CREMER

GmbH

1.180°C 1.200°C 1.250°C 1.280°C 1.390°C
C-Level Bainit Martensite TTT density grainboundaries
Pore morphology Partial pressure

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Preface

High-temperature furnaces are becoming more and more important. At the same time, there is a strong tendency to combine several process steps. A hot item is to incorporate rapid cooling directly after the sintering zone, so called “direct hardening”.

The following overview is intended as an introduction to high-temperature sintering, describing which process steps can be combined, how the individual sections operate and which problems have to be accounted for.

The information is based on experience with fully operational high-temperature sintering systems and rapid cooling units.

The overview is restricted to technically feasible and practically usable solutions, using the long time experience in our company. The information given is specific and may vary from case to case.

We prefer to combine construction units that have proven themselves over the years. This allows the development of installations used for a specific product, as well as the construction of universal systems with a wide range of applications. The total process has become so complex, that a 100% new development will not only involve long development times, but will also pose an unacceptable risk.

For more technical data and consumption figures or even commercial details, we would like to invite you to a personal conversation. We will be honored to visit your company. This will allow us to offer you a tailor made solution, consisting of modern, reliable and efficient installations, which will set new standards in powder metallurgy.

We hope this overview will be of interest to you and will be looking forward to meeting you.

Kind regards,

Ingo Cremer, Dipl.-Ing.
CREMER Thermoprozessanlagen GmbH

Charge carrier

Due to the different process steps and the temperatures encountered, the parts have to be transported through the furnace on special carriers. The word “sintertray” is avoided on purpose, as the requirements are far more complex. A suitable charge carrier should have following features:

- Temperature resistance up to 1300 °C (2400 °F) under protective and reductive atmosphere.
- High thermoshock resistance against heating rates and, more critical, rapid cooling.
- Specific heat capacity as low as possible.
- An acceptable balance between cost and life-time of the charge carrier(a cheap one-way carrier can be just as good as a very expensive one with “indefinite” life-time)
- The interactions between parts, atmosphere and charge carrier have to match
- The overall dimensions are limited in order to guarantee a temperature distribution within the limits of the process accuracy.

It is obvious that in the design of a complex high-temperature sintering installation, one is strongly limited by the charge carrier available. The furnace has to be constructed starting from the inside. Starting the development of a charge carrier after the transport system has been fixed, will lead to failure.

Our developments have been aimed at metal charge carriers. They show little or no interaction with the parts. Depending on the geometry of the parts, it may be necessary to use ceramic supports inside the charge carrier. Such supports should be kept as small as possible in order to assure an acceptable thermoshock resistance. The materials to be considered for such ceramic supports are siliconoxide and aluminumoxide. Siliconcarbide, although it has a favorable thermoshock resistance, shows negative interactions with the parts when put into direct contact.

The shape stability of a metal charge carrier can only be achieved by a thermal separation between the frame and the bottom of the carrier. Such a system allows for different cooling rates in the frame and the bottom during rapid cooling. A rigid connection between the cold frame and hot bottom will induce strong deformations.

The inside of the charge carrier has to be adapted to the parts, while the outside dimensions should remain constant in order to maintain a high degree of universality.

Dewaxing – stearate zone

After the charging purgelock with 2 lock doors, the first process step is to remove the lubricant from the parts. This lubricant has been admixed to the metal powder as a pressing aid. The stearate zone has to fulfill following requirements:

- Suitable for different types of lubricants (Ethylene-bisstearamide, Zinc-stearate, Dens-Mix for warm compaction or binder residues from the MIM-process)
- Projected gas flow according to the counter-current principle
- Mechanical transport of the boxes containing the parts with a minimum of vibrations
- Atmosphere control
- Minimum of sooting through controlled addition of reactive components (wet hydrogen, carbondioxide)

Sooting

It is important to make a distinction between external and internal sooting. In external sooting the residues are deposited on the furnace walls and the surface of the parts. In internal sooting carbon is deposited inside the parts which is much worse. Internal sooting may result in crack formation, blistering or pop-corning and consequently in low, non-reproducible tensile properties.

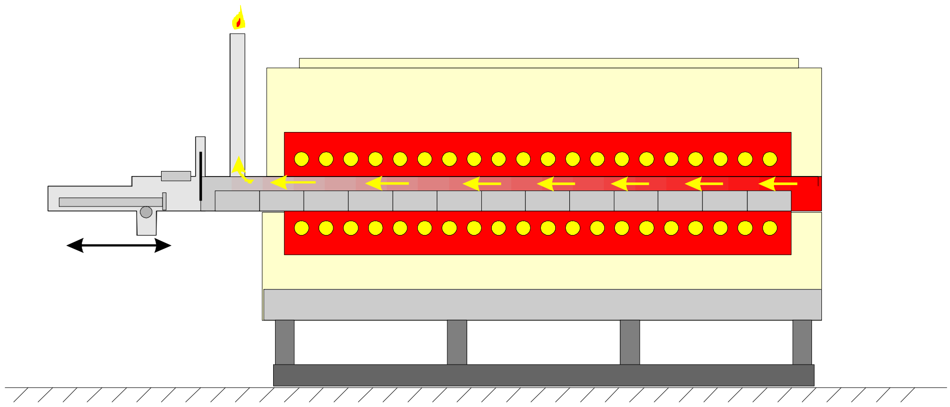
Sooting is promoted by admixing of Ni-powders, which act as a catalyst in the formation of solid carbon (soot). Metal containing lubricants, such as Zn-stearate, are more likely to cause sooting than lubricant based on ethylene bisstearamide. With higher pressed densities, the heating rates should be reduced in order to prevent sooting. Nowadays, furnaces are supplied with longer stearate zones compared to the previous generations.

Sooting can be reduced or even prevented by the following measures:
- High gas velocity by means of reduced cross-sections
- Increasing the hydrogen concentration of the atmosphere
- Increasing the water concentration (dew point) of the atmosphere
- Increasing the CO_2 concentration of the atmosphere
- Gradual heating to 650 °C

For the transport through the stearate zone we offer 3 different designs which can be combined with a high-temperature sintering zone.

Pusher-type stearate zone

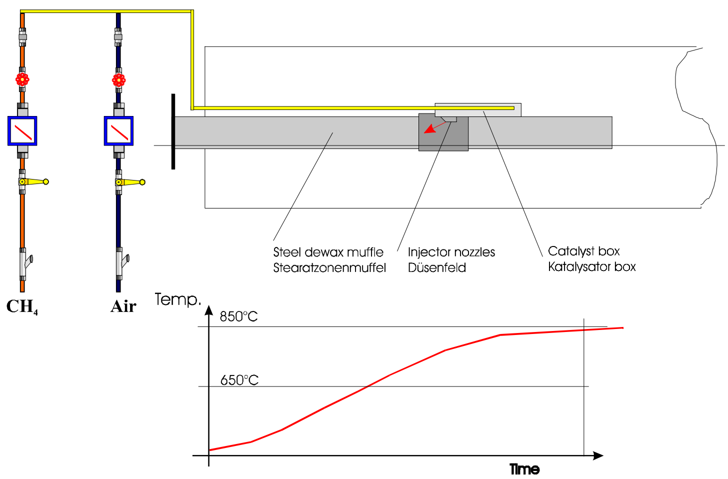
The trays are pushed through the stearate zone one by one. Due to the steel muffle, an unmistakable gasflow in counter-flow direction is achieved.



This type of stearate zone can be connected to the high-temperature zone directly or by a cross conveyor. When a tray is being pushed into the furnace, it has to push forward the other trays in the stearate zone. Consequently, such a system is most suitable for smaller furnaces. In large furnaces the stearate zone will become too long. Since the pusher system is not entirely free from vibrations, it is less suitable for the metal injection molding process. The pusher system has been frequently applied in high-temperature sintering furnaces with capacities up to 600 kg/h.

The system allows for the installation of several feeding points for wet nitrogen or catalytic gas (synthesized from natural gas and air). So far wet nitrogen has been preferred, but from technical point of view there are no objections against application of catalytic gas. Catalytic gas is roughly composed of:

Nitrogen	63%
Hydrogen	20%
CO	12%
CO_2	4%



Important is to prevent the catalytic gas from entering the high-temperature zone.

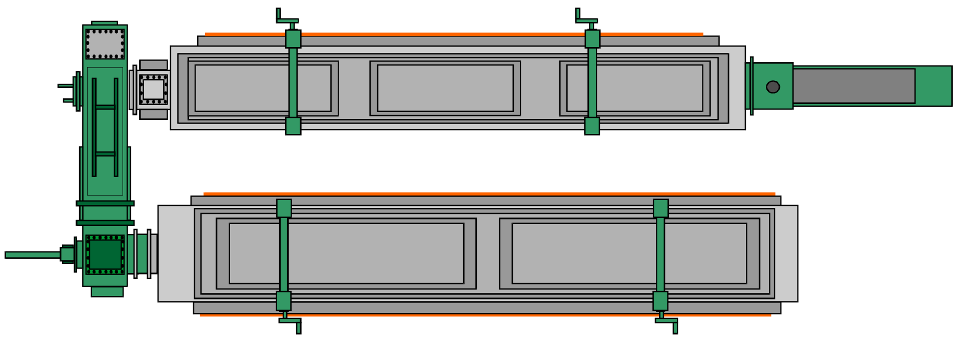
Conveyor belt stearate zone

In this system a conveyor belt moves through the muffle. The trays are positioned on the belt with small spaces in between them. At the end of the belt a belt returning unit is installed. This return station should have a cold part to assure a long life time of the belt. The entrance of the furnace does not feature a lock door system. Therefore a purgelock is installed at the end of the stearate zone. This guarantees that all gases flow towards the entrance of the stearate zone, subscribing the counter-current principle.

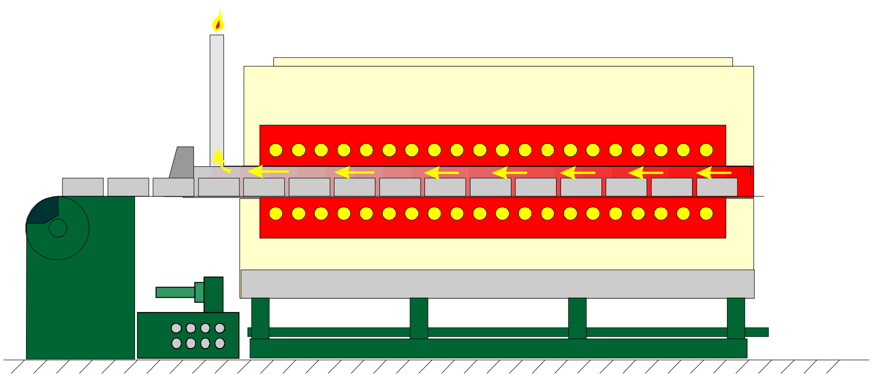
A purgelock positioned in-line between 2 zones is not very reliable. Therefore it is better to install a cross conveyor system. In such a system the mechanics will remain rather cold. It is important to realize that this may also cause a small cooling down of the parts. Whether this affects the parts, could not be determined so far.

The conveyor belt system offers a very smooth transport and, in combination with the cross conveyor and purge lock, it allows for a clear atmosphere separation between sintering zone and stearate zone. Nevertheless a part of the belt has to be heated up with each cycle.

The two furnace bodies, stearate zone and sintering zone, can be positioned either in "U-shape" or in-line with an off-set at the cross conveyor, so called "Z-shape".



Top stearate zone, bottom sintering zone



Side view of stearate zone with conveyor belt

Walking beam type stearate zone

A new development is the “muffled walking beam”. A walking beam in the stearate zone is connected directly to that of the sintering zone. A walking beam lifts up the carriers, moves forward and puts the carriers down on the side supports. The walking beam moves further down and returns to the starting position, moving underneath the carriers. A detailed description of the walking beam mechanism can be found in the next chapter.

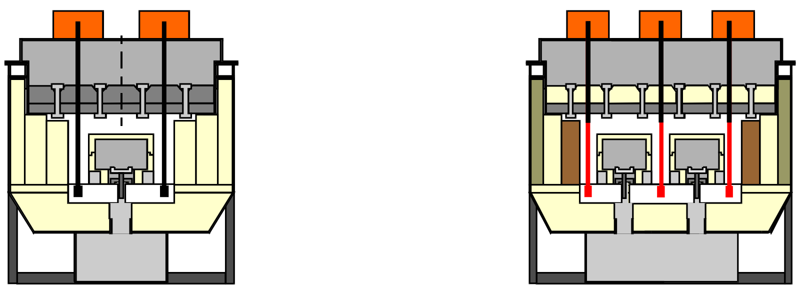
Through the application of special ceramic parts, an atmospheric separation is obtained between the charge on one side, and the heating elements and mechanics on the other side. By nature the ceramic materials are not as gas-tight as a steel muffle. On the long run this could lead to severe contamination, therefore an annual cleaning of the stearate zone is recommended.

The muffled walking beam system combines the high energy efficiency of the pusher system, with the smooth vibration free transport of the conveyor belt system.

This type of stearate zone can be connected to the sintering zone directly (in-line) or through a purgelock.

As an alternative to the used NiCr-heating elements, SiC-elements can be installed.

To save working space without loss of capacity, the walking beam system allows for two charge carriers to be transported side by side, as described below.



Cross section view of a stearate zone with a single and double walking beam

High-temperature Sintering Zone

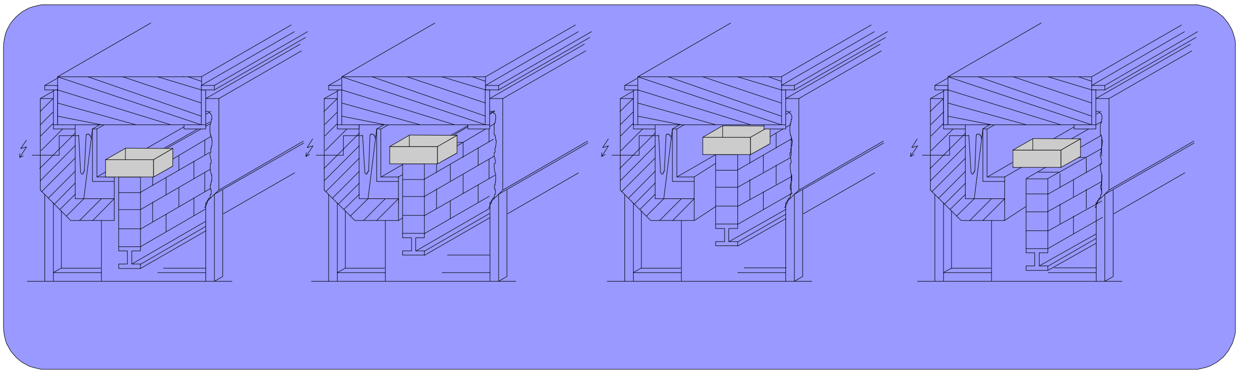
The key component of the complex high-temperature sintering furnace is the sintering zone. Here the carrier and parts are heated up to 1150°C (2100°F), 1280°C (2333°F) or even 1400°C (2550°F). Installation with throughput rates of 1200 kg/hr (2650 lb./hr) have been running for several years. The residence time at maximum temperature is usually set at 30 minutes. This can be increased when high additions of alloying elements such as Ni, Mo and Cu are used, as they will diffuse slower than for instance carbon.
For example, high-temperature sintering of iron, molybdenum, copper alloys (e.g. Hoeganas' Astaloy Mo mixed with 1 %Cu) can offers following advantages:

- Better homogenization of the alloying elements
- Higher densities
- Formation of smaller, rounded pores reducing notch effects
- Much higher yield strength
- Improved UTS
- Increased hardness

Next to the improved mechanical properties, it is much easier to reduce oxygen-sensitive alloying elements at 1280°C (2333°F) than at 1120°C (2048°F). This allows for the use of alloying elements such as Cr, V or Mn.

For the transport mechanism in the high-temperature sintering zone a walking beam system is applied. This system operates stepwise:

1. Step The walking beam moves up, lifting the charge carriers.
2. Step The beam moves forward.
3. Step The beam moves down, putting the charge carriers onto the bed on both sides of the beam.
4. Step The beam moves back without touching the charge trays.
5. Step The walking beam moves up to the original position, at an equal level as the bed with the charge carriers. The beam remains in this position till the next cycle starts.



Usually the forward movement of the beam is somewhat larger than the length of one charge carrier, but in applications where carefully controlled heating rates are essential, such as MIM, this movement can be divided in smaller steps. It can take up to four complete cycles to move the charge carrier one length forward. Due to this, parts in the front of the carrier will be exposed to the same heating rates as parts in the back.

The isolation and supports are made of ceramics. High purity aluminumoxide (>98%) is applied at critical sections. For temperatures exceeding 1150 °C (2100°F) fiber isolation can not be used, since the fibers consist of SiO_2. Exposed to pure hydrogen atmospheres, these fibers will be reduced to siliconmonoxide, which is gaseous as 1000°C. Thus, the lifetime of isolation with large amounts of SiO_2 is very much limited.

The inner walls of the furnace should not be too cold, to prevent condensation. If this is not accounted for, it will take a very long time before reducing atmospheric condition are obtained.

The walking beam concept has been well established. But nowadays the requirements have moved to higher throughput rates on as little as possible floor space. For this the "double walking beam" has been developed. Combined with a double walking beam in the stearate zone, it allows for the charge carriers to move side by side through the furnace. This is called the "Twin-runner".

Cross section view of a conventional high-temperature sintering zone (left) and the sintering zone of a "twin runner" (right)

For heating elements molybdenum meanders are used. In the charge carriers the parts can be stacked, so one has to be cautious that non of them is exposed to direct radiation from the heating elements. This would lead to inhomogeneous temperature distribution or even local overheating. To prevent this the charge carriers are moving in the "shade" of the ceramic bricks, assuring a homogeneous temperature distribution within the carrier of +/- 5°C. Trials with ceramic temperature control rings have demonstrated that in a loaded charge carrier of $330x330x80mm^3$ it was impossible to detect any systematic temperature inhomogeneity. At a sintering temperature of 1280°C (2333°F), there was a random temperature distribution of +/- 3 °C, which is even within the accuracy of the measurement.

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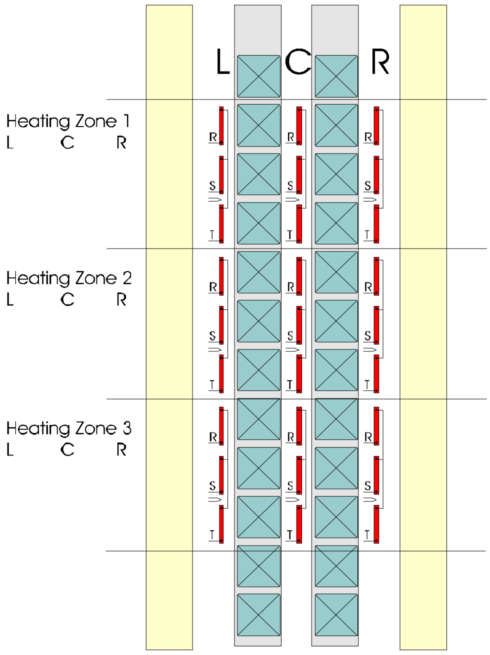
Nowadays the heating zones of the high-temperature section are fitted with thyristor controllers. In the installation several heating zones are installed to allow for a specific temperature profile to be set. In the **Twin-runner** system, there is an additional subdivision of the heating elements perpendicular to the walking beam. This enables a temperature accuracy comparable with that of the conventional walking beam systems. The heating elements in the center will heat up half of the material in the adjacent charge carriers, while the outer heating elements will heat up the remaining part of the material and the furnace walls. Each set of heating elements is fitted with its own thermocouples and temperature controller, to compensate for fluctuations in weight between two charge carriers.



The sintering atmosphere is usually composed of mixtures of nitrogen and hydrogen. Cracked ammonia (75% H_2 and 25% N_2) can be applied alternatively, although we recommend the use of storage tanks to get the best homogeneity. For the sintering of carbon containing parts without decarburization, the hydrogen content of the gas should be under 5% (even with 100% nitrogen proper sinter conditions can be achieved). Stainless steels are usually sintered under full hydrogen, but if the installation is fitted with a rapid cooling unit, N_2/H_2-mixtures can be used as well. The rapid cooling will prevent excessive nitrogen pick-up, enabling controlled hardening without loss of corrosion resistance. Controlling the sintering atmosphere is described in the next chapters.

Carbon restoration zone

Depending on the application, it may be interesting to restore the carbon concentration in the edges after the sintering. This should be achieved by an increase of the carbon potential in the gas phase, for which endogas is very suitable. If the alloy composition requires a carbon restoration at temperatures above 1000 °C (> 1832°F), the endogas should be generated in a separate generator. Nevertheless one should strive for a carbon restoration at the lowest possible temperatures, e.g. 860°C (1580°F). This allows for a high carbon potential with a minimum risk of sooting.

Sooting is a phenomena, one has to reckon with during the design of the restoration zone. An open walking beam system, like the high-temperature zone, is not suitable, as soot will contaminate and damage the isolation. The design should be comparable with that of the stearate zone, but the maximum temperature allowed should be higher, around 1150°C (2100°F). Therefore, a conveyor belt or a muffled walking beam are the only transport systems to be considered.

A purgelock is installed between sintering zone and carbon restoration zone. To prevent unwanted cooling down of the parts, a gaslock or diffusion lock will be mounted. Suck a lock operates without mechanical movements using differences in pressure, cross-section and flow.

Sooting problems / Boudouard-equilibrium sooting by endogas

Endogas is commonly used in the heat treatment (carburizing) and powder metallurgical industry. It is usually manufactured in a separate generator. At around 1000°C a mixture of air and hydrocarbon gas (e.g. methane, propane, natural gas) will react endothermically in the presence of a nickel catalyst, forming hydrogen, nitrogen, carbonmonoxide and carbondioxide (the remaining hydrocarbons are neglected).

Endogas from methane:

$$2CH_4 + O_2 + 79/21\ N_2 = 2CO + 4H_2 + 79/21N_2$$

Endogas from propane:

$$2C_3H_8 + 3O_2 + 3*79/21N_2 = 6CO + 8H_2 + 3*79/21N_2$$

This will lead to the following compositions for the endogas:

nitrogen	: 45,1 - 39,8%
hydrogen	: 34,6 - 38,7%
carbonmonoxide	: 19,6 - 20,7%
carbondioxide	: 0,6 - 0,01%

The C-level of the atmosphere is determined by the carbon activity, which is a function of the amount of carbon in the part and the temperature. A useful approximation is given by:

$$\log_{10} a(c) = (2300K / T) -2,21 + 0,15 * (\%C) + \log_{10} (\%C)$$

The effect of alloying elements is not taken into account in this formula.

The Boudoir reaction describes the equilibrium conditions between the carbon activity, carbon monoxide and carbon dioxide.

Boudouard: $2CO(g) = C(s) + CO_2(g)$

p_{ges}=1,013E5 Pa

Equilibrium constant: $$k_B = \frac{a(C)\ p(CO_2)}{p^2(CO)}$$

R = 8,31441 J/(mol *K)

ln 10 = 2,302585

$a(C) > 1$ => sooting

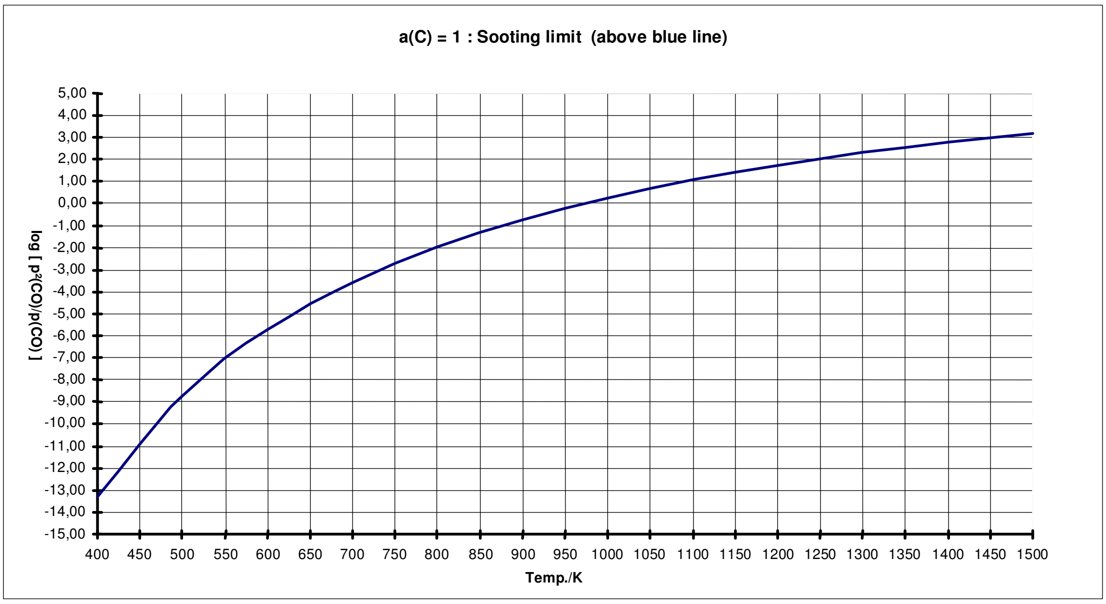
$a(C) < 1$ => no sooting

$a(C) = 1$ => sooting limit

$$\ln(10) * R * \log k_B =)_R H(T)/T+)_R S(T)$$

Theoretical sooting limit

When the carbon activity becomes larger that 1, carbon will sedimentate in the form of graphite (sooting). This usually takes place on the parts or the furnace refractory, because of catalytic effects of the surface. In the diagram below, the relation between $p^2(CO)/p(CO_2)$, which equals $1/k_B$, and the temperature is depicted for a carbon activity of 1. Sooting will take place in the area above the blue line.



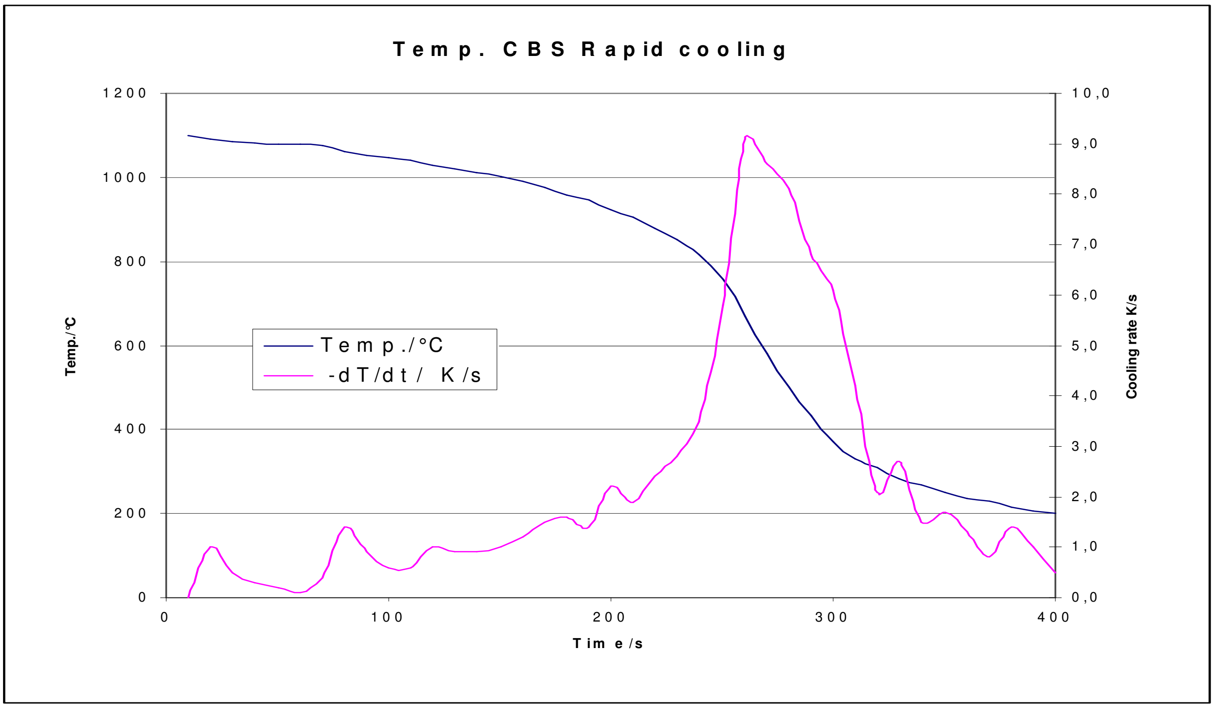
From the diagram it is obvious that given a constant gas composition, the chances for sooting increase with decreasing temperature. Therefore this problem is most pronounced in the cooling zone. Especially, if the furnace is operated at high temperatures, which is the case for the sintering process (ca. 1120°C). On top of that, it is necessary to use a high carbon monoxide pressure, in order to prevent decarburization of the parts.

Fortunately the reaction kinetics of the sooting decrease when the temperature drops. Empirically it was found that little sooting takes place below 600°C; the gas is 'frozen'.

Rapid cooling

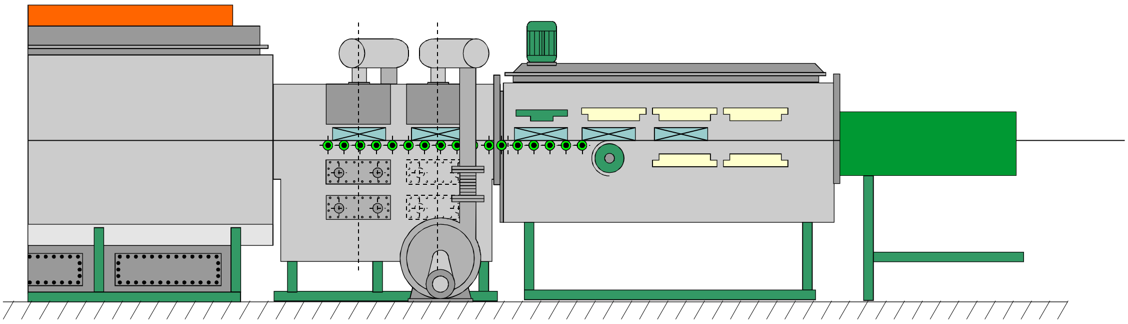
Behind the high-temperature zone or carbon restoration zone a rapid cooling installation can be mounted. In here the parts can be cooled in a controlled way, following the TTT-diagrams. The system is fitted with shaft mounted rollers. Ventilators are circulation the process gas, which is chilled in water cooled heat exchangers. The cold gas is aimed at the charge carrier and parts.

The benefit of the rollers as a transport system is that the charge carriers can be moved independently of the walking beam movements. The carrier will move rapidly into the high speed gas circulation. And, if necessary, the charge carrier can be moved just as fast out of the gas circulation at any time. This makes it possible to control the metallurgical transformations allowing the formation of different specific microstructures, such as bainite, martensite or mixtures thereof.



The rapid cooling unit may be followed by an annealing zone. A very interesting process is the following:

- High-temperature sintering
- Carburizing the edges with 0,7% C
- Rapid cooling, forming martensite on the edges
- Interruption of the cooling and keeping at a constant temperature for an isothermal transformation to bainite in the remaining material.



The temperature control, essential in such a system, is carried out using a pyrometer. The pyrometer monitors the temperature of the parts, using a wide focus to catch a mean temperature and not the temperature of a small section of a part. Controlling on a time basis has been tried as well, demonstrating remarkable homogeneity.

Example of an application:
Powder Distaloy HP, xq=350 HV10 after 1200°C. The parts have been positioned in several layers. A difference in hardness values over the charge carrier could not be determined. Please, bear in mind that this data is specific to the product. The configuration of the installation is as follows:

- Stearate zone with pusher mechanism
- High-temperature sintering zone with walking beam
- Rapid cooling with shaft-mounted rollers
- Cooling zone with conveyor belt and outlet purgelock

The results were comparable with sintering in a conventional high-temperature sintering furnace, followed by heat treatment in a conveyor belt sintering furnace with rapid cooling. Exact data concerning e.g. press densities or carbon contents are confidential.

Atmosphere measuring devices

NDIR gas-analyzing equipment with C-level control for endogas

Using a two-channel NDIR-analyzer (**N**on-**D**ispersing **I**nfrared **A**nalyzer), the partial pressures of CO and CO_2 are determined. Together with the temperature, the C-level can be calculated.

Measurements range between 0..30 Vol% for CO and 0..2% for CO_2. Optional in Nitrogen/Hydrogen sintering atmospheres, these channels can be used for 0..2 Vol.% CH_4 and 0..1 Vol% H_2O, which equals a dewpoint of –30 to +8°C.

The gas is sampled through an analyzing connection from the sintering zone or from the carbon restoration zone and led towards the NDIR-analyzer, passing a filter on the way.

The analyzing connection forms a direct connection with the muffle atmosphere through a 1" tube. The gas is samples through a T-joint. This T-joint is fitted with a ball valve on the non-used outlet, through which the analyzing tube can be cleaned when sooted. From the T-joint the gas will pass a spiral metal tube to chill the gas before the filter is reached.

This analyzing connection can also be used for a oxygen probe.

A NDIR-analyzer has to be cleaned regularly, once every week. For this a bottle with calibration gas and the required fittings are part of the supply.

Regulating the C-level is done by a separate controller, which uses the partial CO2 pressure as a set point. Depending on the composition of the gas, the carbon rich gas is added (e.g. methane, natural gas, propane,..).

When the furnace is fitted with a built in endothermic gas generator, the controller will adjust the air/gas ratio.

Gas analyzing unit with oxygen sensor

The oxygen sensors is suitable for atmosphere control in endogas or hydrogen/nitrogen mixtures.

Oxygen is in equilibrium with CO, CO_2, H_2 and H_2O, so once the partial pressure of oxygen has been determined, the composition of the atmosphere can be characterized.

In endogas the carbon activity (C-level) of the atmosphere can be calculated from the partial pressure of oxygen using the CO/CO_2 equilibrium.

Consequently, this analyzing unit can be used to measure and control the C-level of the atmosphere. Different from the NDIR-analyzer, the risk of sooting is reduced to a minimum. Neither is a weekly calibration required.

In nitrogen/hydrogen mixtures the atmosphere can never be "too good", so sampling alone will do; there is no need for regulating. The H2/H2O ratio, which is in direct equilibrium with the partial pressure of oxygen, enables a clear definition of the atmosphere conditions. We recommend to show the $\log(pO_2)$ on the display. It is also possible to display a dew point, but from scientific point of view this is not entirely correct and rather dated. We will be happy to advice you on this issue.

Oxygen sensors need reference air to measure accurately. The appropriate fittings are included.

Gas analyzing unit with a lambda-sensor

The lambda-sensor is a price favorable alternative to the oxygen sensor. In contrast to the oxygen sensor, this type of sensor can not be installed directly in the muffle. Using a pump, the furnaces atmosphere is sampled at an analyzing opening and led over the lambda-probe. With endogas this may result in sooting of the fittings, but by installation of a T-joint and a ball valve, these can be cleaned easily. In nitrogen/hydrogen mixtures this sooting problem does not exist.

As with the oxygen probe, the lambda sensor allows the measurement of the partial pressure of oxygen, through which the atmosphere can be characterized clearly. The calculations are analogue to the oxygen probe. There is no need for reference air.

If you have questions concerning measuring and controlling of atmosphere or are in need of additional documentation, please do not hesitate to contact us.