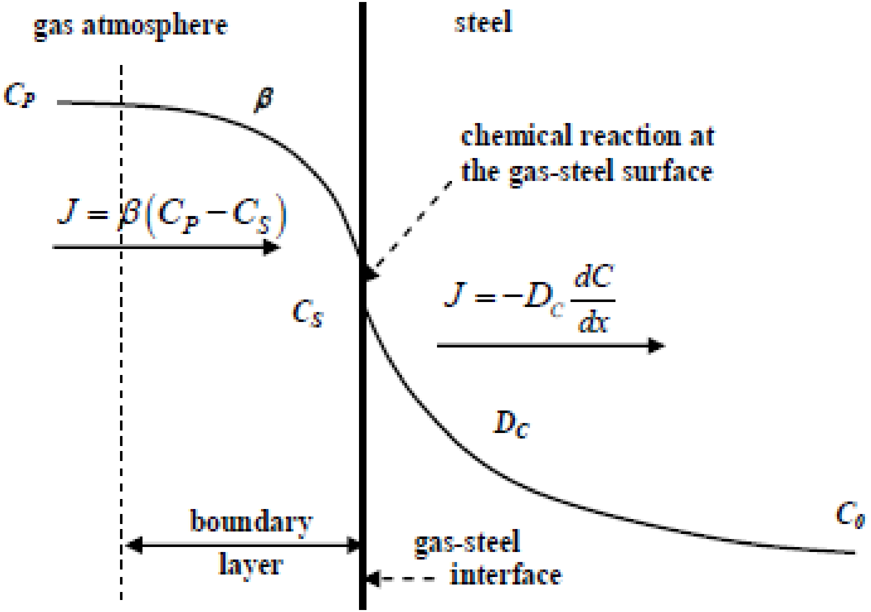
- Furnace atmospheres are usually controlled by the carbon potential Cp
- Definition: **The carbon content that pure iron in austenite form would have when in equilibrium with the gas**.

$$a_c = \gamma^0 \frac{x_C}{1-2x_C} \qquad x_C = \frac{\dfrac{C_p}{12{,}01}}{\dfrac{C_p}{12{,}01}+\dfrac{(100-C_p)}{55{,}85}}$$

- Cp is proportional to $(P_{CO})^2/P_{CO2}$

# Carbon mass transfer coefficient, β

- β controls the rate of carbon uptake during the initial stage of carburizing



Karabelchtchikova (2007)

$$J = \beta(C_p - C_S)$$

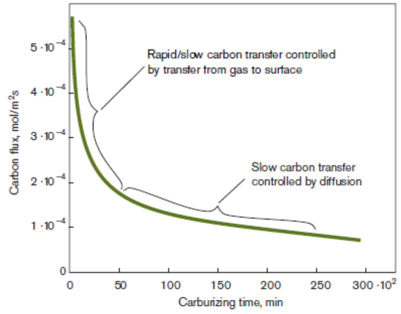
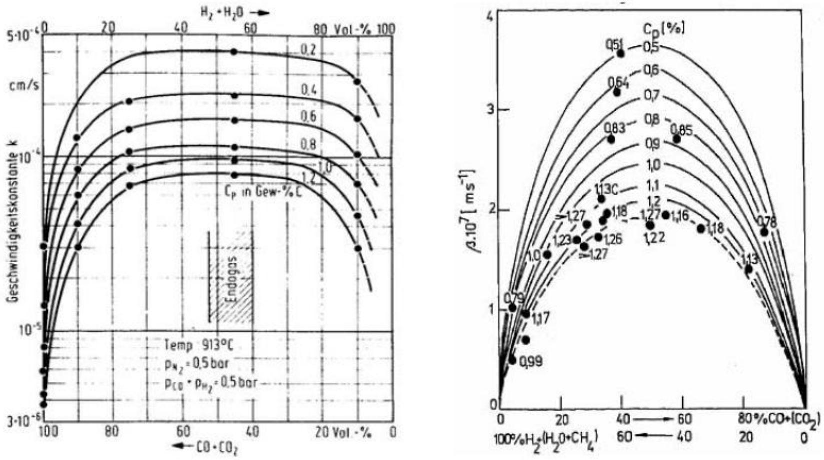


*Figure 8.4.10 The flux of carbon as a function of carburizing time. [4]*

From ”Steel and its Heat Treatment – a handbook”

# Variation of β with CO content

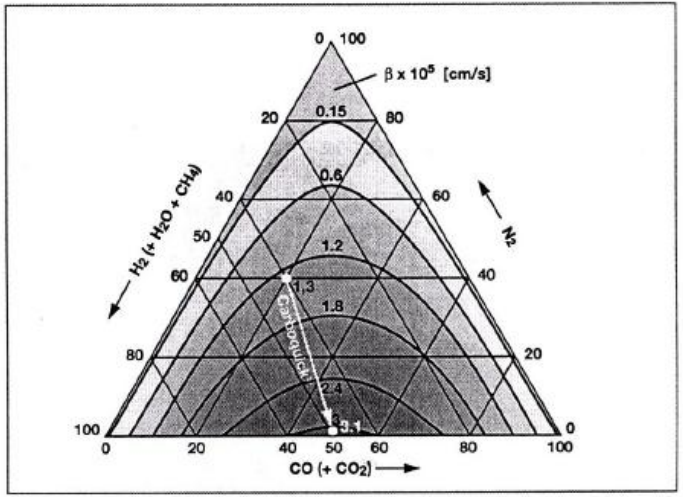


a)

b)

Figure 3. Variation in $\beta$ with gas atmosphere composition and $C_P$: (a) according to Rimmer et.al. at 913 °C [2], and (b) according to Stolar at 920 °C [1].

P. Stolar and B. Prenosil (1984)



***Determination of the carbon transfer rate $\beta$ at 900°C from the composition of the carburising atmosphere.***
***$\beta$ rises from 1.3 x 10⁻⁵ cm/s with endothermic gas to 3.1 x 10⁻⁵ cm/s with CARBOQUICK®.***
***n according to Neumann and Wyss)***

$$\beta = \frac{6.31\cdot10^{5}\cdot\exp\left(\frac{-22350}{T}\right)\cdot\frac{P_{H_2O}}{\sqrt{P_{H_2}}}}{1+5.6\cdot10^{6}\cdot\exp\left(\frac{-12900}{T}\right)\cdot\frac{P_{H_2O}}{\sqrt{P_{H_2}}}}$$

Collin et al 1972

LINDE GAS – CARBOQUICK – product sheet

# Carbon profiles at different β

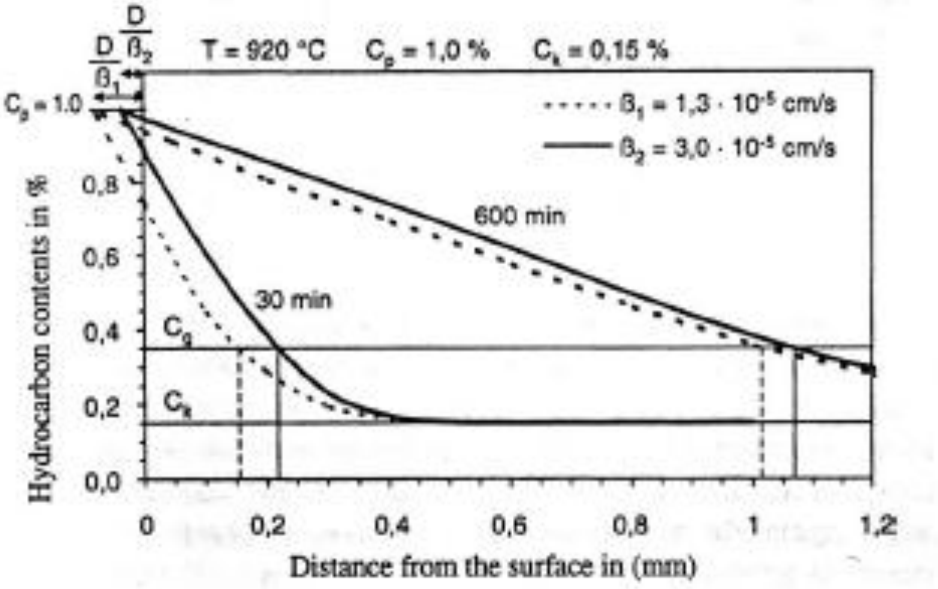


*Fig. 1. C-profile = f (Cd, β), left graph always β = 1,3, right graph β = 3,0 · 10⁻⁵ cm/sec*

Jurmann (1999)

# Cp and CO

- Most important factor for heat treatment result is a correct Cp
- Cp is proportional to $(P_{CO})^2/P_{CO2}$
- Cp can be controlled independently of the CO content, just keep the relation $(P_{CO})^2/P_{CO2}$ constant

- If CO is lowered emissions are lowered
- If CO is increased carbon mass transfer is increased
- This opens for dynamic control of CO content

# Dynamic control of CO content

- If CO-content is varied during the heat treatment one could:
  - Boost with high CO in initial stage to increase carbon flux
  - Reduce CO in later stages where diffusion is dominant

- For a given carbon profile this could:
  - Reduce furnace time and/or
  - Reduce $CO_2$-emissions

# Influence of CO on internal oxidation

- Cp is proportional to $(P_{CO})^2/P_{CO2}$
- Higher $CO_2$ concentration increase oxidation potential

- Reduced CO for a given Cp should decrease $CO_2$ and thus also internal oxidation

- For instance, Daves and Cooksey (1966) reported doubled internal oxidation when increasing CO from 20% to 40%

# The idea behind the DynaSty project

- Through the use of dynamic CO-content and a digital twin
  - Reduce $CO_2$-emission
  - Optimize furnace recipes
  - Increase product quality through reduced scrap

# DynaSty

- Duration: 2021-10-01 - 2024-12-31
- Budget: 5,3 MSEK (Vinnova 2,65 MSEK)
- Project leader: Sven Haglund, Swerim

**Participants**

- Swerim AB
- RISE
- Sandvik Mining & Construction
- Bodycote Värmebehandling AB
- Volvo Lastvagnar AB
- Linde Gas
- Bulten

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# Digital twin

- Basic components: Fick’s second law, mass transfer equation and Collins evaluation of β

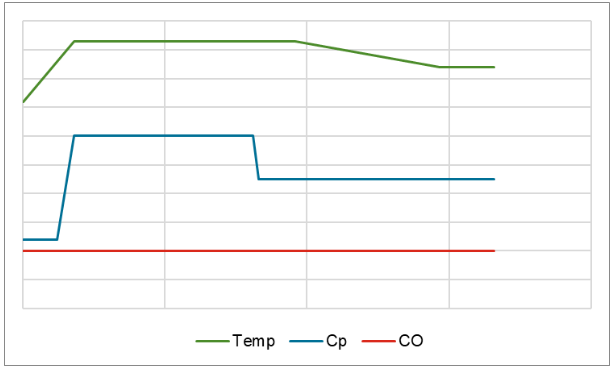
$$\frac{\partial C_c}{\partial t} = D_C \frac{\partial^2 C_C}{\partial x^2} \qquad D = D_o \exp(-Q/RT) \qquad J = \beta(C_p - C_S) \qquad \beta = \frac{6.31\cdot 10^5 \cdot \exp\left(\frac{-22350}{T}\right)\cdot \frac{P_{H_2O}}{\sqrt{P_{H_2}}}}{1+5.6\cdot 10^6 \cdot \exp\left(\frac{-12900}{T}\right)\cdot \frac{P_{H_2O}}{\sqrt{P_{H_2}}}}$$

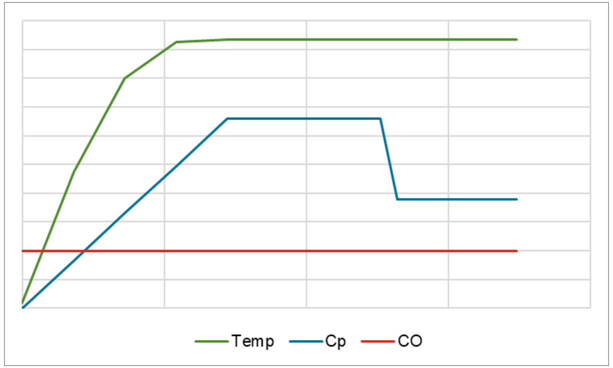
- Input data: Furnace program, T, Cp, CO, either nominal or measured
- Output data: carbon profile, estimate of $CO_2$-emission
- Model tuned to experiments with different CO contents
- Model can be used with an optimizer to optimize recipes with respect to desired outcome (i.e. low $CO_2$, fast process, …)

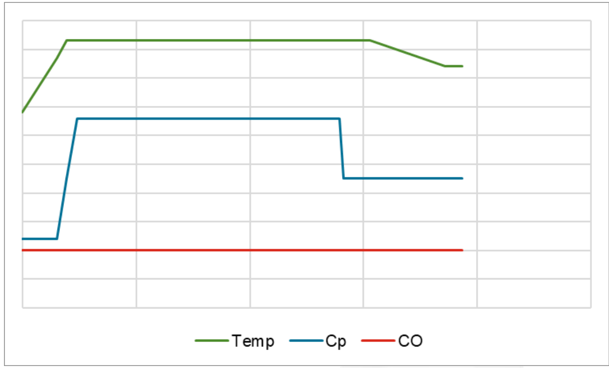
# Optimization

- Three case hardening cycles at Sandvik and Bodycote
- Boost-diffusion, 0.7, 0.9 and 1.3 mm case depth
- Fixed total furnace time but lowest possible $CO_2$-emission

# Original recipes







- 0.7 mm 0.9 mm 1.3 mm

- Parameters to optimize: CO-content, Cp, time for boost and diffusion

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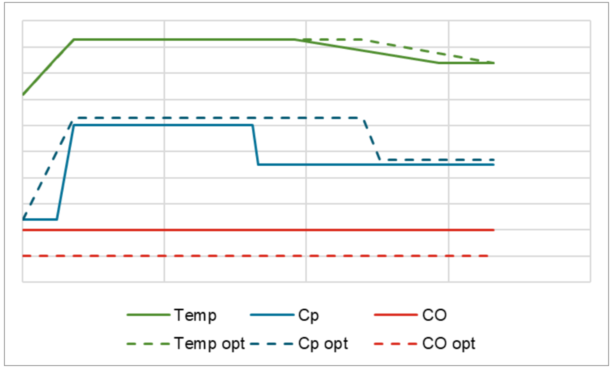
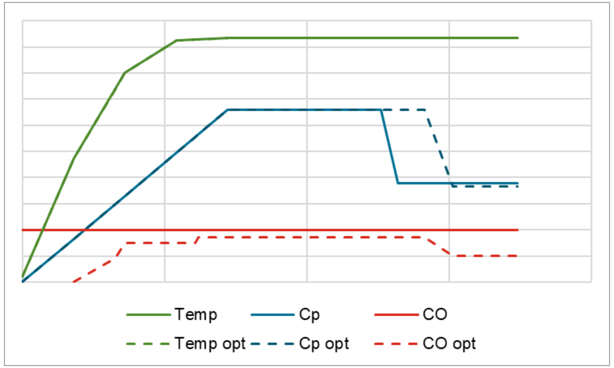
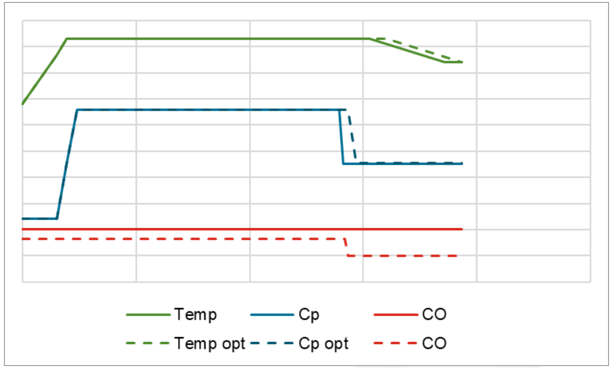
# Optimized cases







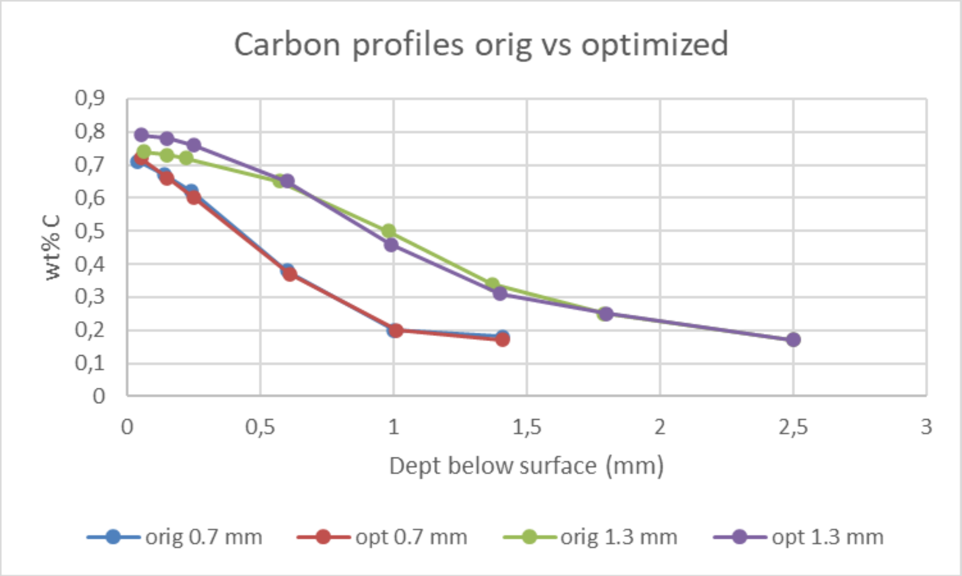
| | | |
|---|---|---|
| Case depth: 0.7 mm | 0.9 mm | 1.3 mm |
| $CO_2$ reduction: 50% | 33% | 26% |

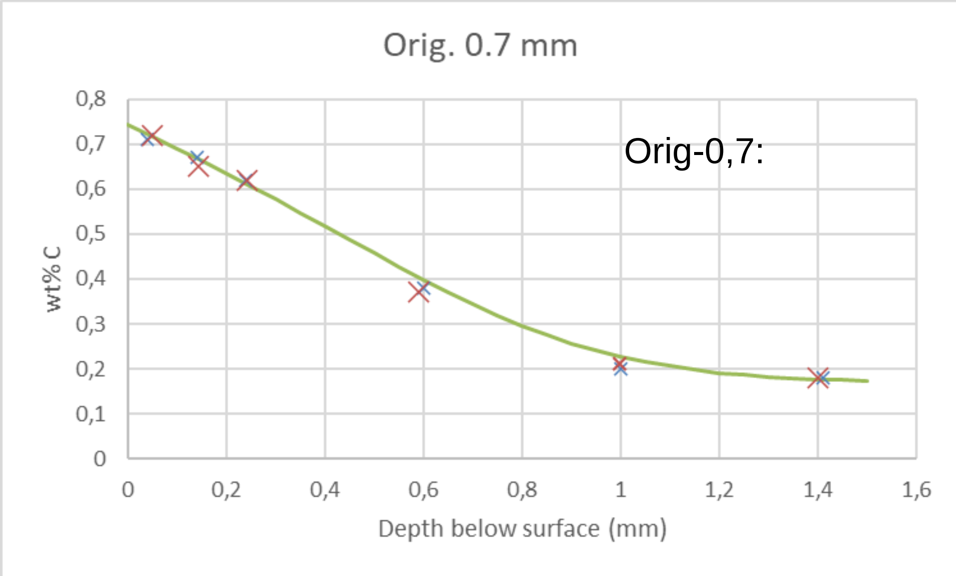
Optimizer gives overall low CO-contents

Prefer high Cp

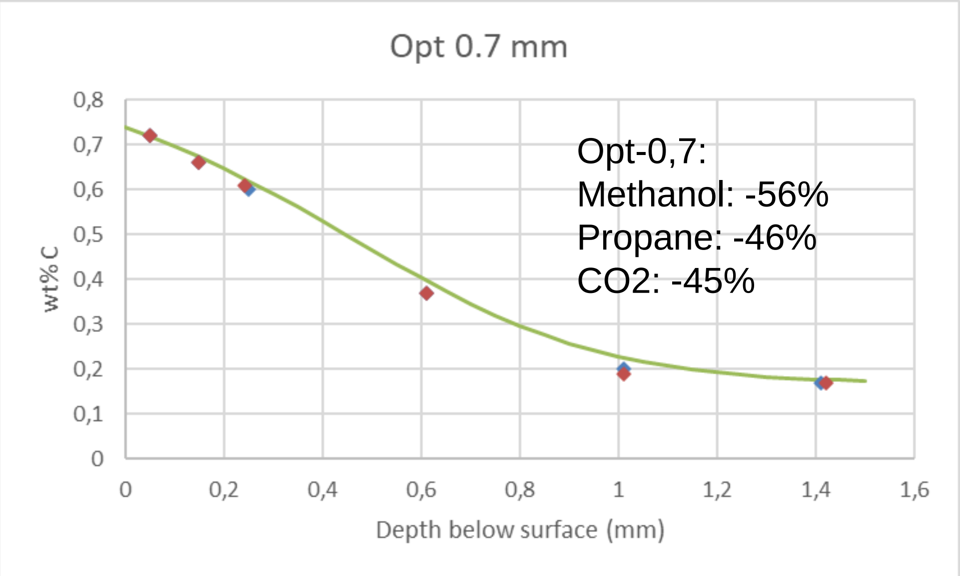
# Experimental results of furnace trials

- Almost identical carbon profiles in original and optimized recipes




Orig. 0.7 mm

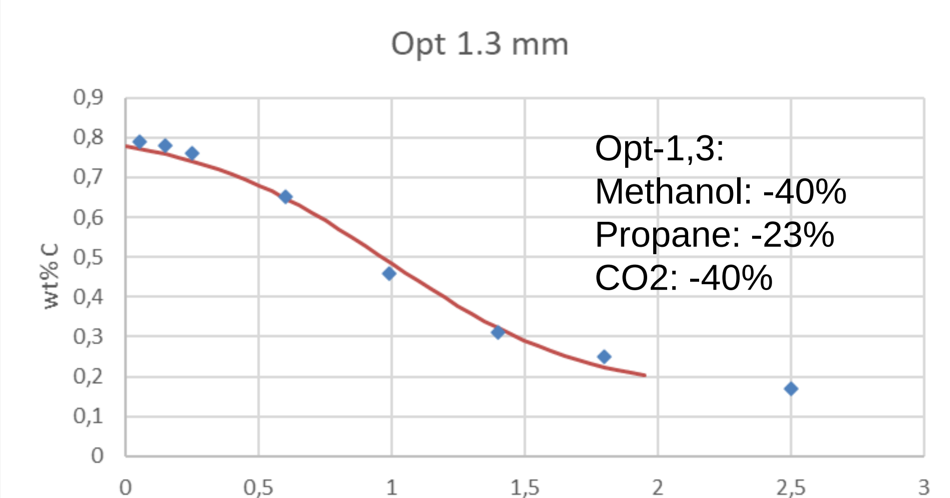
Orig-0,7:


Opt 0.7 mm

Opt-0,7:
Methanol: -56%
Propane: -46%
CO2: -45%


Orig 1.3 mm

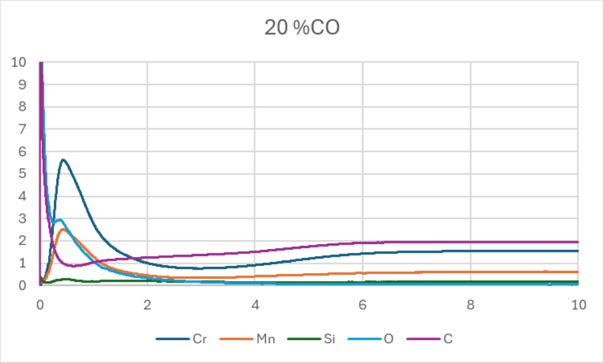
Orig-1,3:

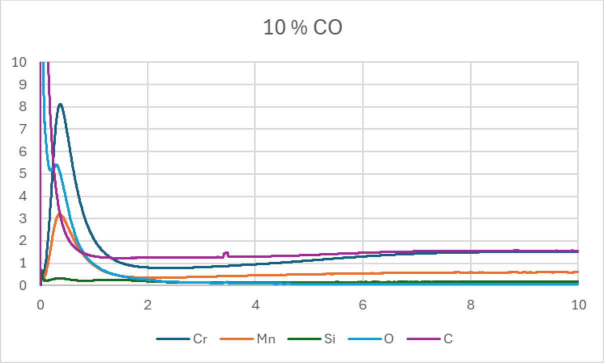

Opt 1.3 mm

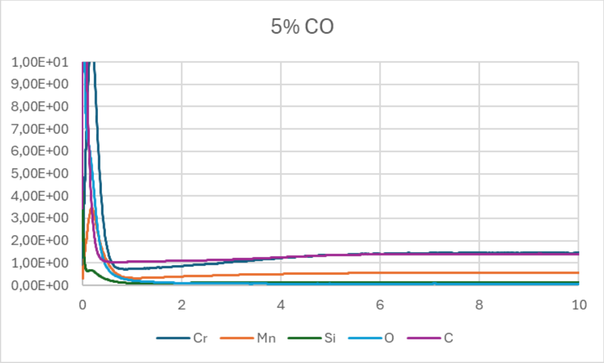
Opt-1,3:
Methanol: -40%
Propane: -23%
CO2: -40%

# Internal oxidation

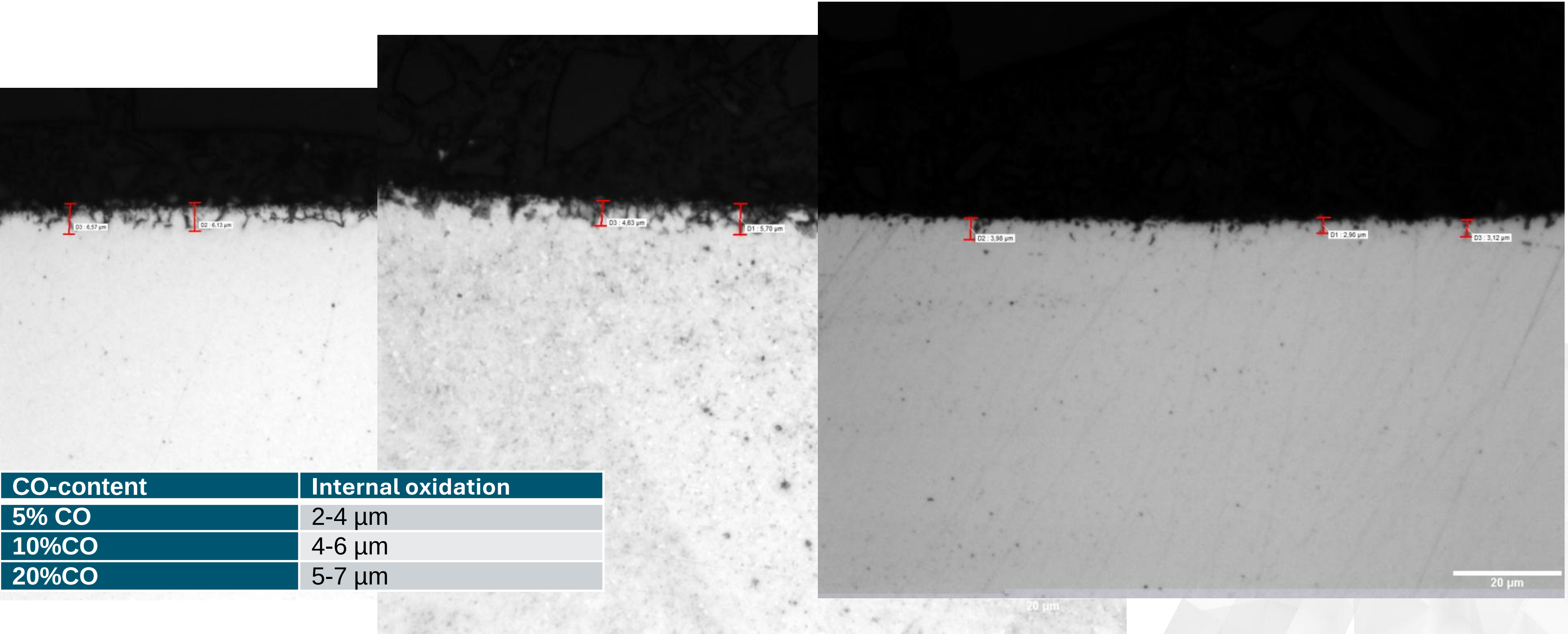
- Neutral hardening experiments at Bodycote
- 20, 10, 5% CO
- 100Cr6 specimen
- GD-OES







# Internal oxidation 20-10-5% CO



| CO-content | Internal oxidation |
|---|---|
| 5% CO | 2-4 µm |
| 10%CO | 4-6 µm |
| 20%CO | 5-7 µm |

- Could $CO_2$-emissions be reduced by 75% in neutral hardening?

# Industrial full-scale test at Bulten

- Successful full-scale test was performed at Bulten in Hallstahammar 2024
- Four tests, CO=10%, 15% and Cp=0.25%, 0.53%
- A couple of tons of bolts were heat treated in each test

- All products passed quality tests. Hardness OK and microstructure OK.
- CO2 emissions reduced up to 50%
- Bulten also sees a potential for a more stable process and estimates that this could be implemented without increasing costs

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# Conclusions

- $CO_2$ emissions can be reduced with up to ~50% by reducing the CO-content in the furnace
- Internal oxidation is reduced with lower CO-content
- Reduced CO-content requires less methanol input →lower costs
- Reducing CO from 20% to 10% did not result in major furnace instabilities

- As a result of the project:
- Bodycote has already lowered CO-content to 10% in one furnace
- Bulten plans to reduce CO-content to 10% in Hallstahammar in 2025

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