SHTE Heat treatment conference 2017

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Basics of (Gas-) Nitrocarburizing

and how to steer and control the process

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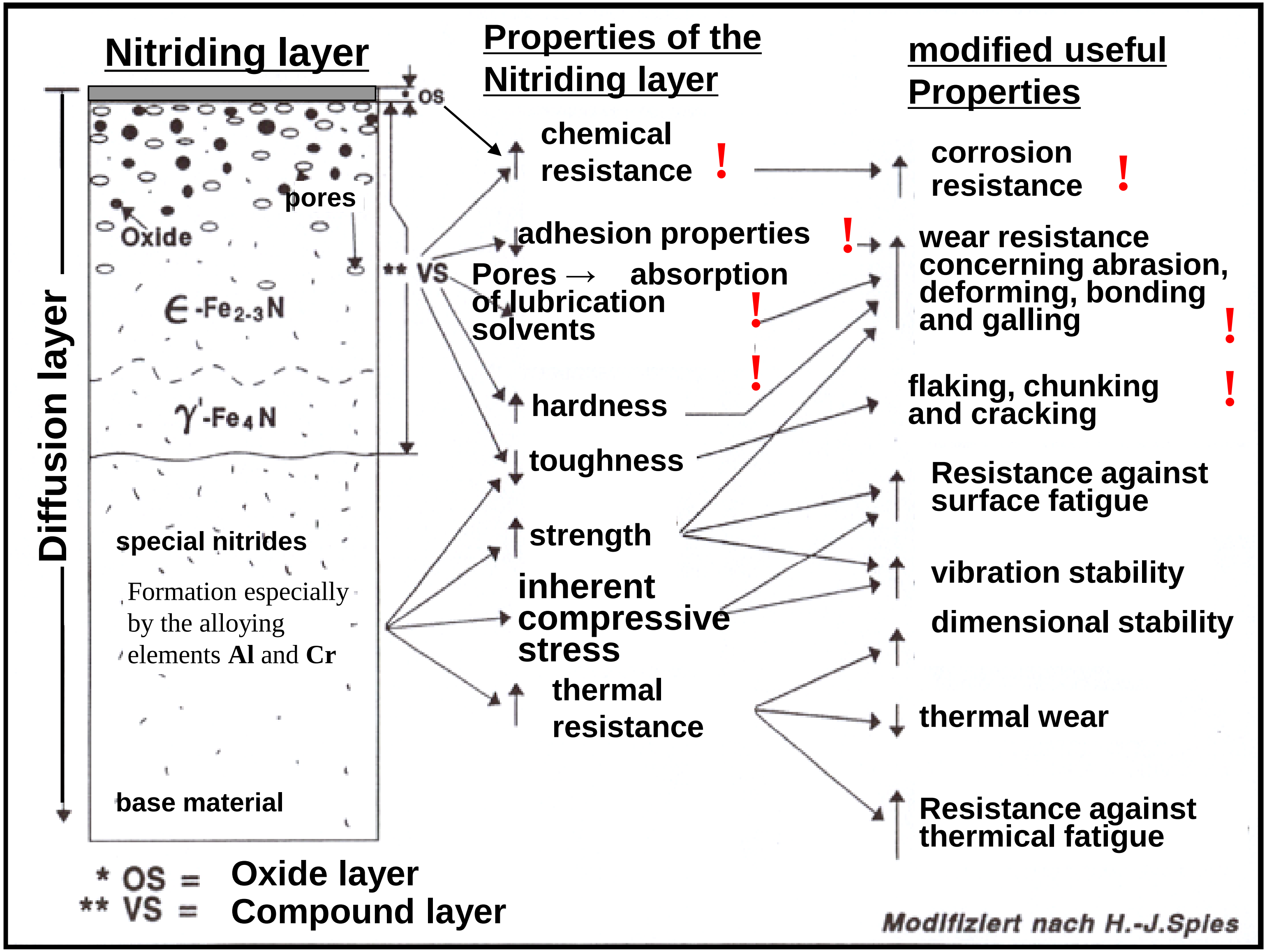
Content

- Basics of (gas-) nitriding / (gas-) nitrocarburizing
- Standard and controlled processes
- Oxinitriding / Oxinitrocarburizing processes
- Postoxidation processes
- Processes with additional hydrocarbons
- Furnace technology

Basics of (gas-) nitriding / (gas-) nitrocarburizing

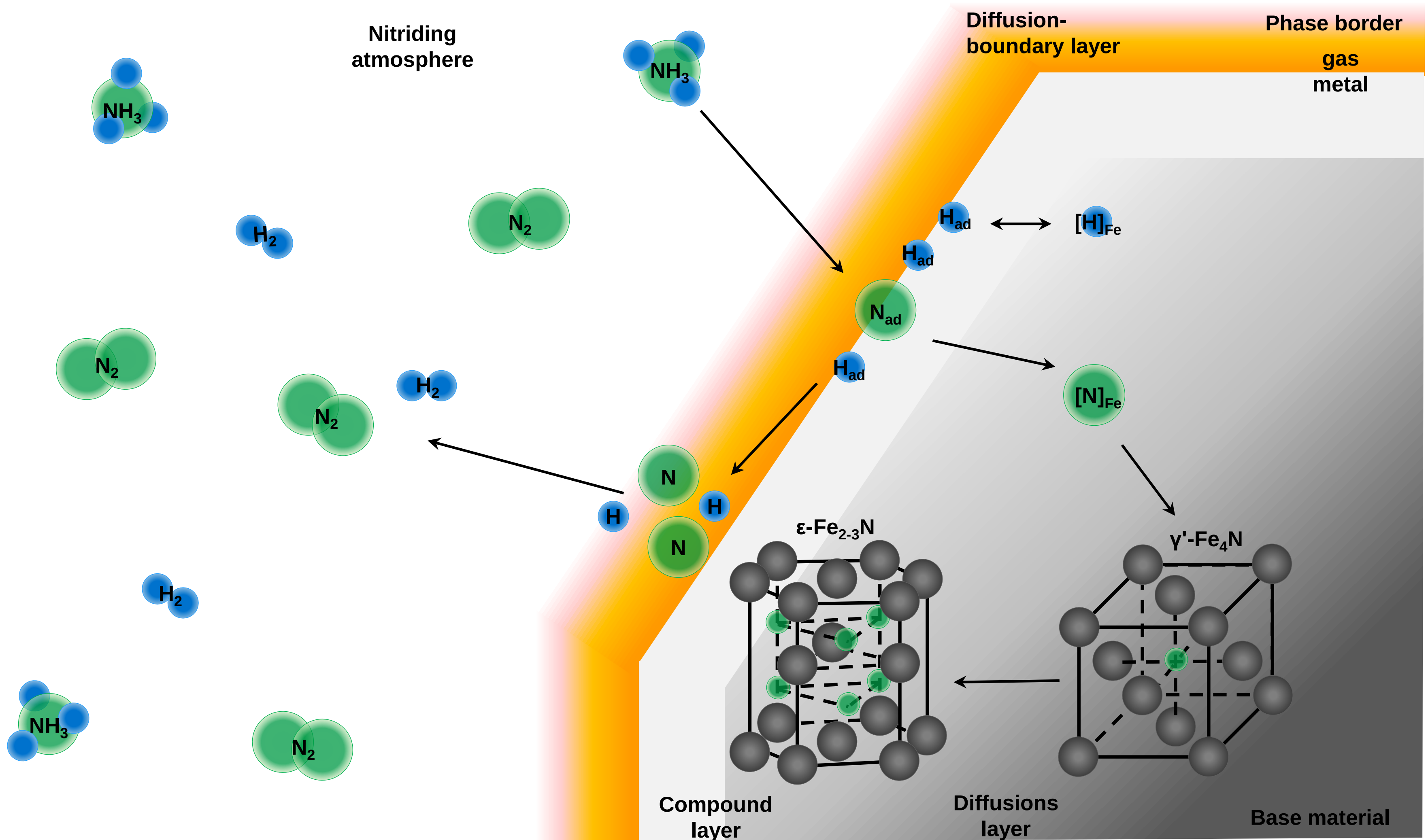
Basics of (gas-) nitriding / (gas-) nitrocarburizing



Reaction Agents for gas nitriding and gas nitrocarburizing

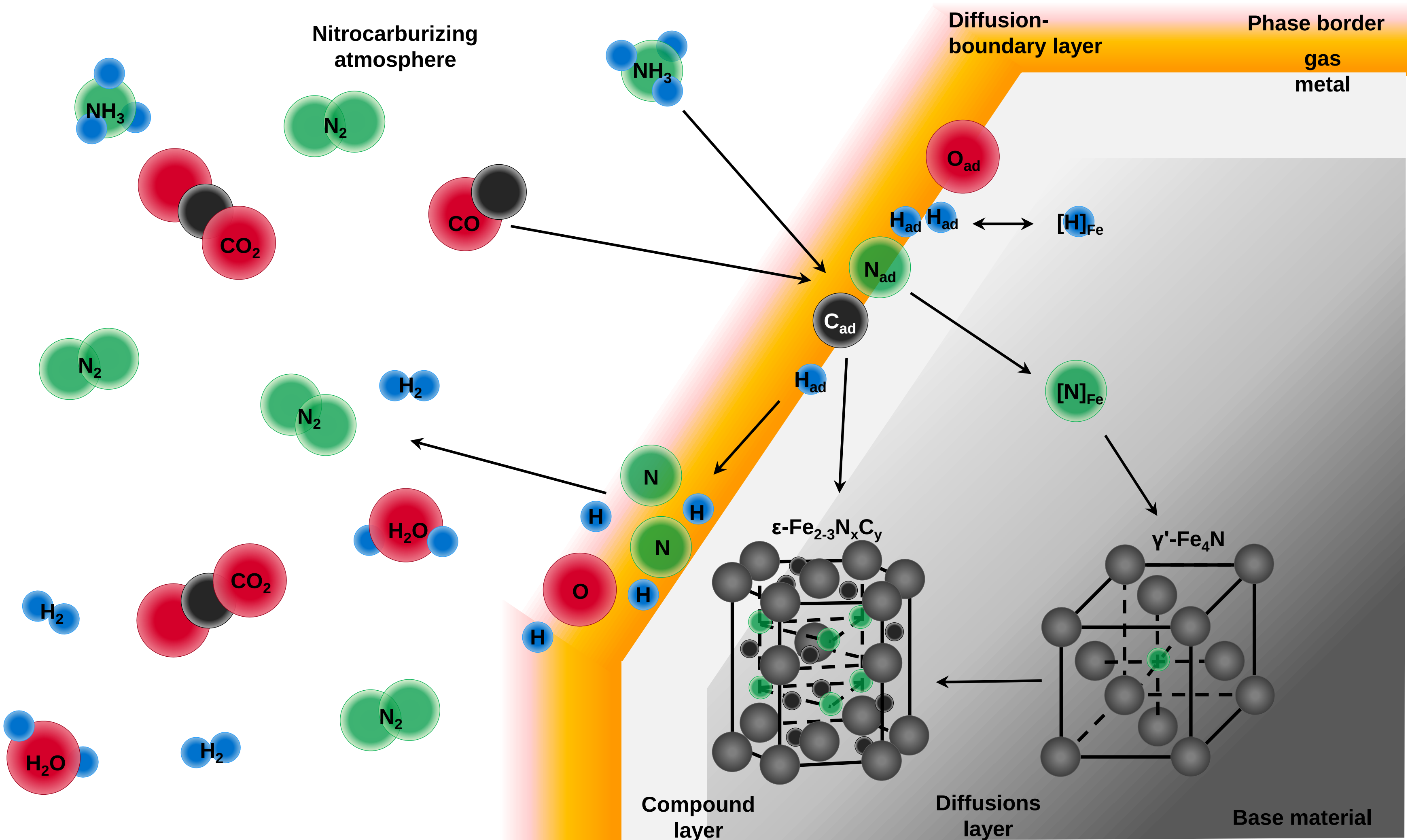
Diffusion Element	Process	Reaction Agents
N	Nitriding	NH_3, NH_3 & N_2, NH_3 & H_2, NH_3 & N_2 & H_2
N, C,	Nitrocarburizing	NH_3 & Endothermic gas, NH_3 & CO_2 & (N_2), NH_3 & C_mH_n, & (N_2)

Reactions during (gas-) nitriding



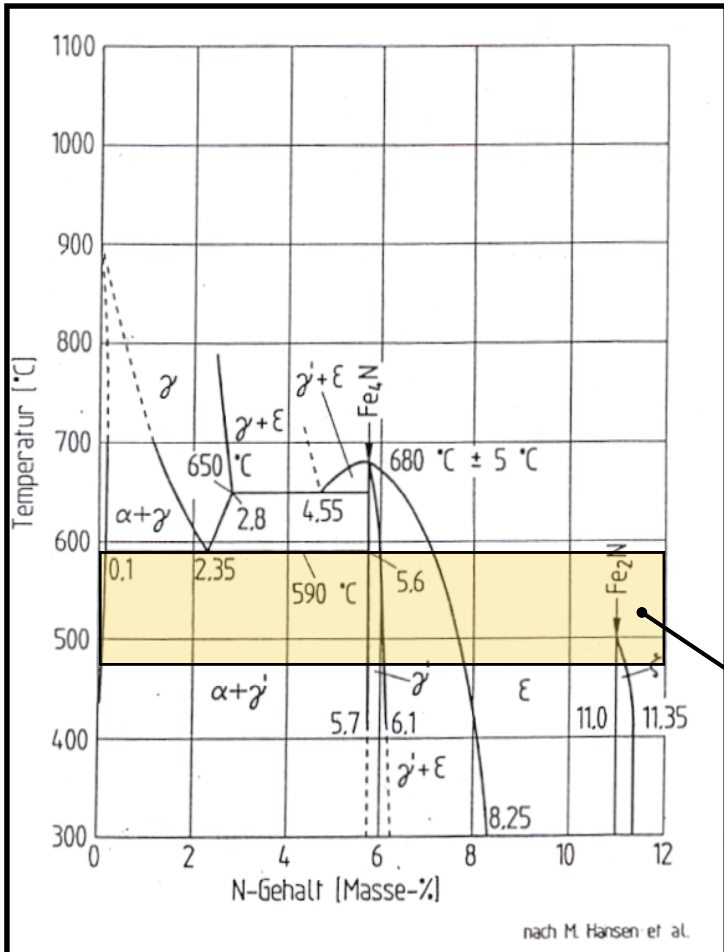
R. Kaden, Ipsen

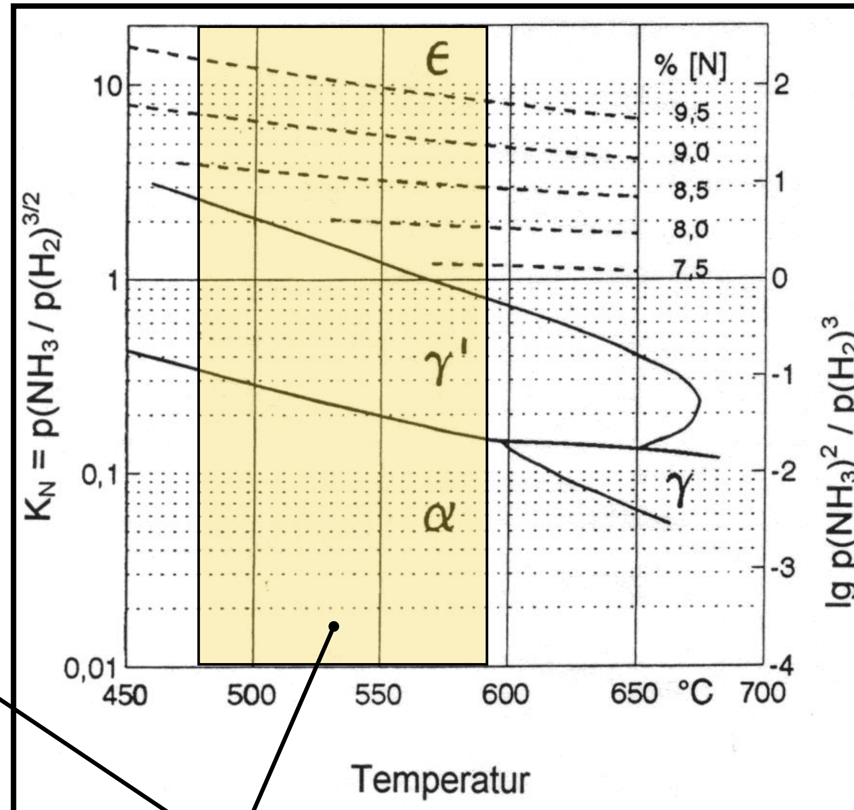
Reactions during (gas-) nitrocarburizing



R. Kaden, Ipsen

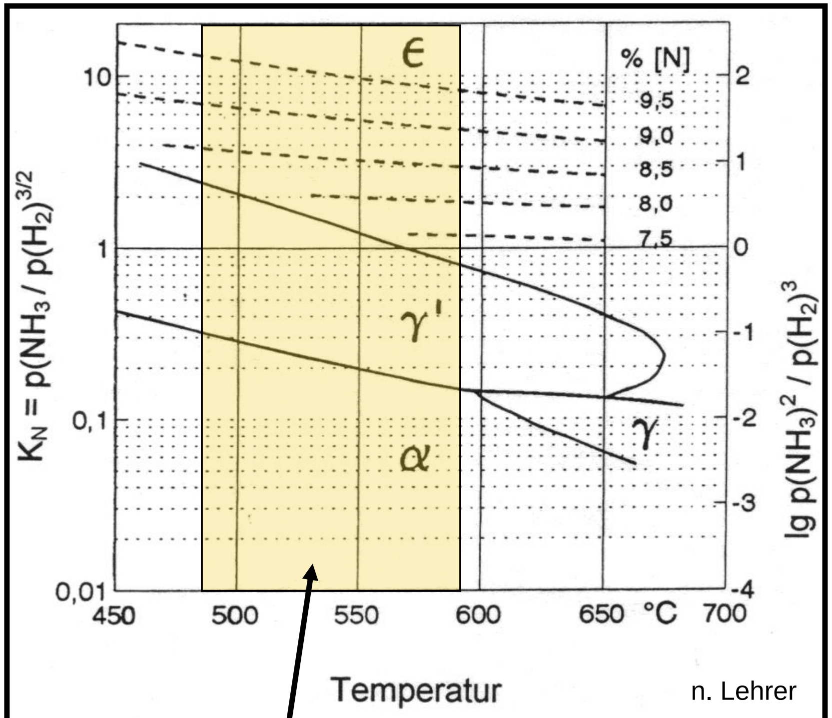
Background of Nitrocarburizing

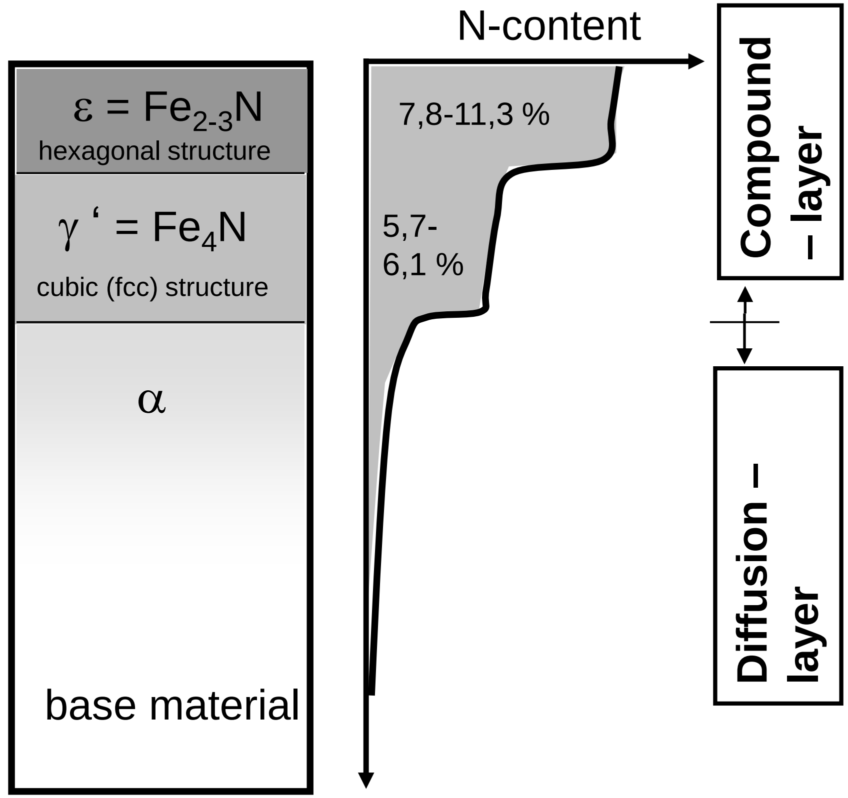




Temperature range normally used for Nitriding or Nitrocarburizing processes

Nitriding potential and Nitriding layer structure

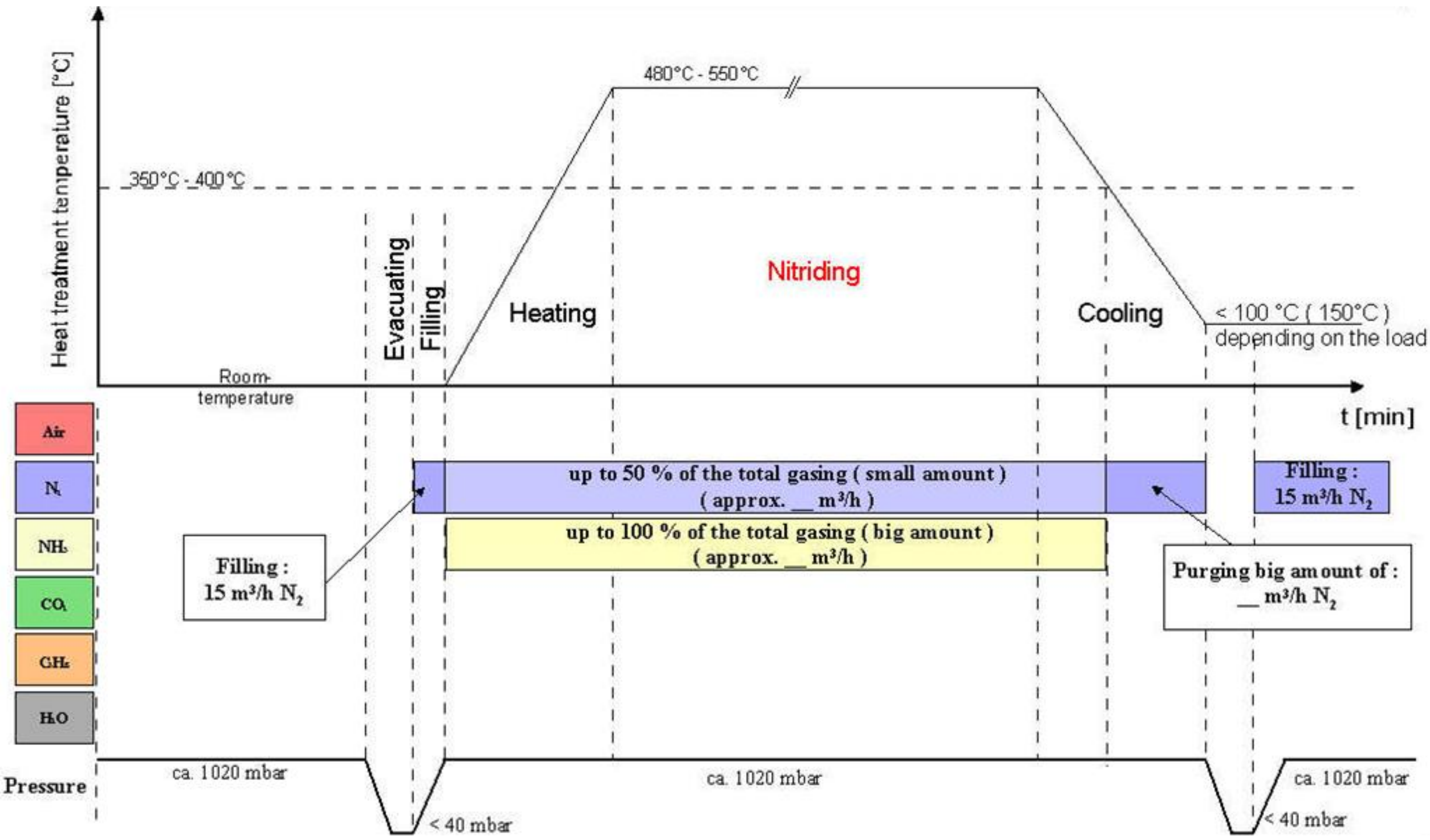




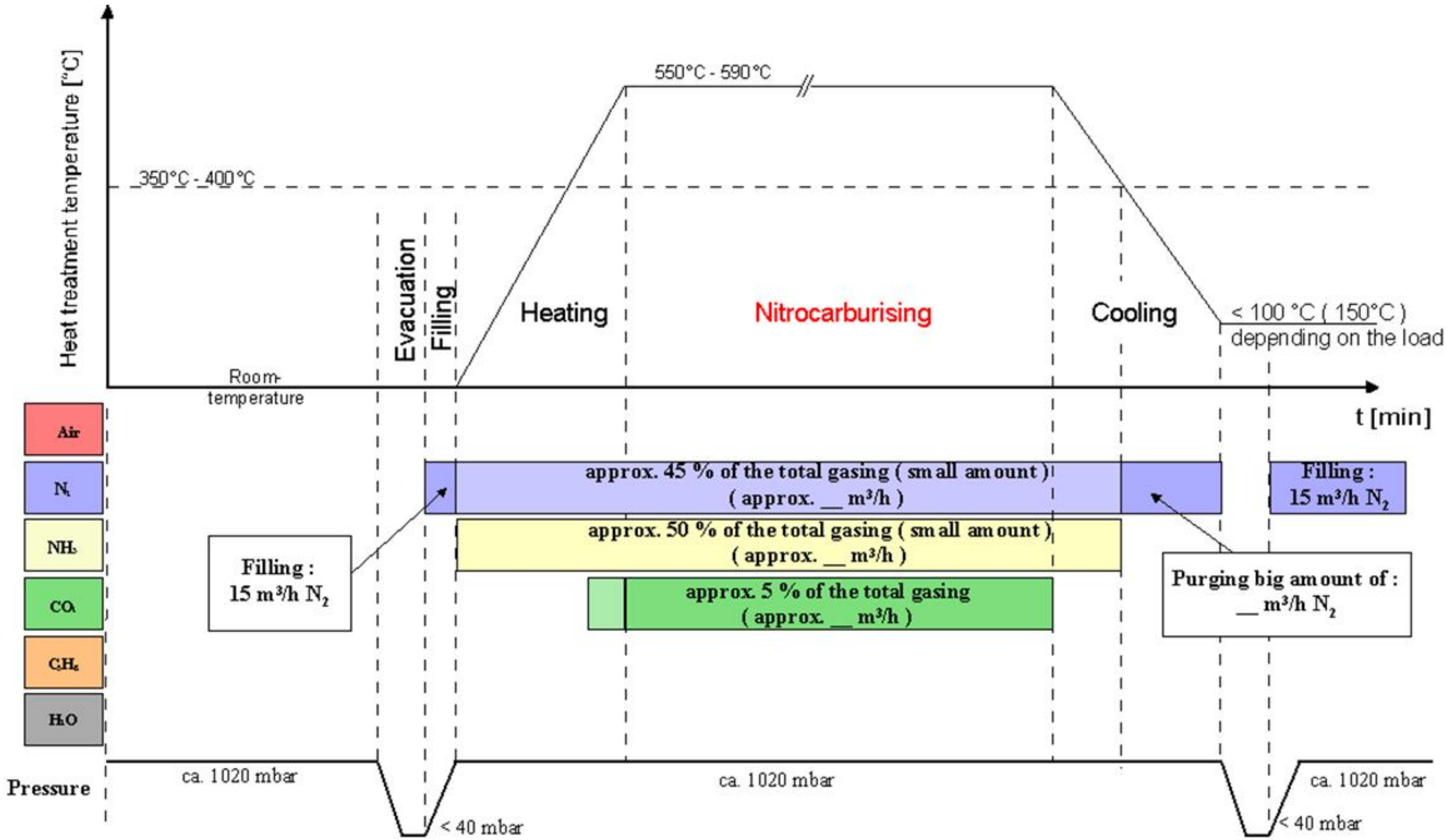
Normally used range of temperature for the gas nitriding or nitrocarburizing (480° C – 590° C)

Standard processes

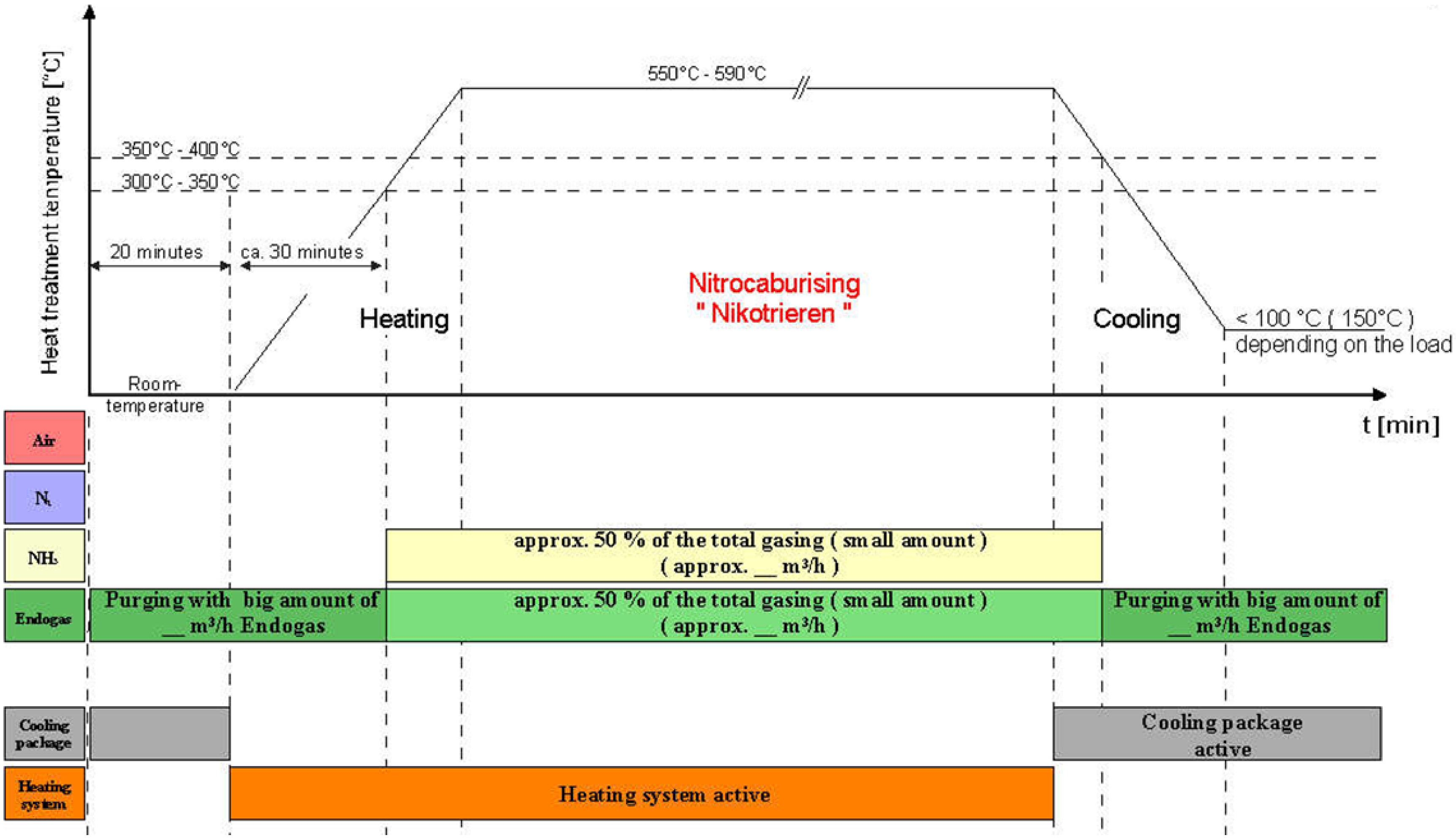
Standard process for nitriding



Standard process for nitrocarburizing



Standard process for nitrocarburizing



controlled processes

Benefits of K_N controlled nitrocarburizing

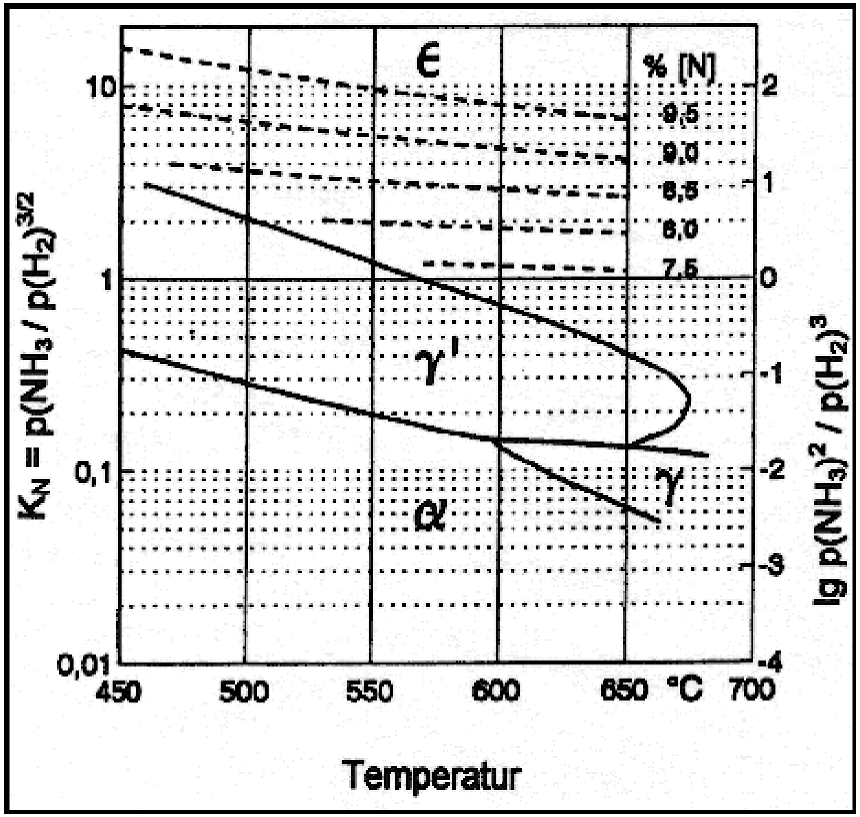
Goals:

- Controlled layer structure generation
- Reproducible layer structure and thickness
- Minimal process duration

Requirements:

- Measurement device for the continuous monitoring of an atmospheric component (e.g. H_2)
- Continuous monitoring of the input gases
- Atmosphere and Nitriding potential - Algorithm
- Cracked ammonia or pure hydrogen for the reduction of the nitriding potential
- Automatic gas flow controller

Theoretic Background of the Nitriding Potential



Lehrer Diagram for pure Iron

$$NH_3 \rightarrow [N] + \frac{3}{2} H_2$$

nitriding reaction

$$NH_3 \rightarrow \frac{1}{2} N_2 + \frac{3}{2} H_2$$

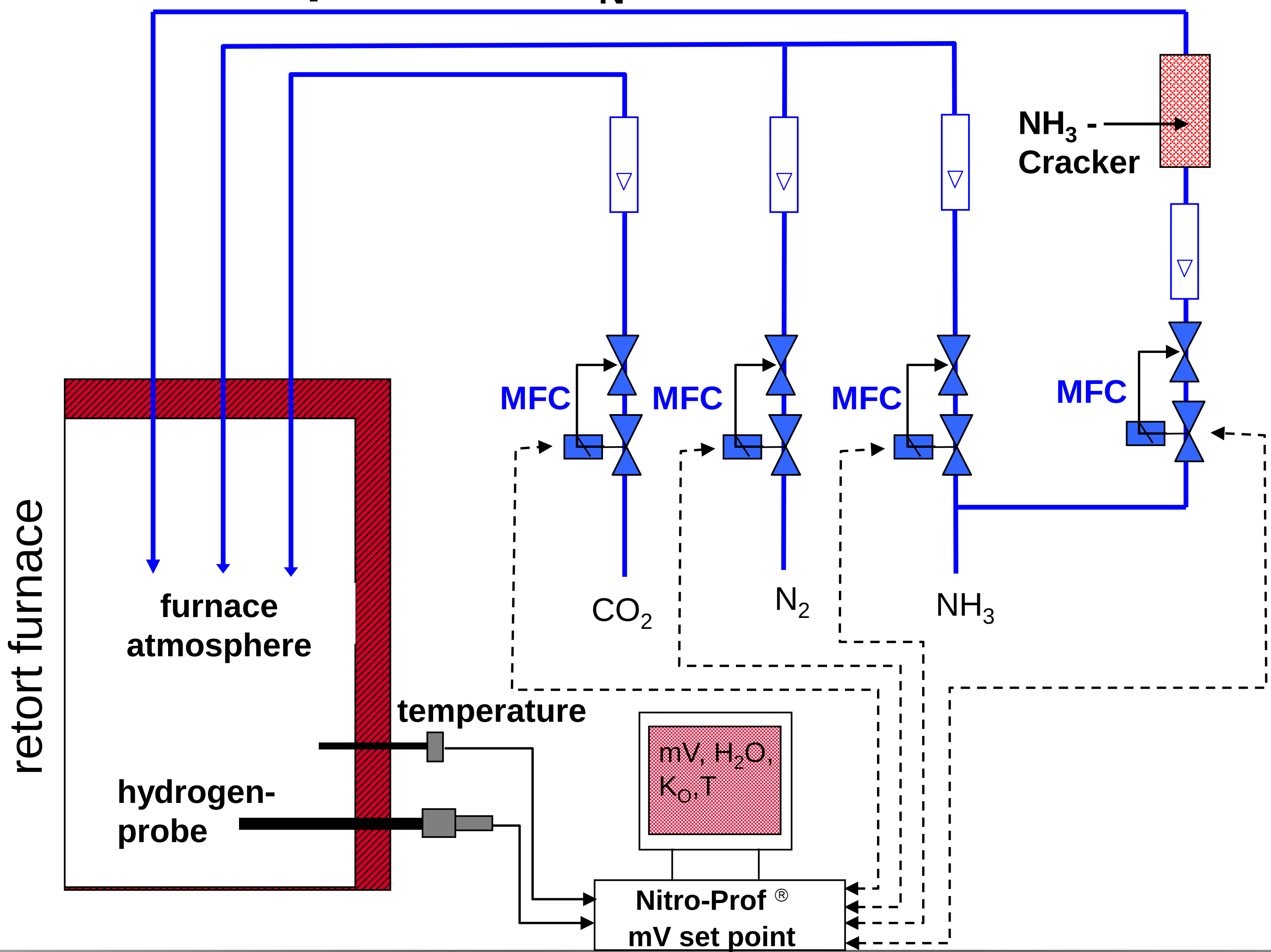
$$K_N = \frac{p(NH_3)}{p(H_2)^{3/2}}$$

nitriding potential

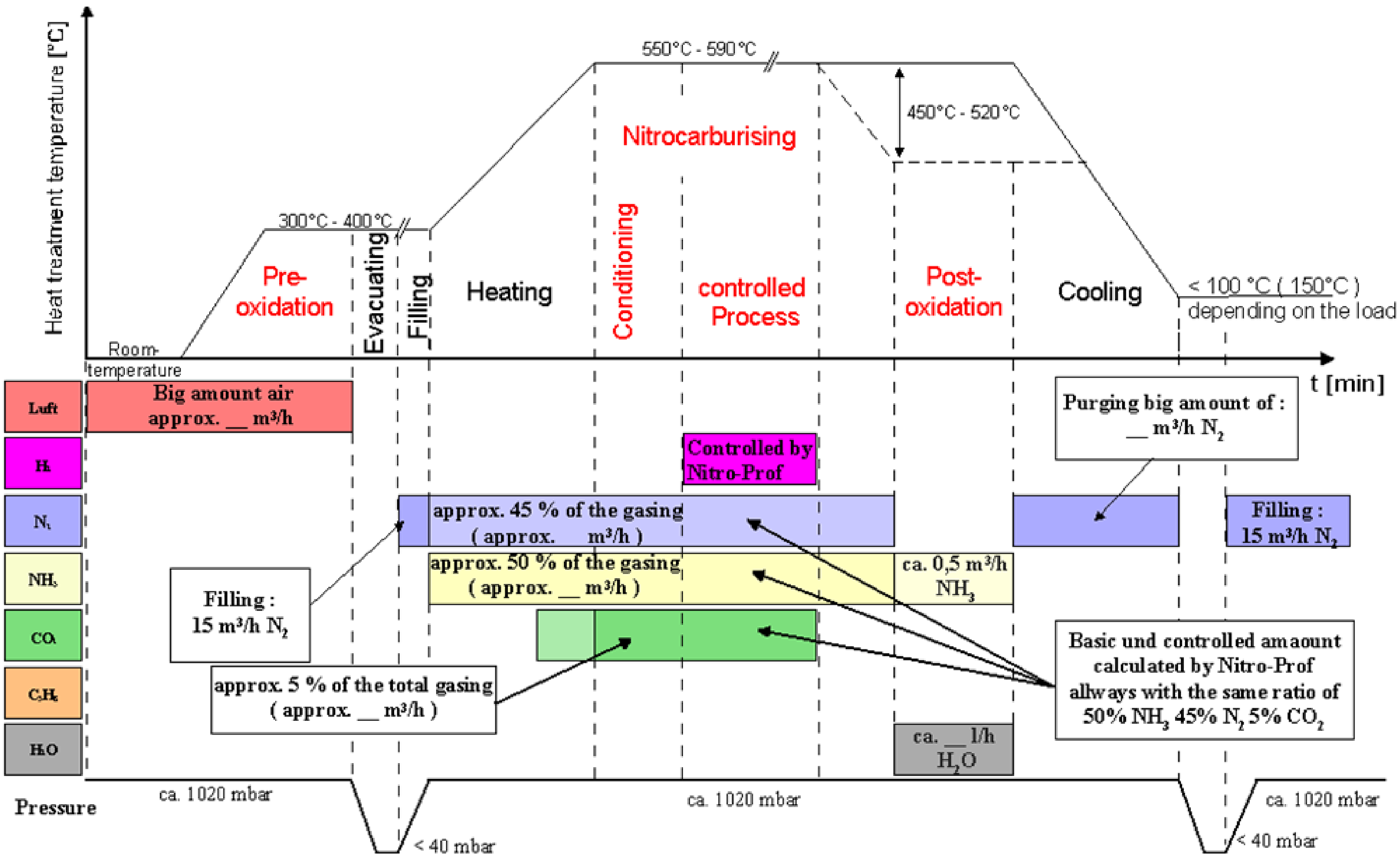
Hydrogen sensors

For documentation and control of
nitriding- and nitrocarburizing processes

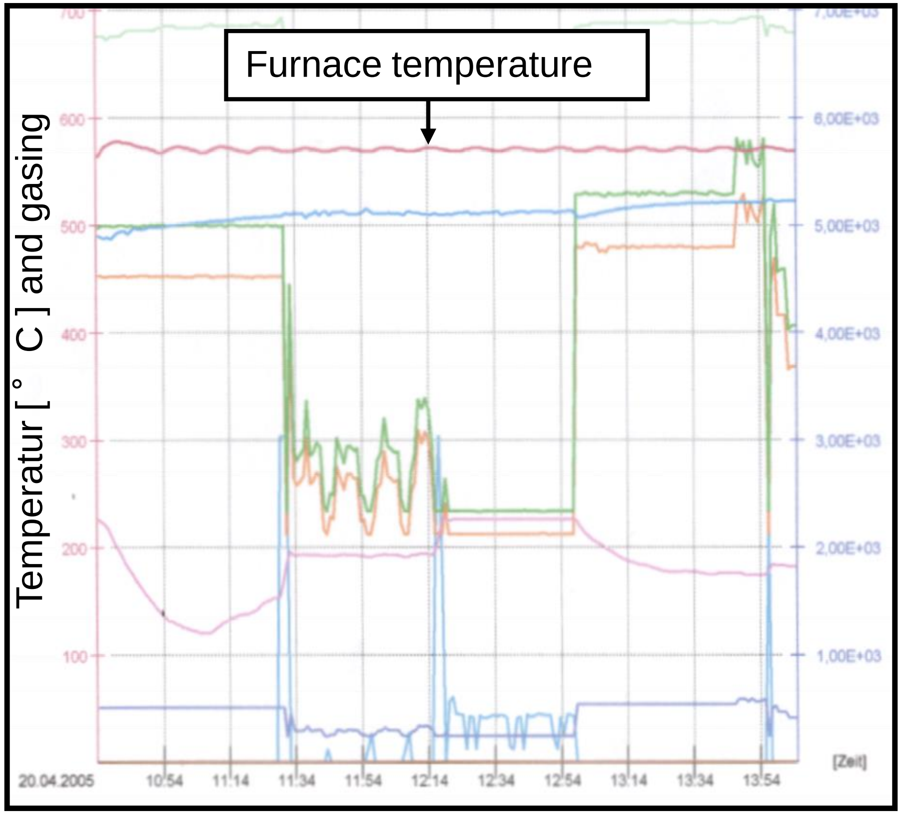
CN panel for K_N controlled nitrocarburizing

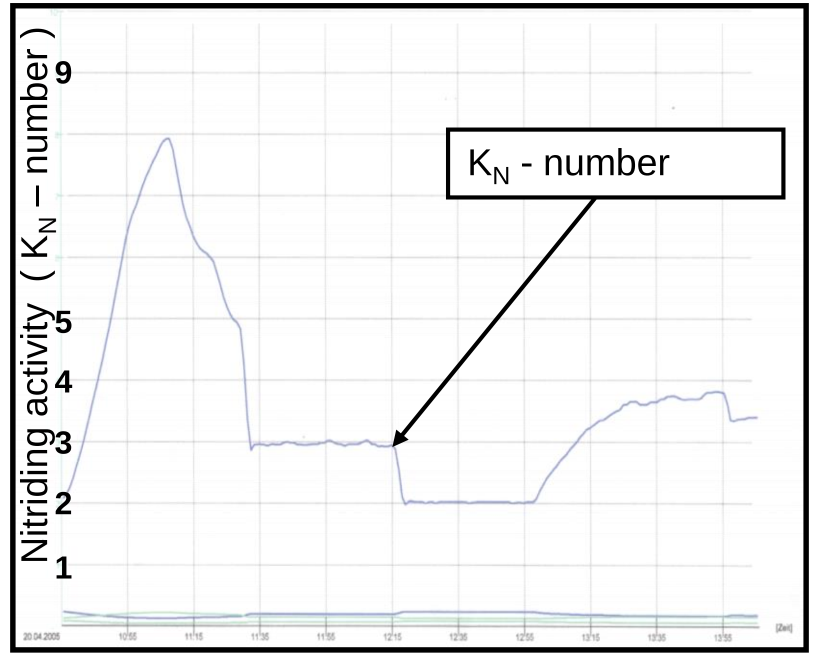


process for K_N controlled nitrocarburizing



Process printout K_N controlled nitrocarburizing





Carbondioxid (CO_2)

Hydrogen (H_2)

Nitrogen (N_2)

Ammonia (NH_3)

Hydrogen (H_2) -Sensor

Oxinitriding / Oxinitrocarburizing processes

Influences on the reaction kinetics

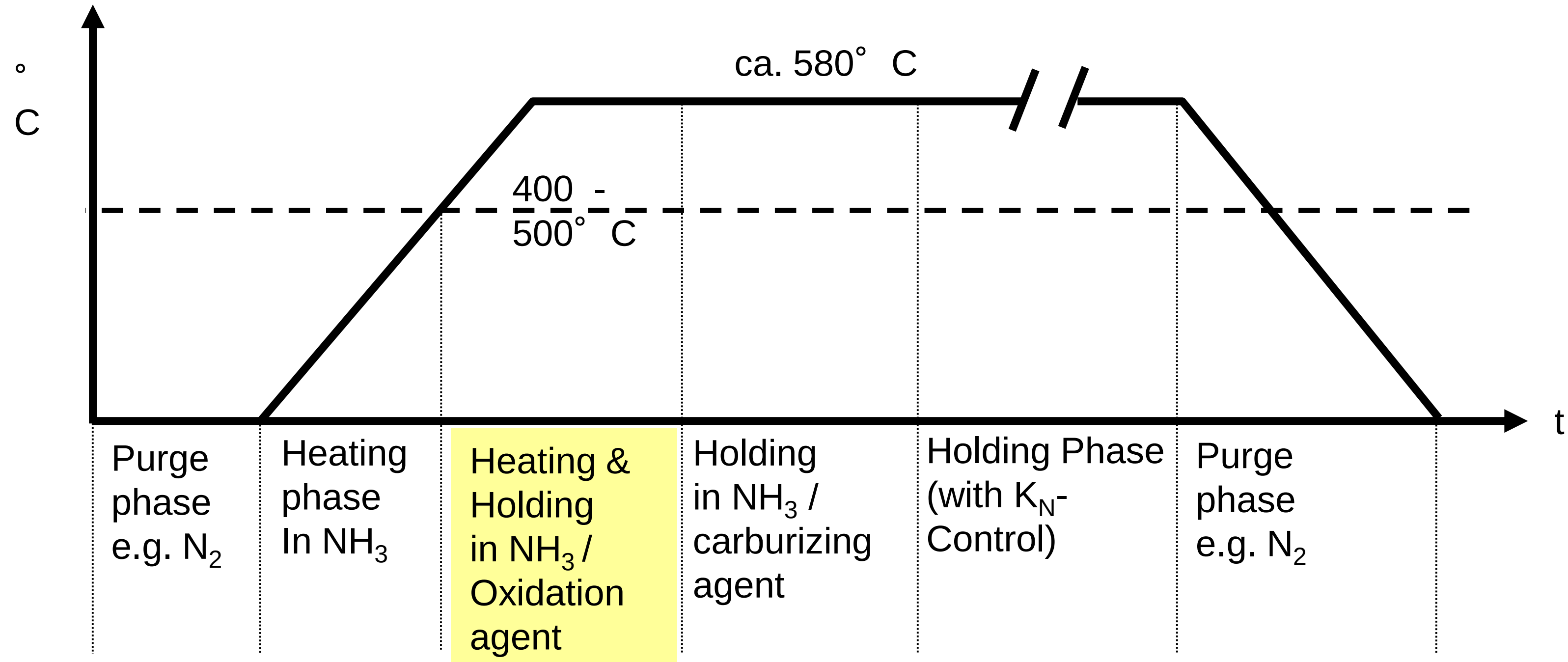
Inhibition, due to:

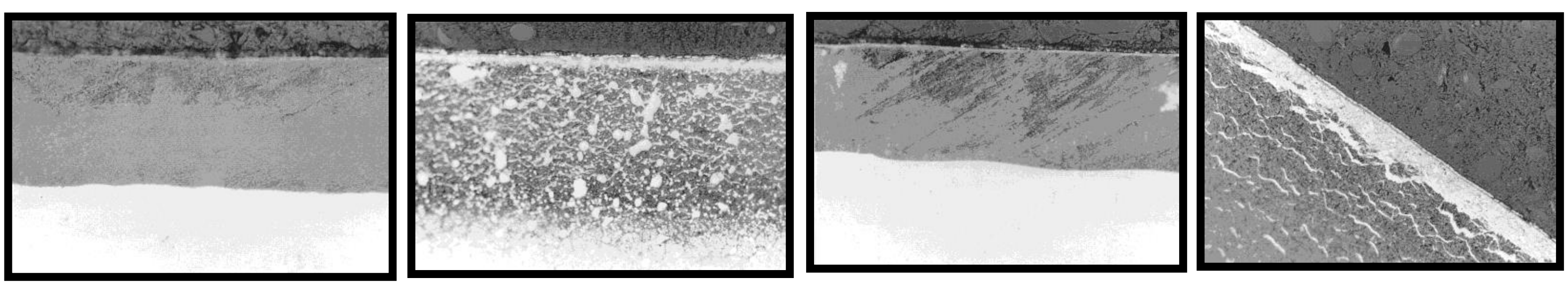
- Fabrication Residues (i.e., cooling oil, grease)
- Detergent Residues
- Surface strengthening
- Surface smoothness
- Passive oxide layer (chromium oxide)

Process sequence for activation:

- Perfect Cleaning and Pre-oxidation
- Oxinitriding or Oxinitrocarburising

Reaction kinetics improvement - Oxinitrocarburizing



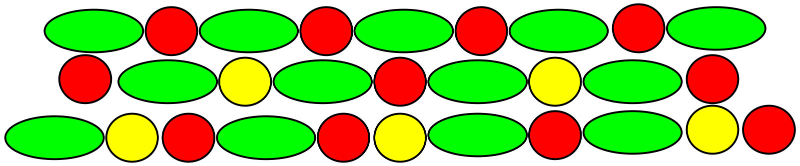


X5CrNiMo17-22-2 X40CrMoV5-1

Modell for the conversion of passive layers

NH_3 → $[NH_3 + N + H]$

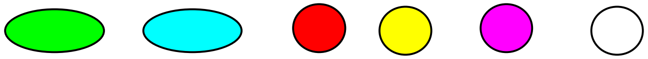
Phase 1



RT – 400° C →

Atmosphere Formation Phase

Explanation:

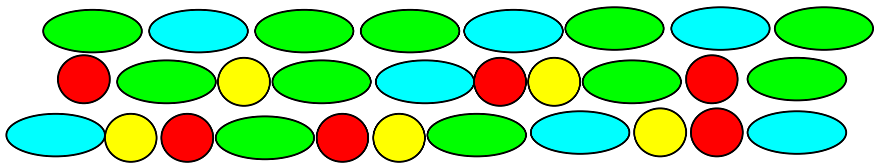


Cr_2O_3 Fe_3O_4 Fe Cr CrN Fe_xN

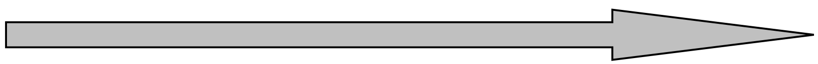
Modell for the conversion of passive layers

NH_3 + Oxidation medium → [NH_3 + N + H + O]

Phase 2

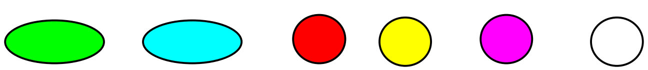


400 – 580° C



Oxinitriding Phase

Explanation:

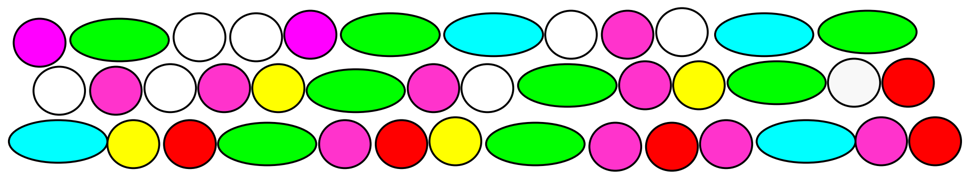


Cr_2O_3 Fe_3O_4 Fe Cr CrN Fe_xN

Modell for the conversion of passive layers

NH_3 + Carburising medium [NH_3 + N + H + C]

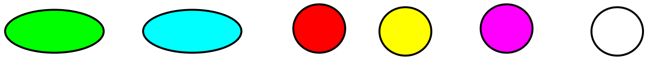
Phase 3



580° C

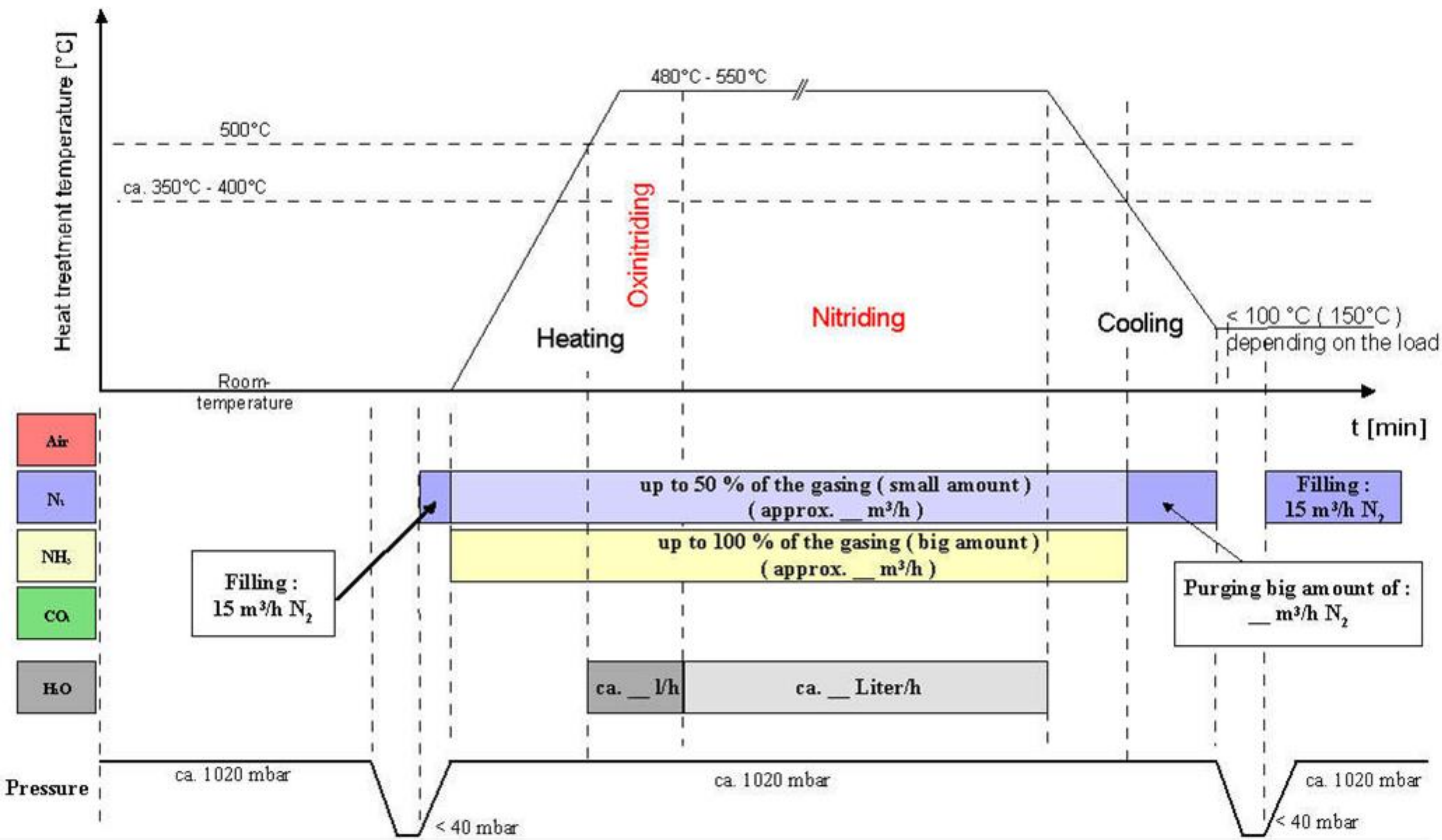
Nitrocarburising / Reduction Phase

Explanation:

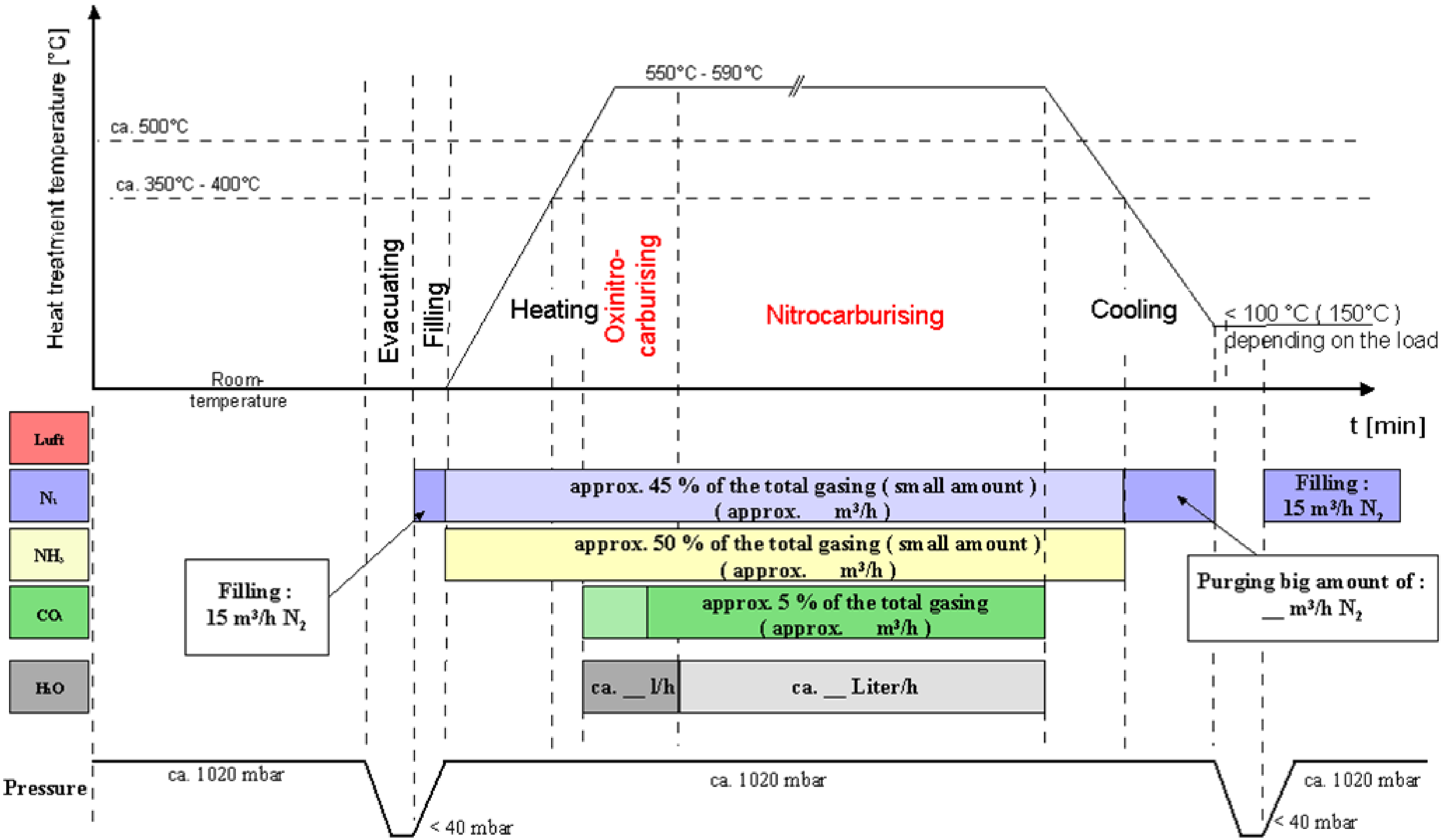


Cr_2O_3 Fe_3O_4 Fe Cr CrN Fe_xN

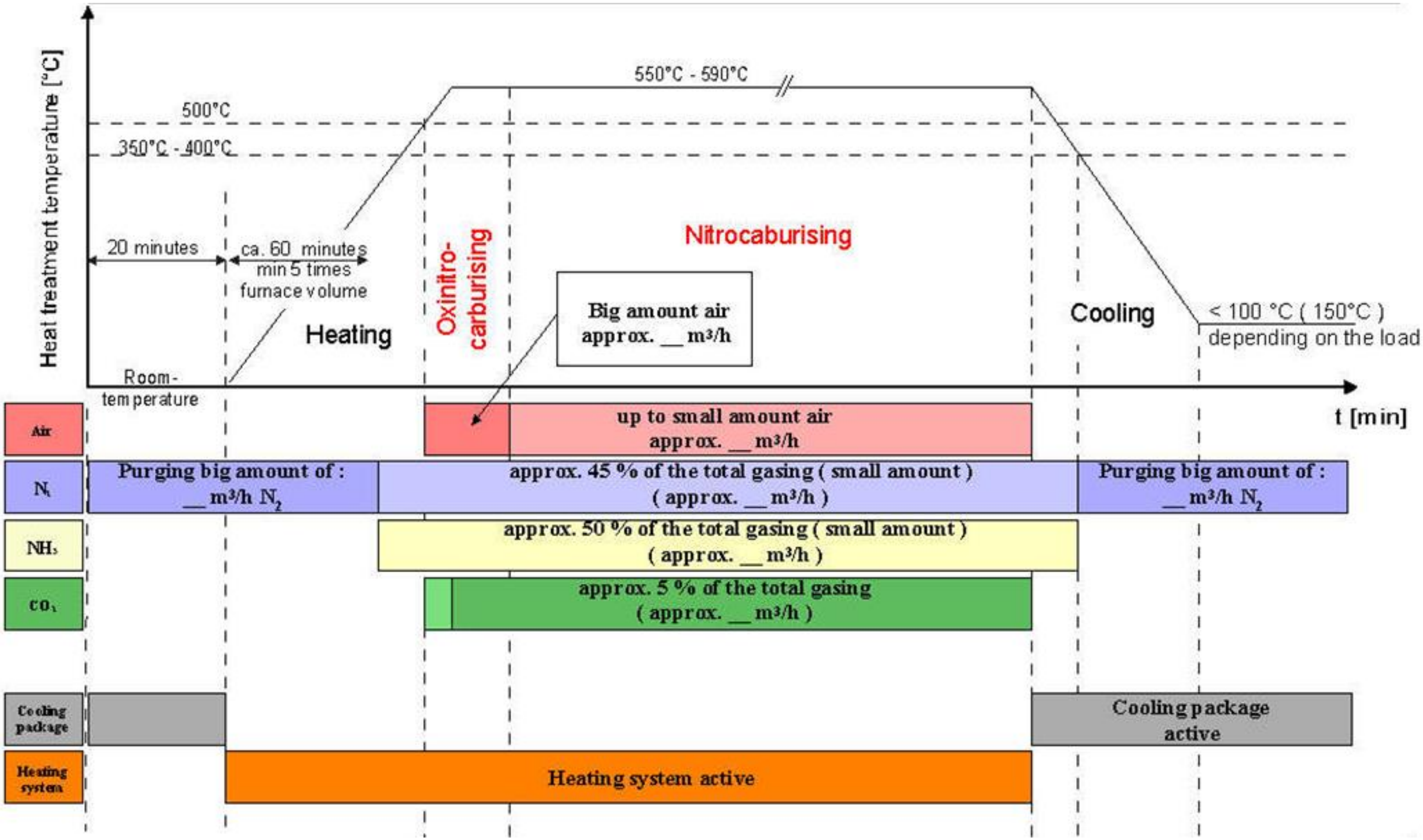
Process for oxinitriding



Process for oxinitrocarburizing



Process for oxinitrocarburizing



(gas-) nitrocarburizing and postoxidation

Benefits due to postoxidation

By running a postoxidation after a normal (gas-) nitriding- or nitrocarburizing process an iron oxide layer will be formed directly on top of the compound layer. This iron oxide layer has to consist of magnetite (Fe_3O_4) and should have a thickness of 1-3 µm.

Benefits of the magnetite layer:

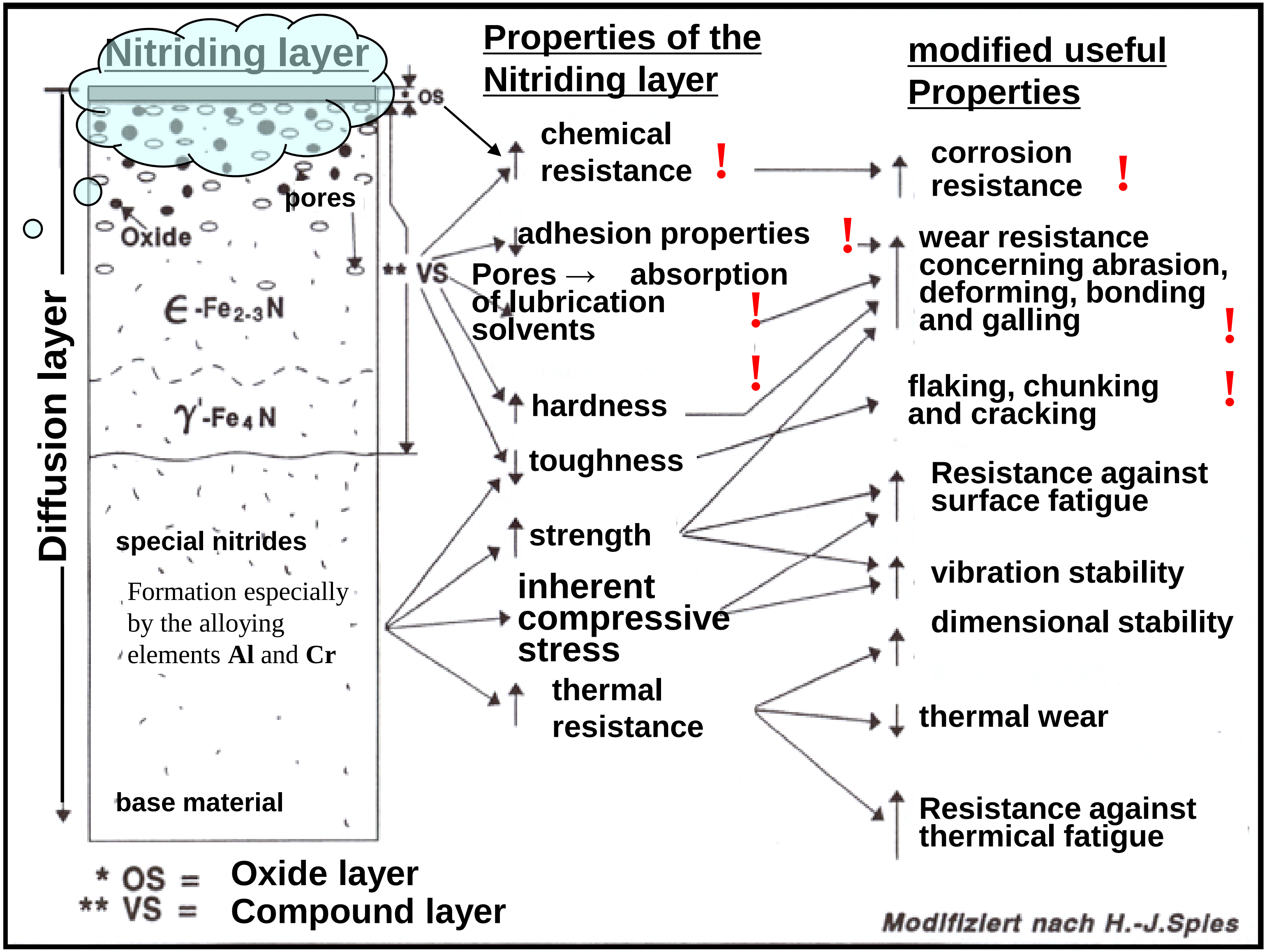
- corrosion resistance : Due chemical composition and the compact design of Fe_3O_4 – oxide layer no oxygen can diffuse into the material and therefore no further corrosion can take place.

- optical effect: By running a postoxidation process (Fe_3O_4 – formation) the surface of the part will become a decorative black color. In some cases / for some customers this black color is more appreciated than the grey color you will get after nitriding or nitrocarburizing.

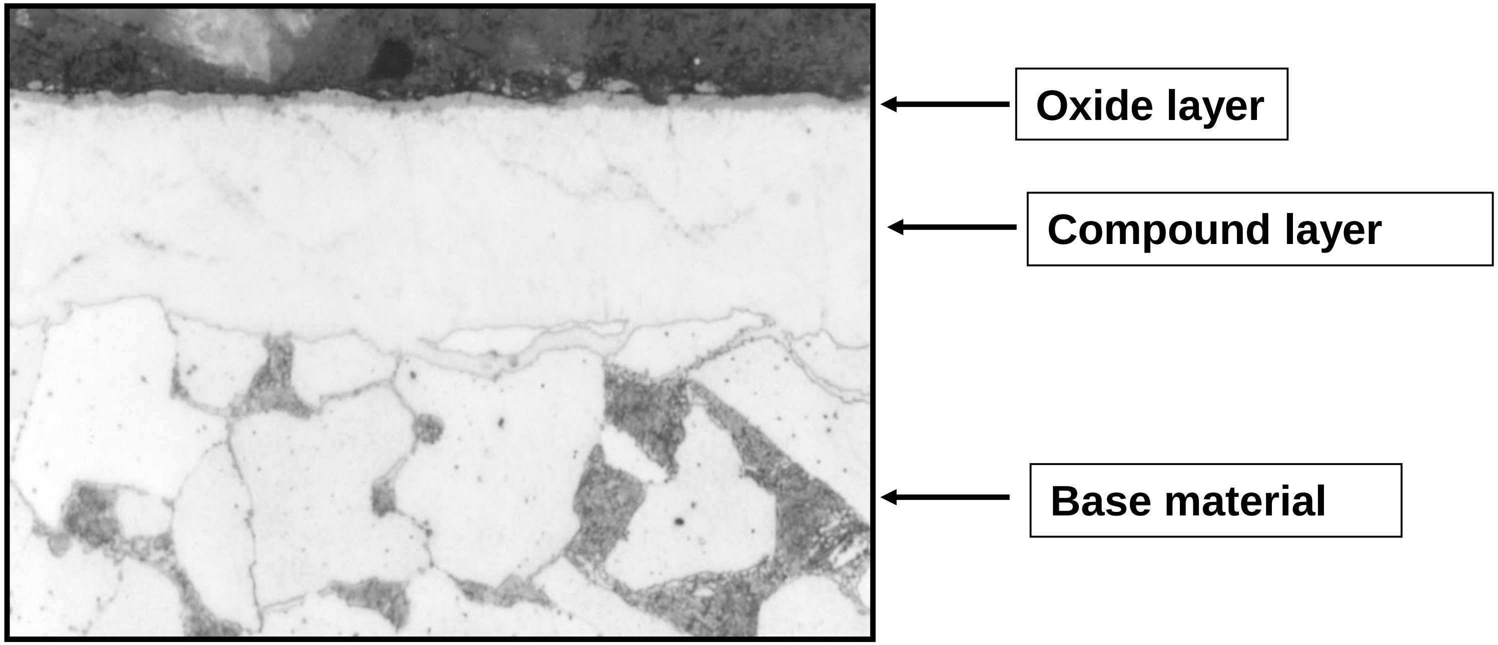
- wear resistance : The oxide layer will always contain a smaller or greater amount of pores and lubricants like oil can get into the oxide layer. This will can cause a higher lubrication effect and therefore a smaller amount of abrasive wear.

Basics of nitrocarburizing and postoxidation

postoxidation



(Gas-) Nitrocarburizing with postoxidation



Different types of iron oxide

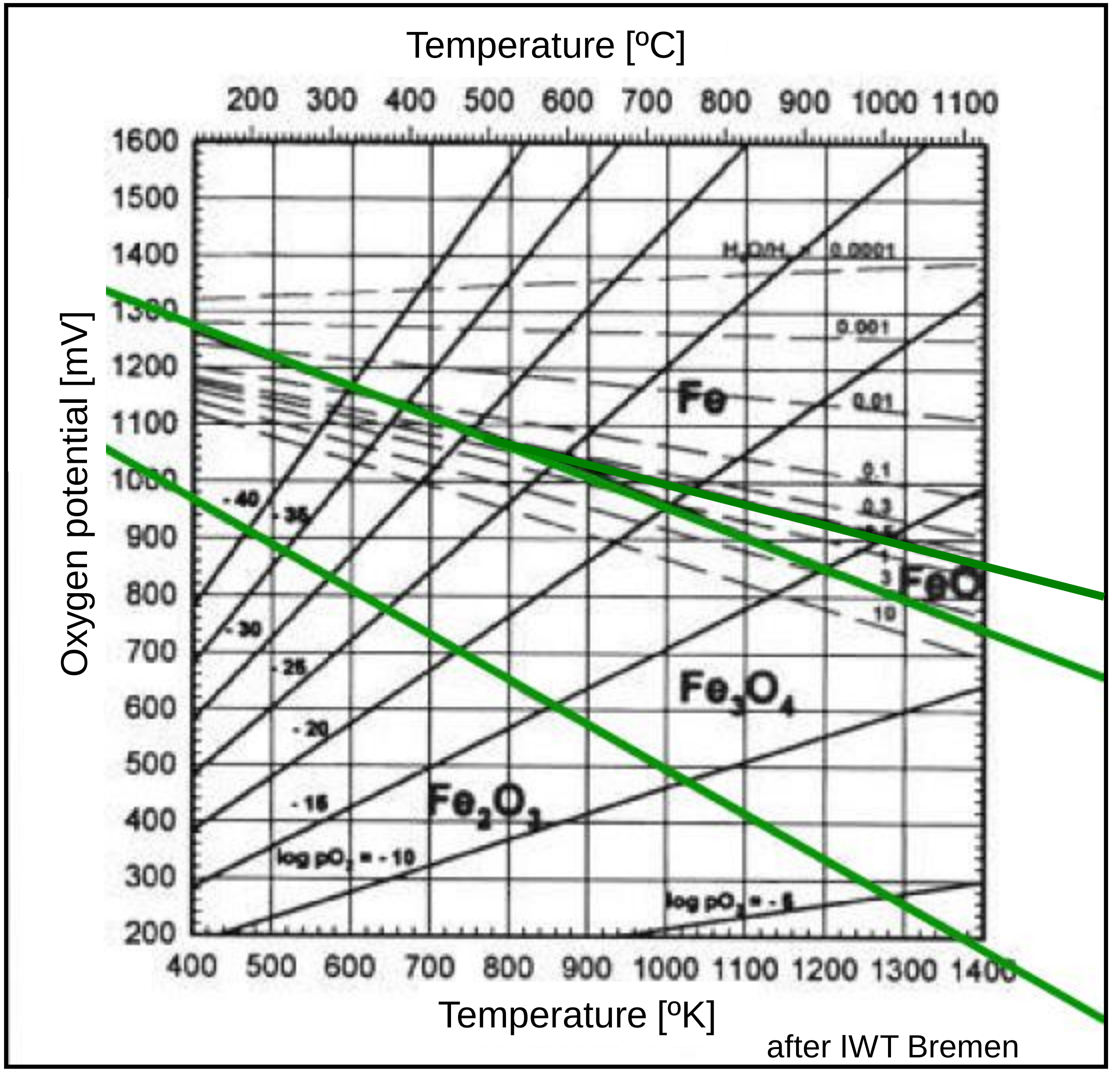
During the oxidation of iron (Fe) three different types of iron oxide can be formed depending on the oxidation conditions like temperature and oxygen potential :

- haematite (Fe_2O_3) : This red iron oxide can be formed at room temperature and ‚normal‘ ambient atmosphere.
  Normally this iron oxide is not magnetic.
  If in general someone talks about ‚the corrosion of iron or steel‘ normally he is talking about haematite.

- magnetite (Fe_3O_4) : This black iron oxide can also be formed at room temperature, but therefore special atmospheres are necessary. Normally this iron oxide is formed at postoxidation temperatures of 450 ºC up to 520 ºC.
  Normally this iron oxide is Ferro magnetic.
  Only this iron oxide creates a corrosion protective layer.

- wustite (FeO) : This black iron oxide is stable in a temperature range of T> 560 ºC, additionally also here specific atmosphere condition are necessary.

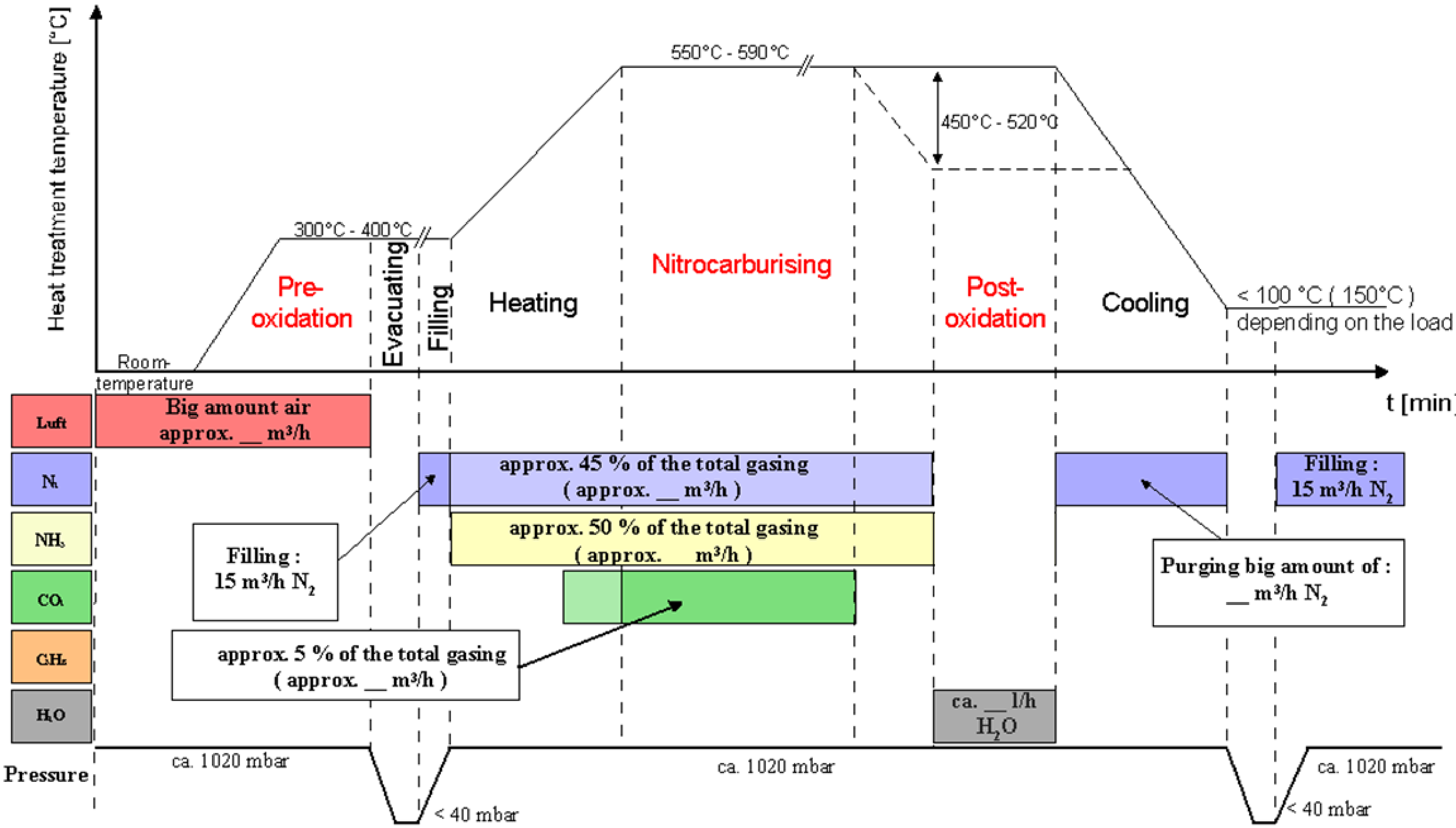
Formation of different iron oxides



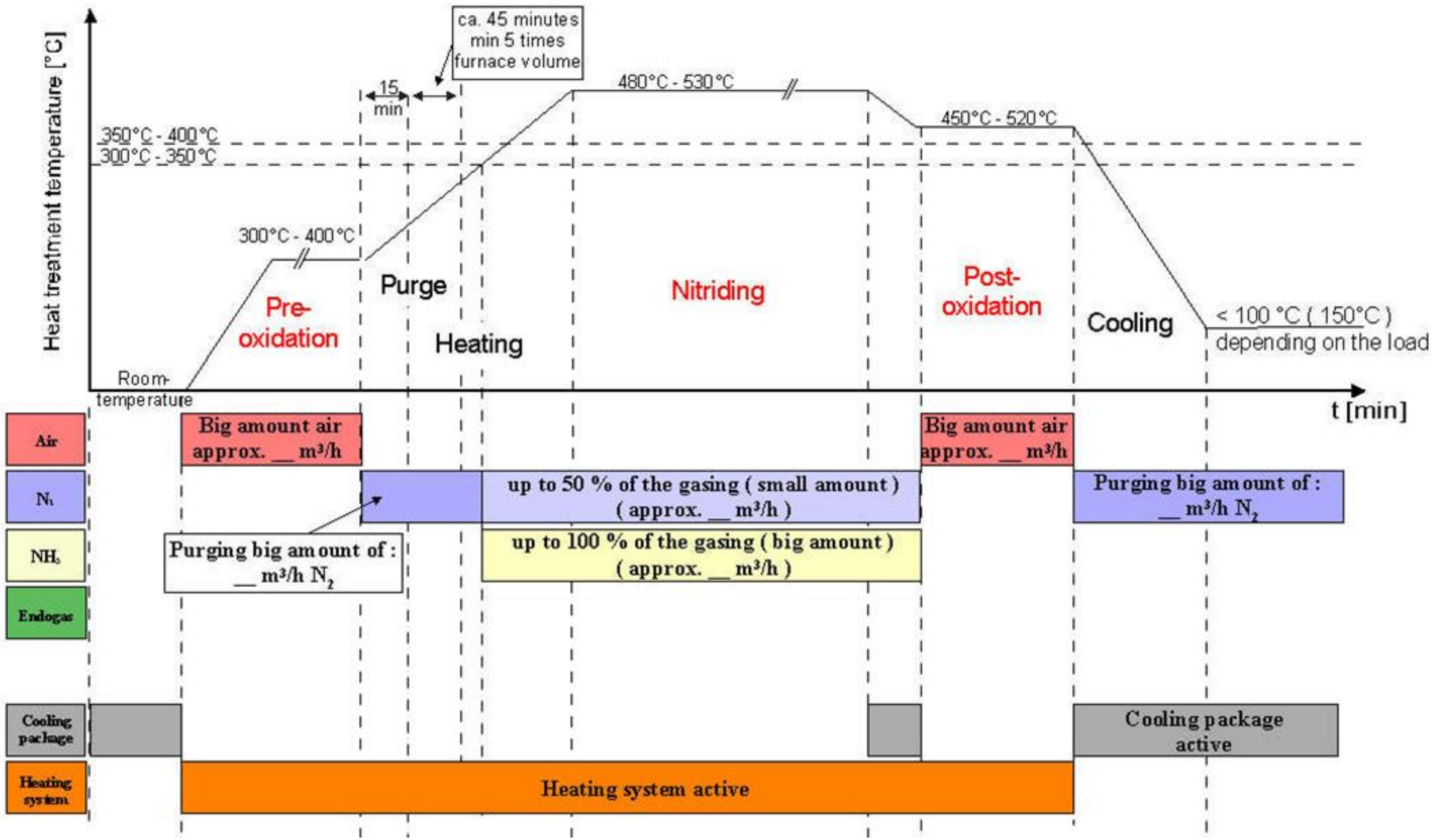
Reaction agents for postoxidation

Diffusion Element	Process	Reaction Agents
N	Nitriding	NH_3, NH_3 & N_2, NH_3 & H_2, NH_3 & N_2 & H_2
N, C,	Nitrocarburizing	NH_3 & Endothermic gas, NH_3 & CO_2 & (N_2), NH_3 & C_mH_n, & (N_2)
O	Postoxidation	demineralized water (H_2O) air (N_2/O_2) laughing gas (N_2O)

Standard process for nitrocarburizing and postoxidation



Standard process for nitrocarburizing and postoxidation



controlled postoxidation processes

Why controlled Post Oxidation??

The amount of oxygen, which is needed for the process, will be different, depending on:

- the temperature of the postoxidation
- the surface size of the load

So – for example – a load with a big surface size will need much more oxygen (here for example demineralized water) to reach the same results in the oxide layer thickness as a load with a small surface size. This is similar to the controlled nitriding or nitrocarburizing, where more ammonia is needed the bigger the surface of the load is.

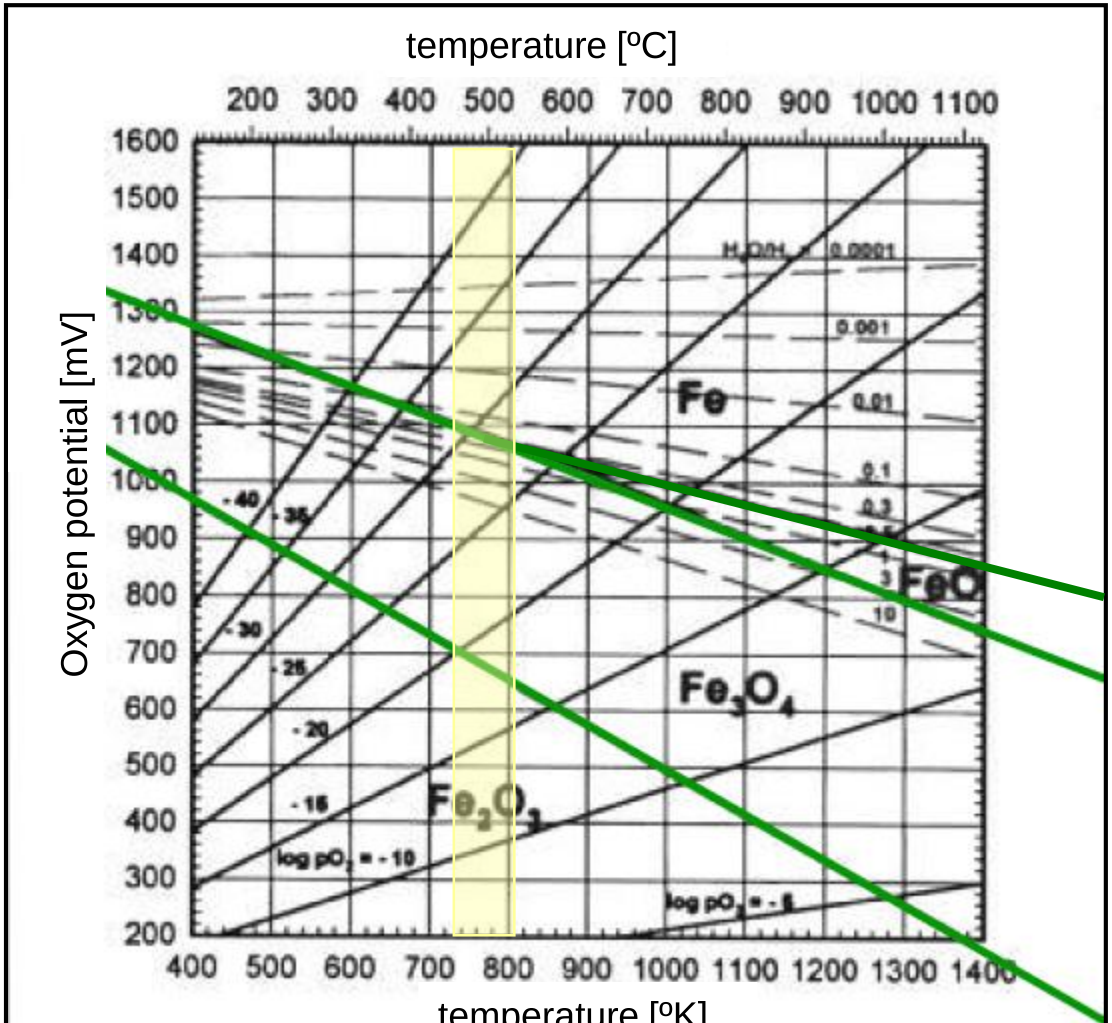
The main reason for a controlled postoxidation process is either the optimised consumption of oxygen and even more important the repeatability of the heat treatment results (independent from the surface size of the load).

↓

Therefore only the optimised mV value is necessary!!

This mV value must be found out by trials for every different part, that should be post oxidated.

Formation areas for the different iron oxides



after IWT Bremen

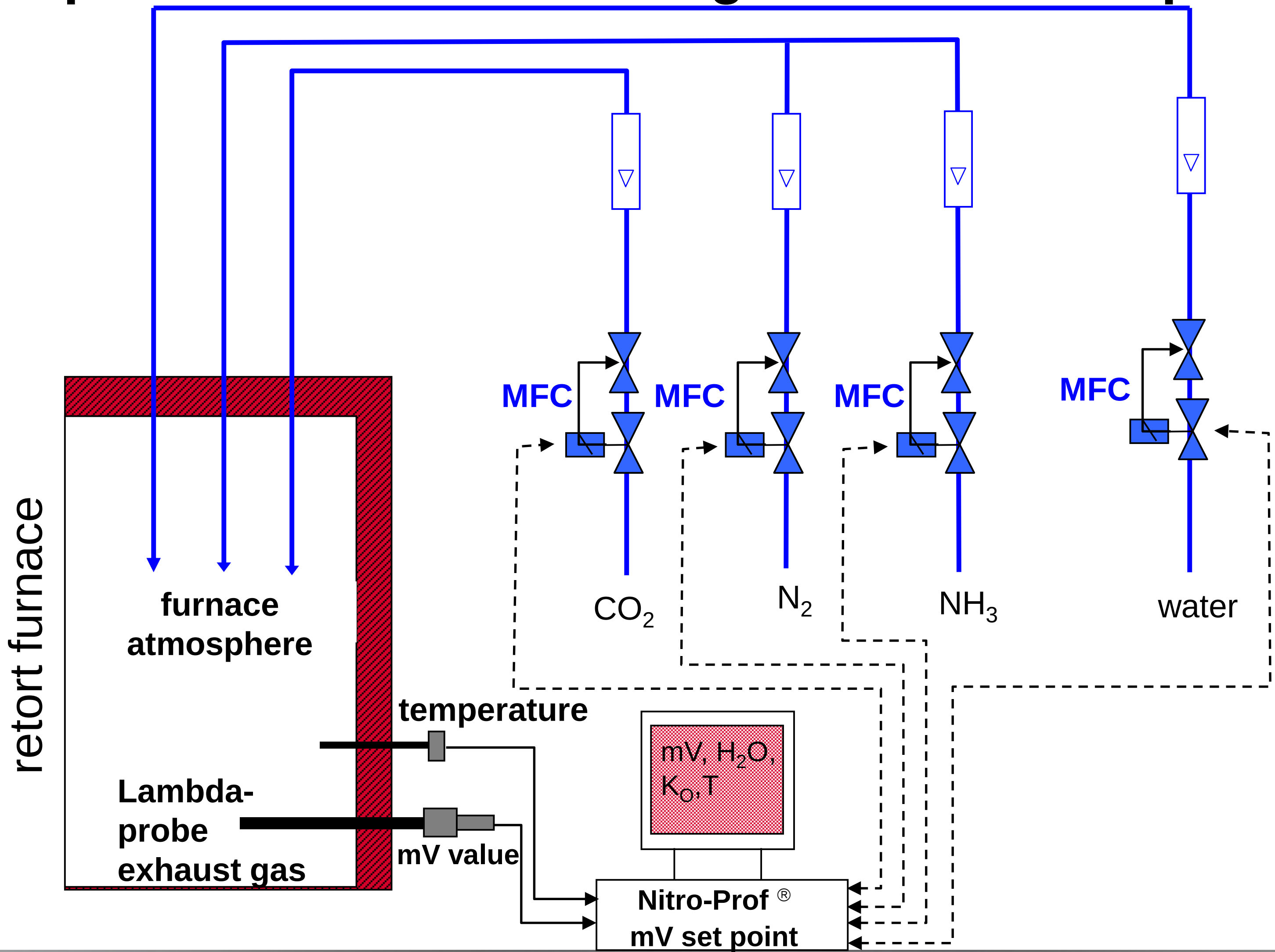
postoxidation- reaction :

$$H_2O \rightarrow [O] + H_2$$

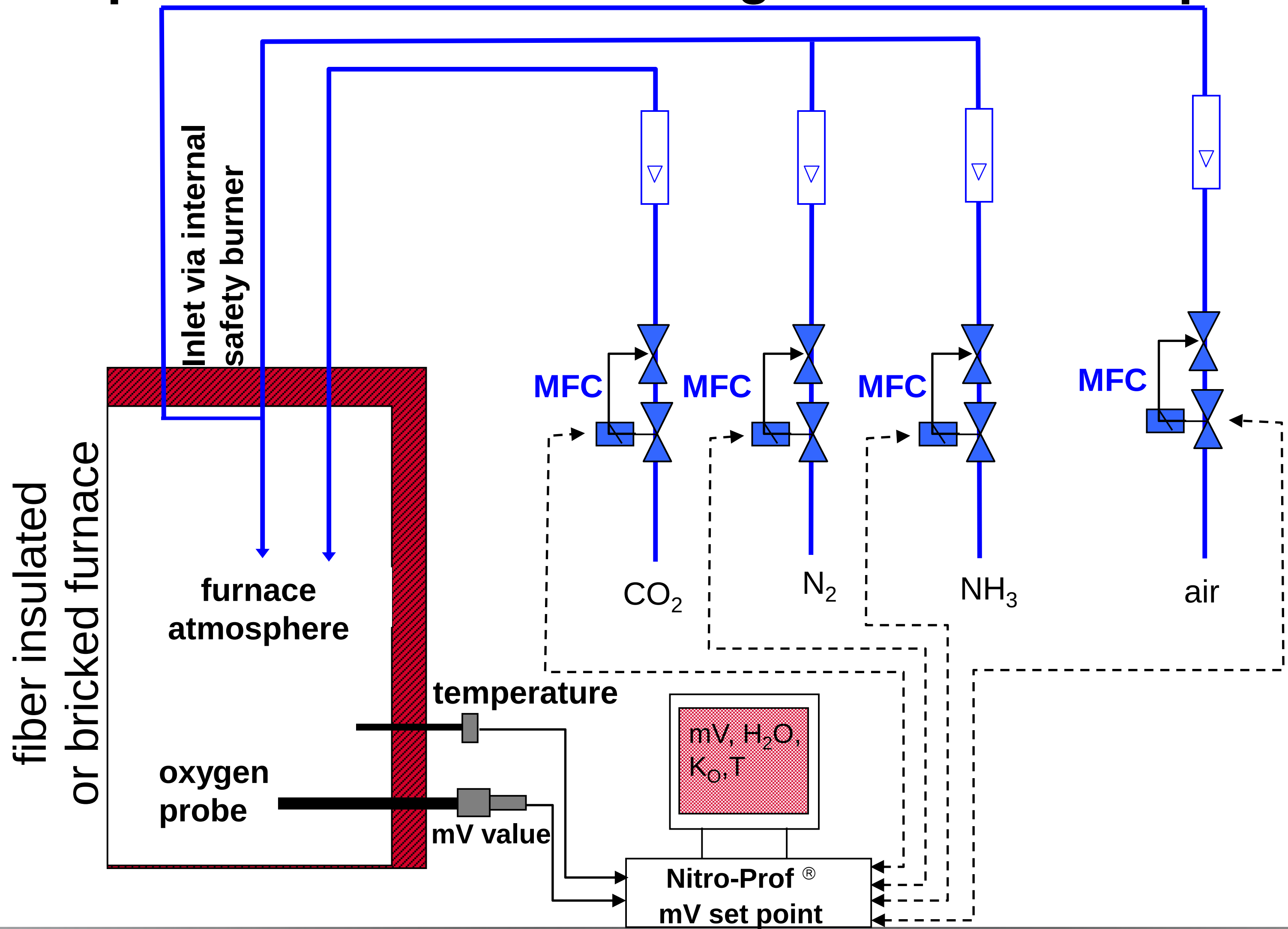
oxidation activity K_O :

$$K_O = \frac{p(H_2O)}{p(H_2)}$$

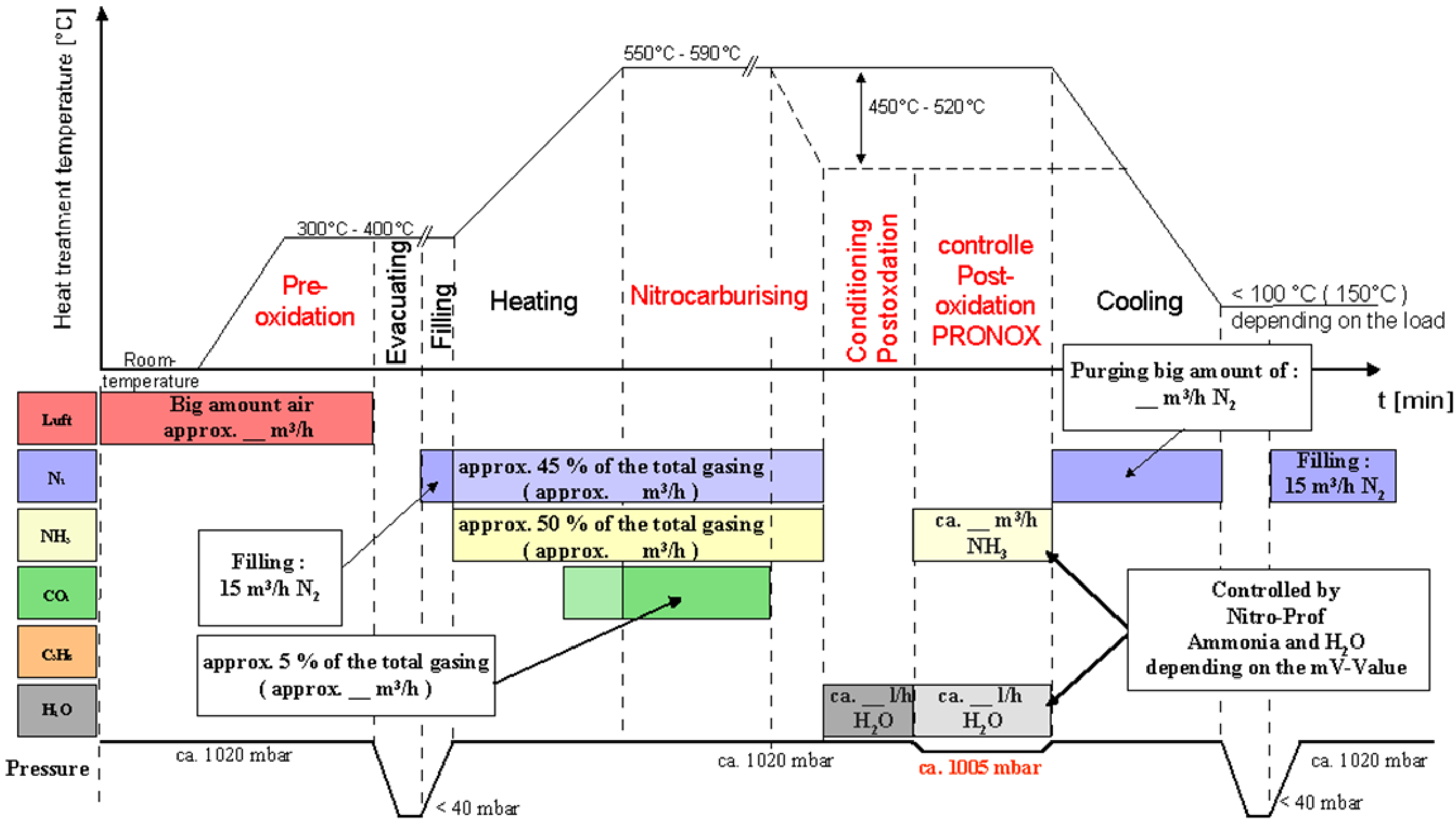
CN panel for nitrocarburizing and controlled postoxidation



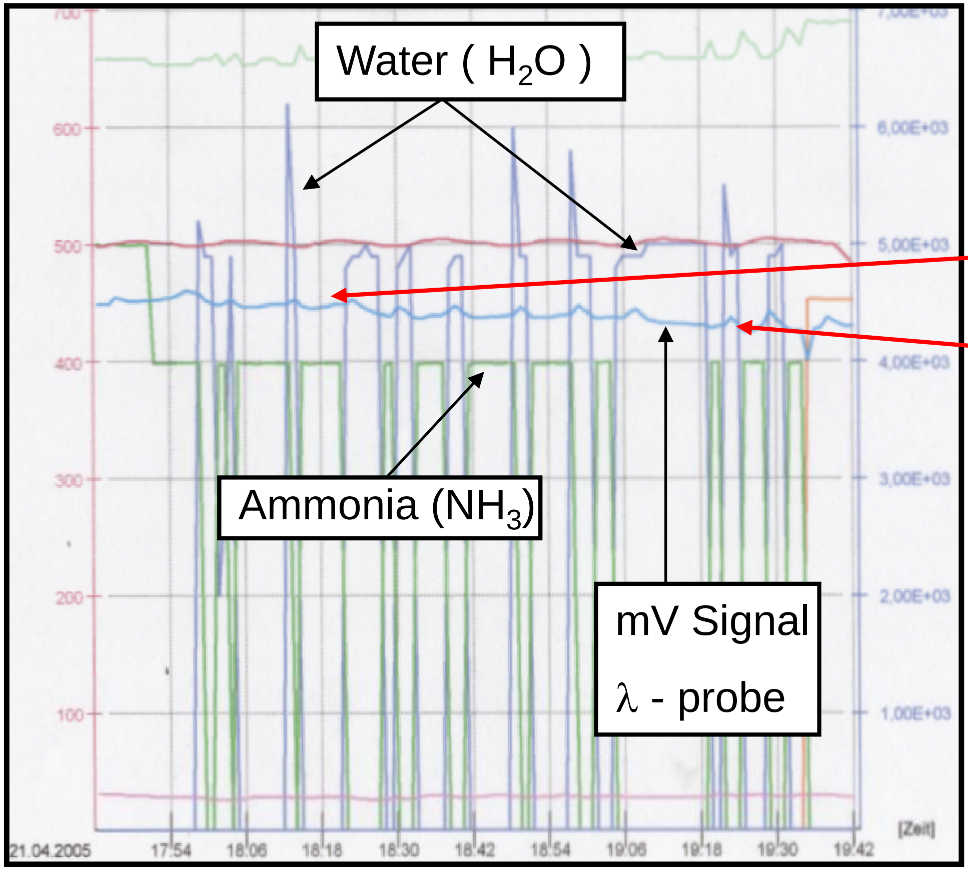
CN panel for nitrocarburizing and controlled postoxidation



Process for nitrocarburizing and controlled postoxidation



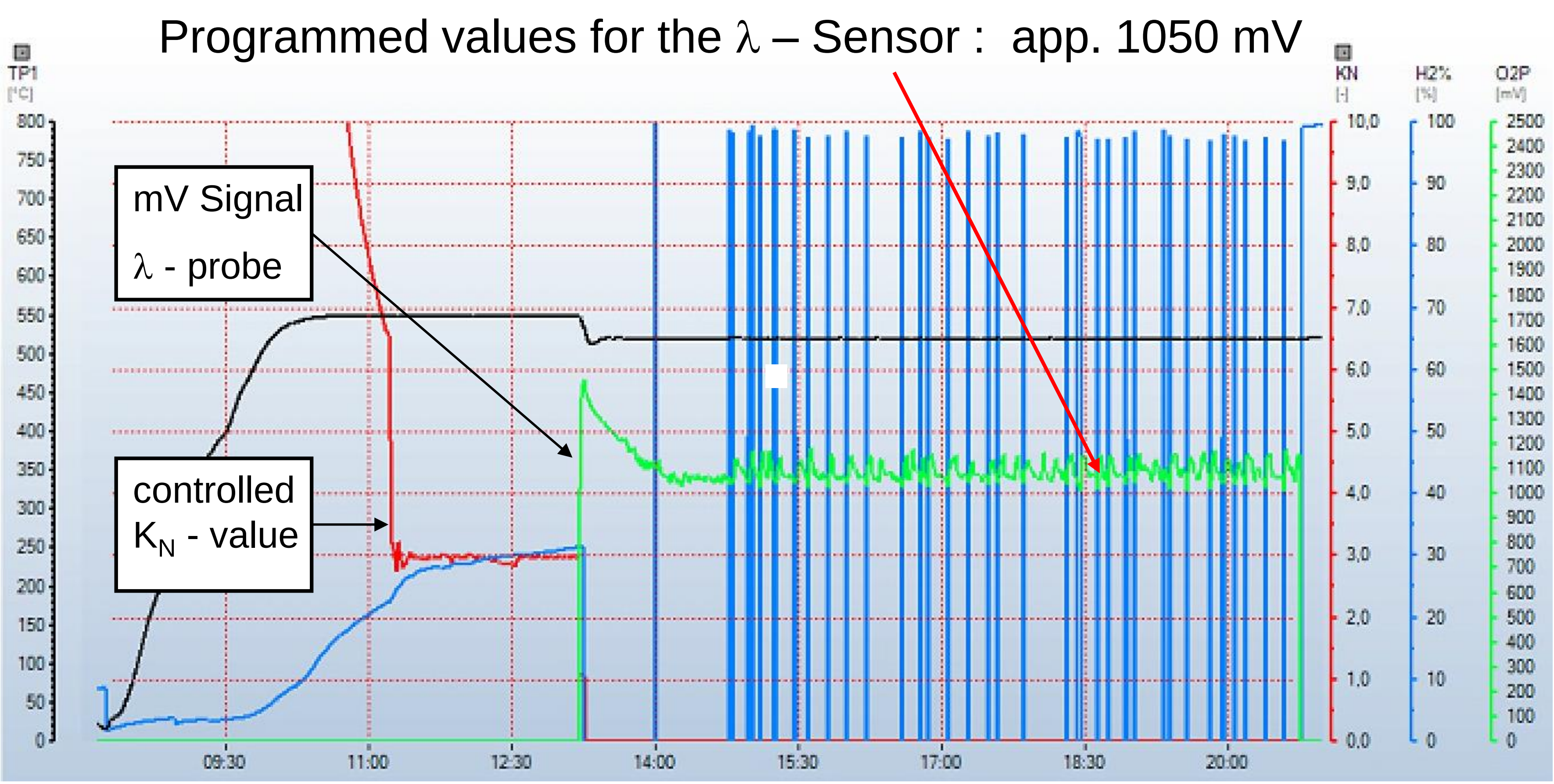
Cycle printout of a controlled postoxidation process – test run -



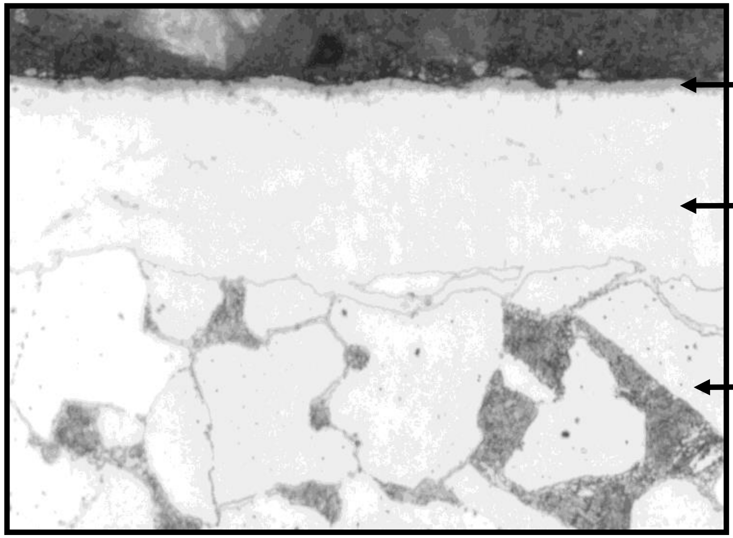
Programmed values for the λ – Sensor :

- app. 880 mV
- app. 860 mV

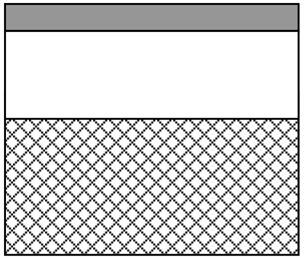
Cycle printout of a controlled postoxidation process – test run -



Gas nitrocarburizing and controlled postoxidation with the addition of propane (C_3H_8) of C15



Requirements for best results in corrosion resistance :



Heat treatment process

1.) nitrocarburizing

- NC temperature: 580° C
- NC time: 5 h
- gasing system: NH_3 & Endogas

2.) cooling down to 450° C

- gasing system : NH_3 & Endogas

3.) controlled postoxidation

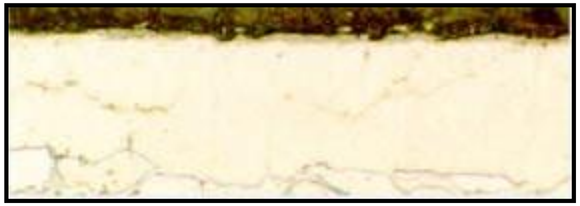
- postoxidation temp.: 450° C
- postoxidation time: 75 min
- gasing system : air & Endogas

4.) cooling down to 150° C

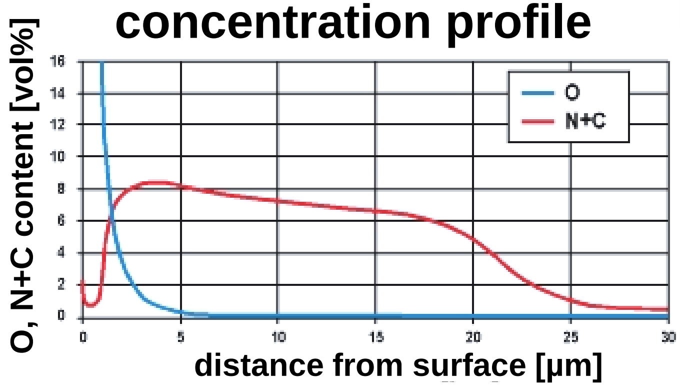
Heat treatment results

Material : C15 ~ 1.0401

Micrographic picture



concentration profile



Time in salt spry test (Din EN ISO 9227):

456 hours !

Postoxidation in a fiber insulated furnace

Heat treatment process

1.) nitrocarburizing

- NC temperature: 580° C
- NC time: 5,5 h
- gasing system: NH_3 & N_2 & CO_2

2.) cooling down to 500° C

- gasing system : NH_3 & N_2 & CO_2

3.) postoxidation

- postoxidation temp.: 450° C
- postoxidation time: 75 min
- gasing system : demineralized water

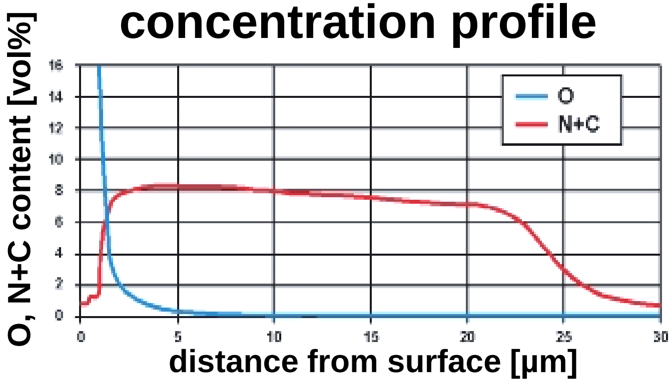
4.) cooling down to 150° C

Heat treatment results

Material : 42CrMo4 ~ 1.7225

Micrographic picture

concentration profile



<u>Time in salt spry test (Din EN ISO 9227):</u>

336 hours !

Processes with additional hydrocarbons

Benefits of additional hydrocarbons in NC processes

By using additional hydrocarbons in nitrocarburizing processes, the carbon content in the surface area of the compound layer is increased.
This will cause two beneficial effects

- The higher carbon content will increase the formation of ε-nitrides.
  The ε : γ' ratio of the compound layer can be increased from 7:1 up to 11:1 and therefore the wear resistance is improved

- The use of hydrocarbons in the last segment of the nitrocarburizing and also in the cooling segment prior to a postoxidation step will increase the N+C content in the top area of the compound layer.
  A N+C content of 8,6 Vol% or more is beneficial for the corrosion resistance

How to use additional hydrocarbons in NC processes

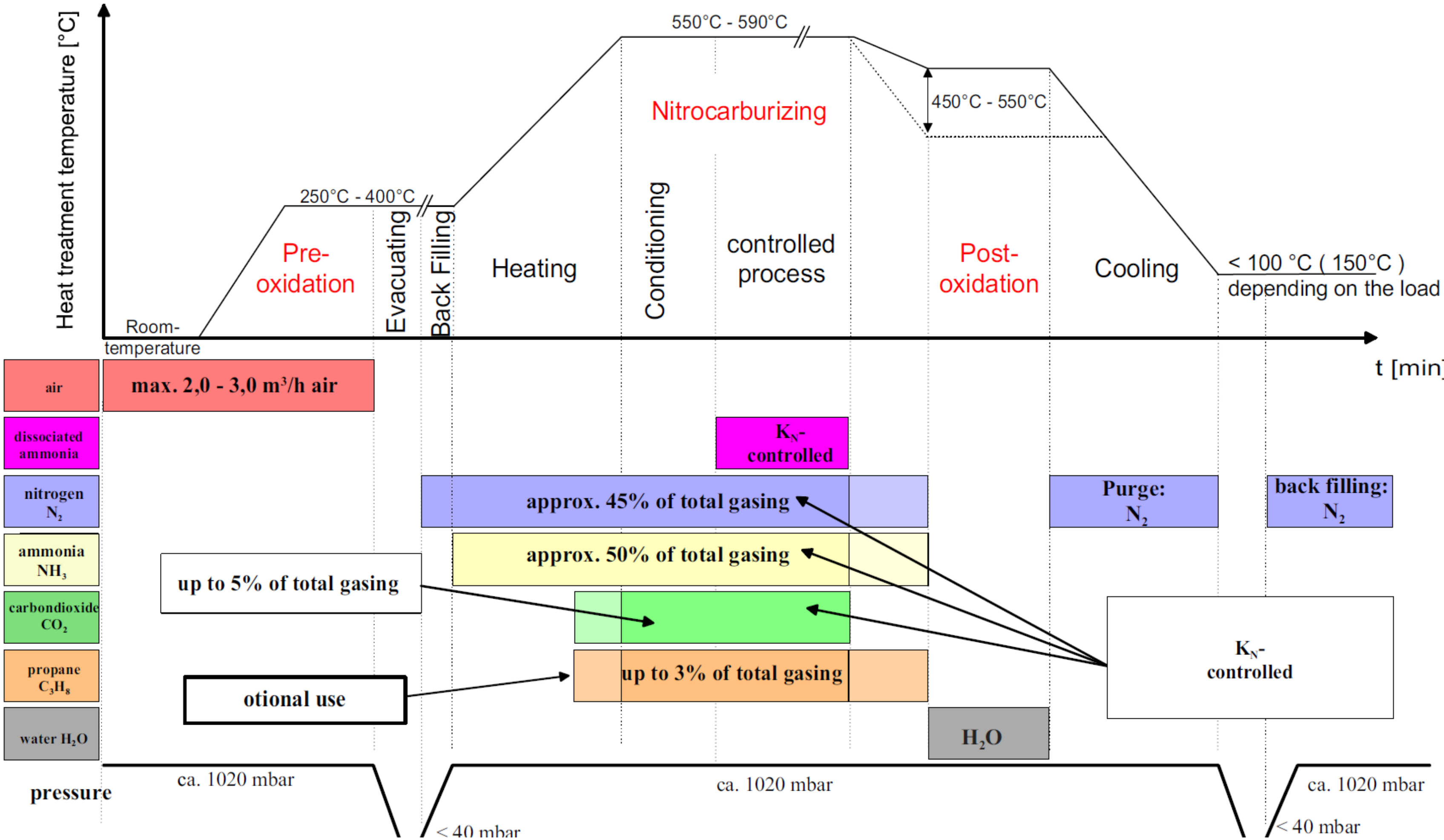
Due to the fact that the nitrocarburizing temperature is in the range of 560 – 590 ºC, the reaction of the hydrocarbons is limited.

In this temperature range propane (C_3H_8) shows the best results compared to methane/natural gas (CH_4) or other hydrocarbons with a higher carbon content regarding the formation of soot during the process.

The amount of propane should not exceed approx. 3-5 Vol% of the total gasing.

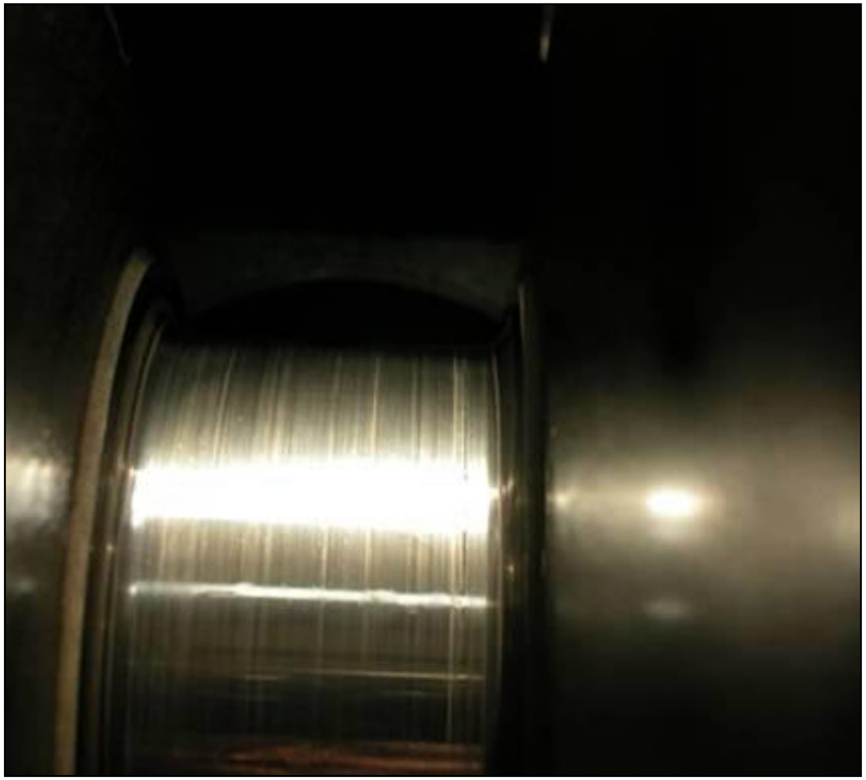
By using the gasing system with ammonia (NH_3), nitrogen (N_2) and carbon dioxide (CO_2) the propane can be used in addition to or instead of the carbon dioxide. Also a double step process (first with CO_2 and second with C_3H_8) is possible.

Process for nitrocarburizing & postoxidation with propane



Gas nitrocarburizing with the addition of propane (C_3H_8)

Increase of wear resistance



CO_2 - process

ε : γ' ratio 4 : 1

CO_2 & Propane - process

ε : γ' ratio 11 : 1

Furnace technology

Furnace technology used for (gas-) nitrocarburizing and postoxidation

Necessary furnace requirements:

exact temperature controlling (± 5 ºC or better)

Adequate amount of gassing (approx. 3 times of the furnace-volume / h)

intensive gas-circulation

↓

Normally used furnaces technology:

Chamber furnace (batch wise treatment)

- sealed heating chamber
- scale resisting retort

Continuously working furnace

- pusher type furnace
- belt furnace

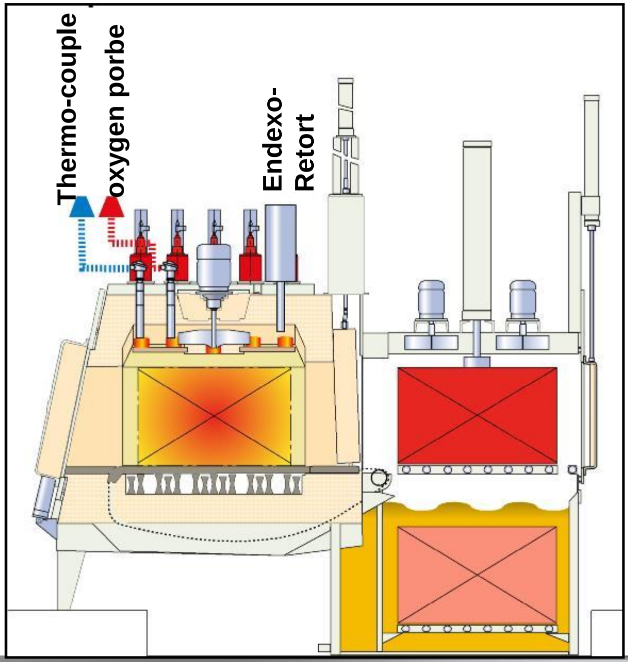
Bricked or fiber insulated chamber furnace

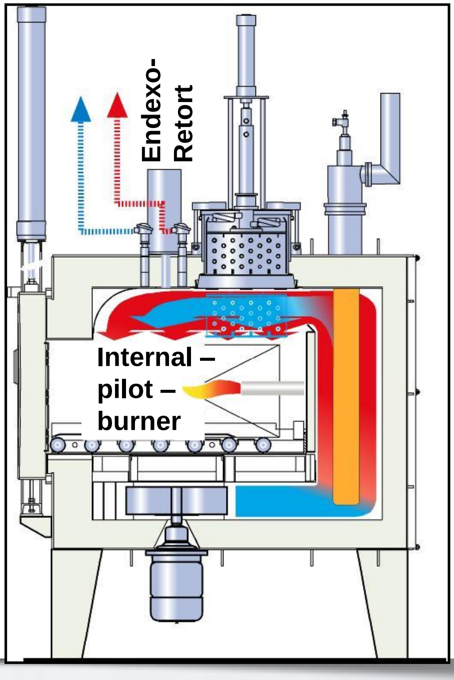
Advantage:

- less catalytic ammonia (NH_3) dissociation
- combination of different chambers possible (modular furnace construction)

Specific feature:

- slow changing of the furnace atmosphere
- **NO** use of demineralized water possible





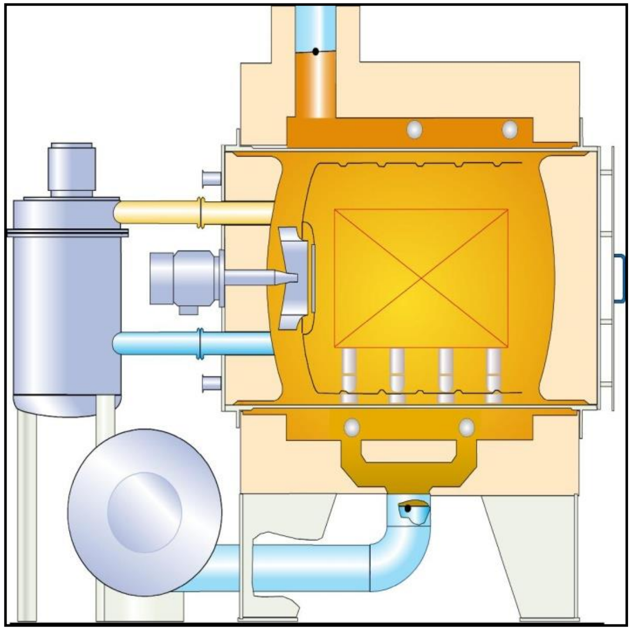
Sealed retort furnace

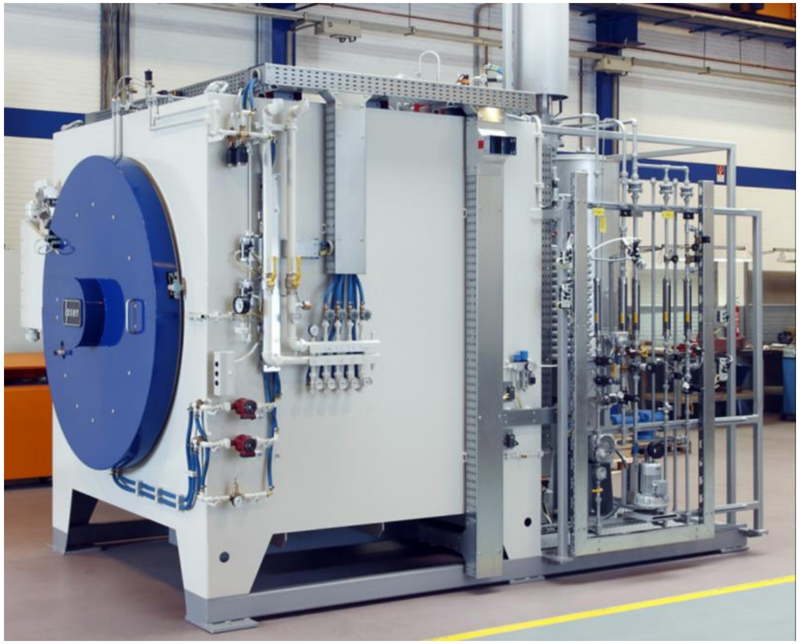
Advantage:

- Fast change of furnace atmosphere possible
- Evacuation is possible
- use of demineralized water possible

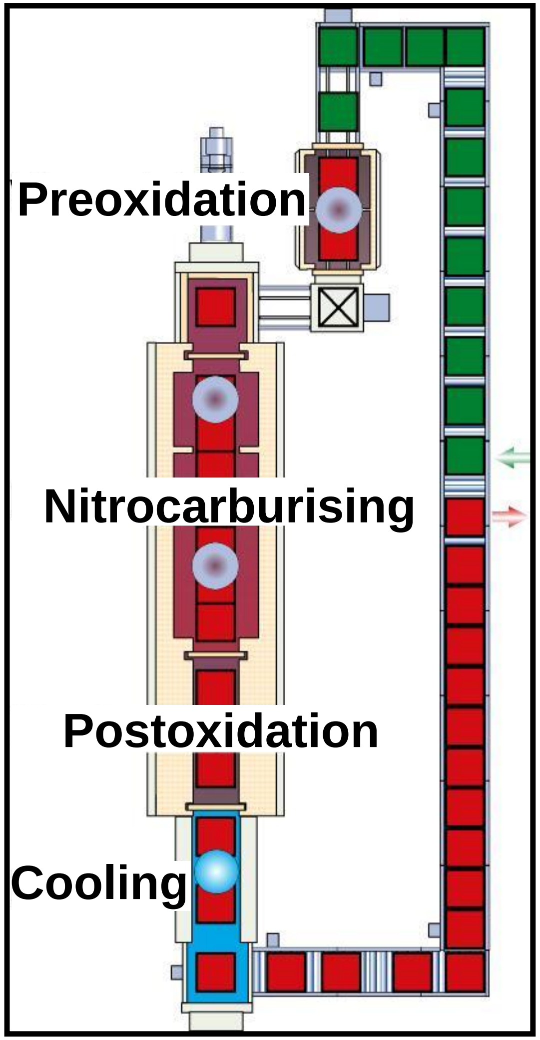
Specific feature:

- limited lifetime of the retort (catalytic and scaling effects)





Continuous furnace



Advantage:

- automated processes

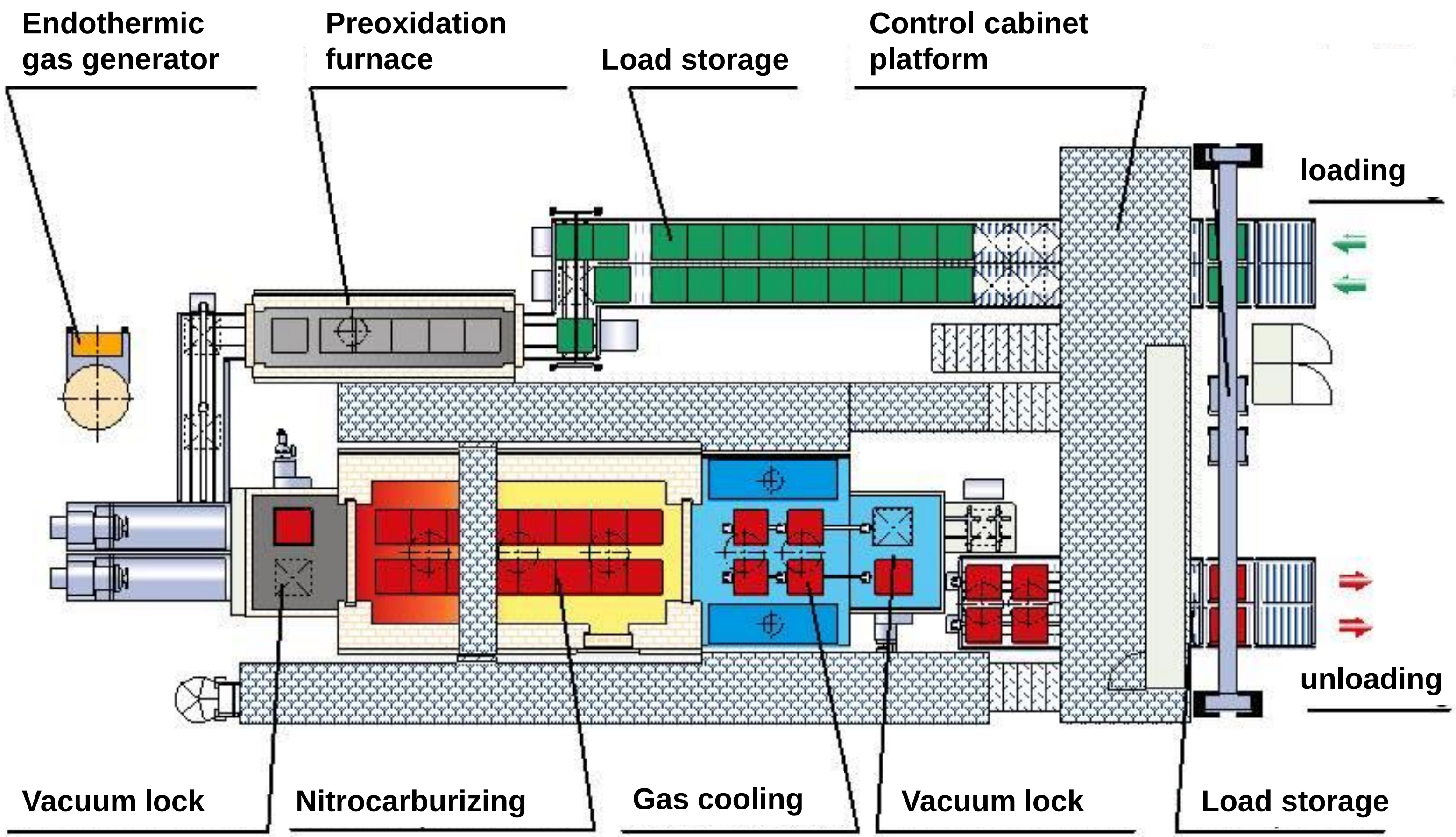
  complex processes can be run in one furnace

- Vacuum locks

Specific feature :

- Low flexibility because of high production capacity
- High costs for the furnace

Pusher type furnace



Double line pusher type furnace for nitrocarburizing

SHTE Heat treatment conference 2017

Västeras, 20th September 2017

Thank you for your attention

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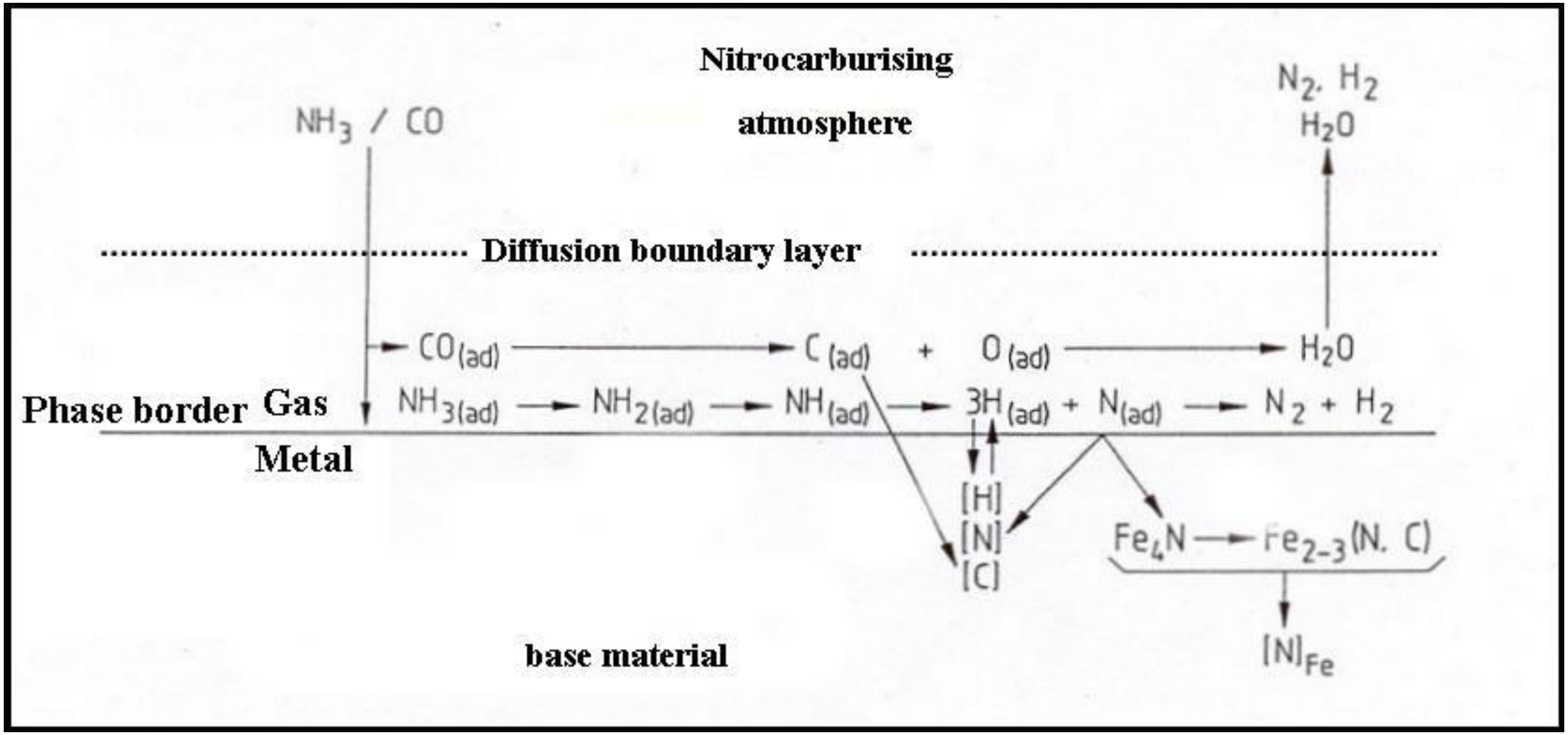
Nitrocarburizing reaction



Conclusions

Conclusions for postoxidation processes

- creation of a magnetite (Fe_3O_4) layer with approx. 1 – 3 µm thickness
- Use of a low temperature (approx. 450 – 480 ºC)
    - Influence on the shape and max. value of the N+C-Profile
- for layers with only decorative purposes the oxide layer may have some more pores than layers for corrosion resistant purposes
    - Higher temperatures (up to 520 ºC) can be used – faster process time

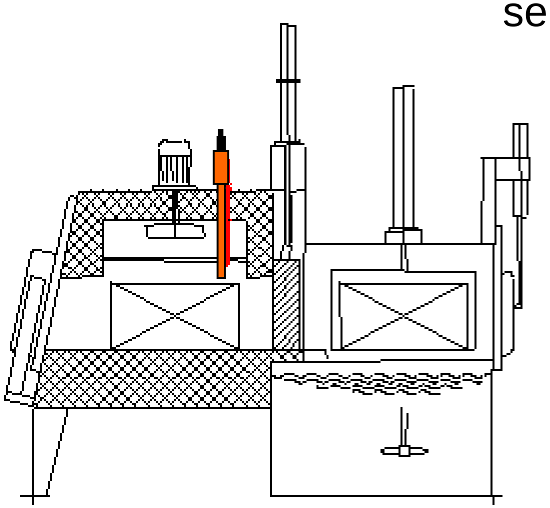
Conclusions for the Post Oxidation

Increase of the corrosion resistance due to :

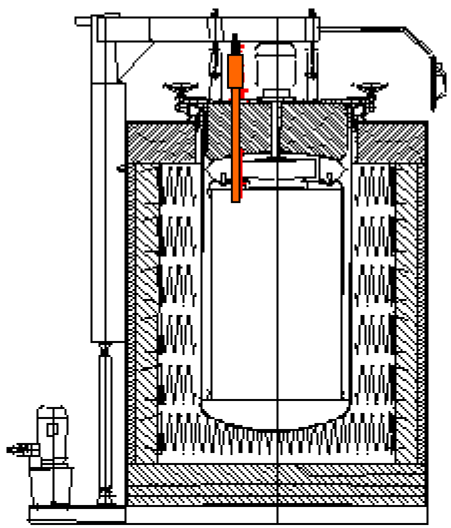
- compound layer thickness of min. 15 µm (mainly consisting of ε nitrides)
- N+C content of > 8,6 Vol% at the top area of the compound layer
- addition of hydrocarbon at the end of the nitrocarburizing
  - Higher max. value of the N+C-Profile
- cooling down to postoxidation temperature under ammonia and hydrocarbon
  - Influence on the shape and max. value of the N+C-Profile
- small difference between end of oxide layer and max. N+C-value

Installation of the oxygen-sensor

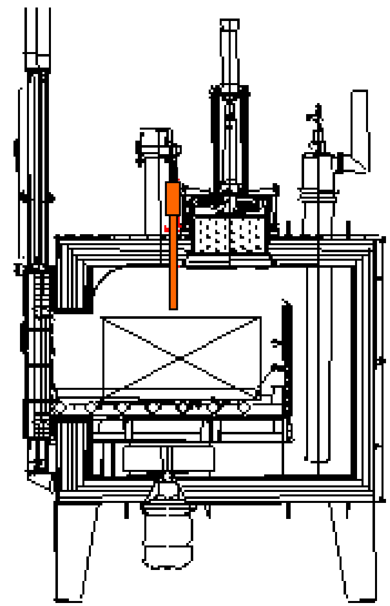
oxygen sensor



Bricked sealed Quench Furnace



Pit Furnace



Fiber insulated furnace