Resistance heated furnaces for protective gas and vacuum operation

Autors: Roland Waitz, Dr. Peter Wübben, Bernd Geiß, Wilhelm Müller

Various types of furnaces for heat treatment of materials under inert gas and vacuum are described. An introduction to the theory of inert gas/vacuum treatments is given. Different types of furnaces are described in their principal structure and in their most important applications. Necessary safety devices for working with combustible and explosive gases are also mentioned.

Most heat treatments are still carried out in air, for instance during ageing of aluminium, hardening and annealing of most steels or sintering of plenty of oxide ceramics.
Normal air contains 78 vol.-% nitrogen, 21 vol.-% oxygen and 1 vol.-% Argon. Alongside trace gases for example carbon dioxide. Frequently the big share of water vapour is forgotten. Accordingly the water content of 1 m^3 air at 30 °C and full saturation can amount to over 30 g in tropical climate, this equals approx. 3 wt.-%. As water vapour always has an oxidizing effect, especially at increased temperatures its share of protection gases is decisive. The indication of the water content is mostly made via the dew point, i.e. the temperate in degrees °C to which the gas has to be cooled until water fully condensates. This can be compared to the dew formation in nature in the morning or evening. Another mostly in diagram used description is the logarithmic relation of H_2O/H_2. Both indications can be converted without any problem.

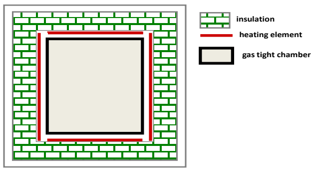
In order to melt metals from ore, protection gases have been applied by mankind since the beginning of the Copper Age approx. 6000 years ago. The main players carbon and ore have remained the same over the millennium. The protection gas atmosphere is generated by the incomplete burning of carbon and carbon monoxide. This reduces ore to metal according to the equation $CO + MeO_x = Me + CO_2$.
Modern applications such as flux-free brazing, sintering of powder-metallurgical parts, silicon carbide and silicon nitride ceramics or the production of graphite parts require an oxygen-free protection gas atmosphere. For special methods during the heat treatment of steel (for instance nitration and carbonitiriding) reactive gases such as ammonia are applied. The change-over between protection gases and reactive gases is fluent and is co-determined by the temperature and the material to be treated. However, it is roughly differed between flammable, explosive and non-flammable or neutral gases or gas mixtures. Apart from that a few special applications gases (compared to air alleviated oxidizing effects) for example carbon dioxide or exogas are used. The main reason for the utilization of protection gases is to reduce or avoid interrupting oxide coatings, which during brazing or sintering aggravate the connection of metals, making it impossible. They should for example also avoid burning of the material during pyrolysis graphite production. Especially when sintering with small grain sizes of the original material, and hence a big specific surface, oxygenic atmosphere would mean a complete conversion to oxide. Which protection gas atmosphere has to be used at which purity depends on the desired effect and on the material. Thereby the stability of the corresponding oxide or its affinity respectively to hydrogen or carbon monoxide, the most important reducing gases, is decisive. In both cases the reaction equilibrium is shifted to the side of the metal with increasing temperature. Materials such as chrome or silicon are always coated with an oxide layer at room temperature in a technical manageable atmosphere. Chromium oxide is still stable at 900°C in hydrogen with dew point of -80 °C, at 1200 °C it is however reduced to chrome in hydrogen with a dew point of -50 °C. The easiest form of protection gas furnace consists of flushing a conventional furnace additionally with the desired gas. Depending on the complexity for additional sealings, for instance in the door area

or the housing, usable results can be achieved in cases of not too sensitive materials, for instance when hardening or steeling. However remaining oxygen content in a one-figure percent range and relatively high protective gas use have to be expected, in order to produce a slight overpressure in the furnace. Due to safety technical reasons no toxic or flammable gases can be applied. As actual protection gas furnaces principally two construction forms can be considered; the hot wall and the cold wall furnace. The latter has to be distinguished between the classic form with shrouds, graphite, fibre, or stone insulation respectively. All construction forms can be combined if required.

A. Furnace Technology

1. The hot wall principle

In a chamber furnace a protection gas or vacuum tight retort (muffle) is inserted. Insulation and heating elements are situated outside the retort, i.e. they are not exposed to the protection gas atmosphere (picture 1-3). For heating elements and insulation the same material for the corresponding temperature range for air can be used.



Picture.1 Plan of hot- wall furnace for protective gas and vacuum

Picture 2
Protective gas furnace KS- S 160 with kiln furniture and changeable door for forced convection up to 950 °C or use in high temperature range up to 1150 °C.

Picture 3
Fibre insulated gastight furnace KF-240 S up to 1200 °C for reduction and sintering of precious metall pellets under hydrogen. Gas recooling by gas/water-heat exchanger for fast cooling. Furnace prepared for clean room installation.

Retort

The muffle can have the shape of a box or cylinder made of steel, quartz glass or ceramic. For quartz and ceramic only the tube cylinder shape is practicable for larger dimensions. The price, especially for larger dimensions, is in comparison to metal very high. Main application

field for ceramic is the high temperature range over 1200 °C, for quartz for high-purity processes until 1150 °C, e.g. in the semiconductor industry.
Disadvantages of the ceramic is the sensitiveness to thermo shock of the gas tight qualities (max. heating speed ranges depending on quality, size, wall thickness and temperature range are between 120 K/h and 400 K/h) and the limited availability of larger dimensions. At temperatures over 1550 °C ceramics are not mechanically of stable shape and vacuum tight anymore. Tubes made of monocrystalline alumina oxide (sapphire) are vacuum tight up to 1850 °C, however at the moment can only be delivered up to max. 40 mm diameter and 1 m length.
Quartz, in amorphous glasslike condition, in contrast has an excellent thermal resistance to changes, yet it tends to re-crystallisation at temperatures over 1050 °C, which during cooling can lead to destruction sooner or later. To achieve a possibly high life time an utmost cleanliness during construction and operation of the furnace has to be followed (cotton gloves). Practically quartz can also be applied up to 1350 °C without deformation, but it has to be held over 300 °C steadily.
The crystallisation to ß- cristobalite employs on the surface and is for instance strongly favoured by water vapour. At temperatures < 275 °C the cubic ß-shape converts into a tetragonal crystal structure with low density, which can lead to flaking and cracks. By regular “chemical stripping” with fluorine- or phosphoric acid a “thorough crystallisation” can be prevented. However, the thickness of the material is reduced with every treatment.
This problem only alleviated appears for opaque fused silicia produced by sintering. Fused silicia normally contains more impurities. Tubes made of both materials are only realizable up to a certain size. Currently diameters to 570 mm for quartz glass and 1000 mm for fused silicia with lengths to 4 meters are available in the industry.

The most common material for protection gas retorts are metals. The alloy qualities have to be adapted to the temperature applied and the process. Mainly austenitic steels such as 1.4541, applicable to 850 °C in air, 1.4841 to 1100 °C, inconel as welded construction to 1150 °C, cast to 1250 °C, APM^{TM} (only as tube) to 1300 °C are utilized.
If applied near to the maximum temperature cylindrical shapes are preferred, as less stress occurs. Same is valid due to the better pressure distribution for vacuum operation. Depending on size and complexity (material thickness, corrugated form) vacuum furnaces with hot-wall design can be realized up to 1100 °C. Thereby it has to be taken into account, that the stability of all established metallic materials decrease significantly between 500 – 800 °C. Under certain circumstances it is possible to work with a supporting vacuum of 80-90 % of the retort vacuum.
The gas inlet into the chamber usually is made by a tube with several bores. The gas thereby is distributed equally into the furnace chamber. At high gas flows, for instance testing capacitors or combustible cell components, the inlet tube is extended meander-shaped. It then serves as gas pre-heating unit.

Door

A special focus has to be put on the door construction.
The area of the door sealing has to be in the cold area due to the seal material which is mostly silicone or viton (max. 280 °C), and therefore the construction corresponds to the one of a cold wall furnace.
The door area is a weak point of construction. The losses in the generally not heated door side should be low and also the temperature change-across seals to the inner furnace should not be chosen to high. Ideal is a small, very deep door. For classic tube furnaces this is the case, however charging and unloading are difficult and only possible for small parts. The alleged

solution is a thick insulation plug in the door. The result from strong temperature gradients is broken ceramic tubes and distorted or cracked metal mufles. The perfect solution are screens towards the hot area, which provide a moderate temperature decrease in the muffle material, a subsequent insulation plug for reducing the remaining temperature and a vertical lead-out of the muffle annulus which decreases the load of the sealing by the thermal conductance of the muffle materials.
A water-cooling of the sealing spaces is still necessary at a furnace temperature over 400 °C. In some special cases (e.g. gas reactors) metal seals can be applied in the hot area; yet they can only be used once or can only be reused with a great effort, respectively. Furthermore the condensation problem has to be taken into consideration in the cold part of the door. A cooling in the door sealing via a temperature control unit with pressurized water (T<130 °C) or heat carrier oil (<220 °C) as fluid, helps to reduce condensation or avoid it completely.

Heating elements

The choice of heating elements for hot wall furnaces is rather unproblematic. As already mentioned the same materials for furnaces using air are applied. Chemical reactions with protection gas do not have to be considered. For tube furnaces T_{max} >1350 °C molybdenum-disilicide heaters ($MoSi_2$) up to 1850 °C can be used, otherwise FeCrAl-heaters as Kanthal A1™ (1400 °C) or APM™ (1420 °C). The rule of thumb is that the max. achievable furnace temperature has to be set approx. 50 °C under the max. temperature of the heating element, in order to achieve a reasonable life time. Max. temperature in a protection gas muffle is approx. 100 °C to max. 50 °C below the furnace temperature.

Insulation

There is no such thing as a perfect insulation for a protection gas furnace. On the one hand the losses of heat during heating up and dwell time should be low in order to save energy and keep the connection value of the furnace low, on the other hand the charged material should mostly cool down quickly, thus loose saved energy in a short time.
The first requirement is fulfilled perfectly by an insulation made of ceramic fibre or microporous material. Both have a very low heat conductance and heat storage capacity. The latter also supports a quick cooling; this however is constricted by the good insulation effect. The price for fibre insulation for temperatures above 1100 °C is relatively high. The design of the heat insulation for hot wall furnaces is therefore always a balancing act between energy consumption, cycle times and furnace price. Crucial is in the end the process security, which marks the limits, in which the furnace can be operated economical and perfectly. A good compromise is the combined insulation of lightweight refractory brick with a back insulation of fibre material or microporous materials. Additionally cool fresh air can be blown into the room between insulation and protection gas muffle by a fan via a distribution system. This way the furnace can be cooled actively. A further possibility, with more effort but really effective is to circulate and re-cool the furnace atmosphere by the means of a side channel blower via an external gas-water heat exchanger. The fan or the side channel blower respectively can be controlled by a frequency converter, depending on the temperature.
The achievable cooling times depend on the starting temperature, charge (weight, specific heat) and the discharging temperature. It is mostly in the range from 1-10h.

An even more effective cooling can be achieved by removing the protection gas muffle of the furnace and inserting a cooling unit, for example with hood kiln.

Temperature distribution

The temperature distribution or uniformity is determined by geometry, radiation conditions, convection and heat conductance of the gases. In general a deep construction form is preferred for hot wall furnaces. Mostly heating is done from 4-5 sides. In the case of unheated doors a strong temperature decrease occurs, which the more it extends into the furnace volume, the larger the furnace surface is. The heat transfer to the gas (except for hydrogen and helium) can mostly be neglected. The main players are convection and radiation. For natural convection the convection remains a ruling factor up to approx. 200 °C, after that the heat transfer and temperature is governed by radiation. In this case of forcing an increased convection by a gas recirculation fan the convection remains assertive up to about 400 °C and is clearly effective until 800 °C. Above that heat transfer and temperature are dominated by radiation. Should a precise temperature distribution over a big volume be necessary, for temperatures up to 400 °C a gas recirculation should be used, above 800 °C more zone heating makes sense, between 400 °C and 800 °C best to use both methods. Gas recirculation can be applied up to 900 °C. Should process require an application to max. 1050 °C (e.g. debinding at 300 °C and presintering at 1100 °C) with good temperature distribution required, the hot gas recirculation fan (with special fan wheel) should control to minimal turning speed, e.g. 1/s to prevent destruction.. Turning the fan wheel is always necessary, as otherwise the drive shaft can be damaged. For more zone heating it is generally worked with 2 or 3 control lines, distributed over the whole length of the furnace (door area, middle part, reverse side wall). With the measures described, temperature deviations of +/- 3 to +/- 7 K over the furnace volume can be achieved. With more effort e.g. 6 side heating and trim capability of the heating zones higher accuracies for special applications can be reached. However it is easier, to restrict the usable furnace volume in relation to the muffle dimensions in order to get a similar good temperature distribution.

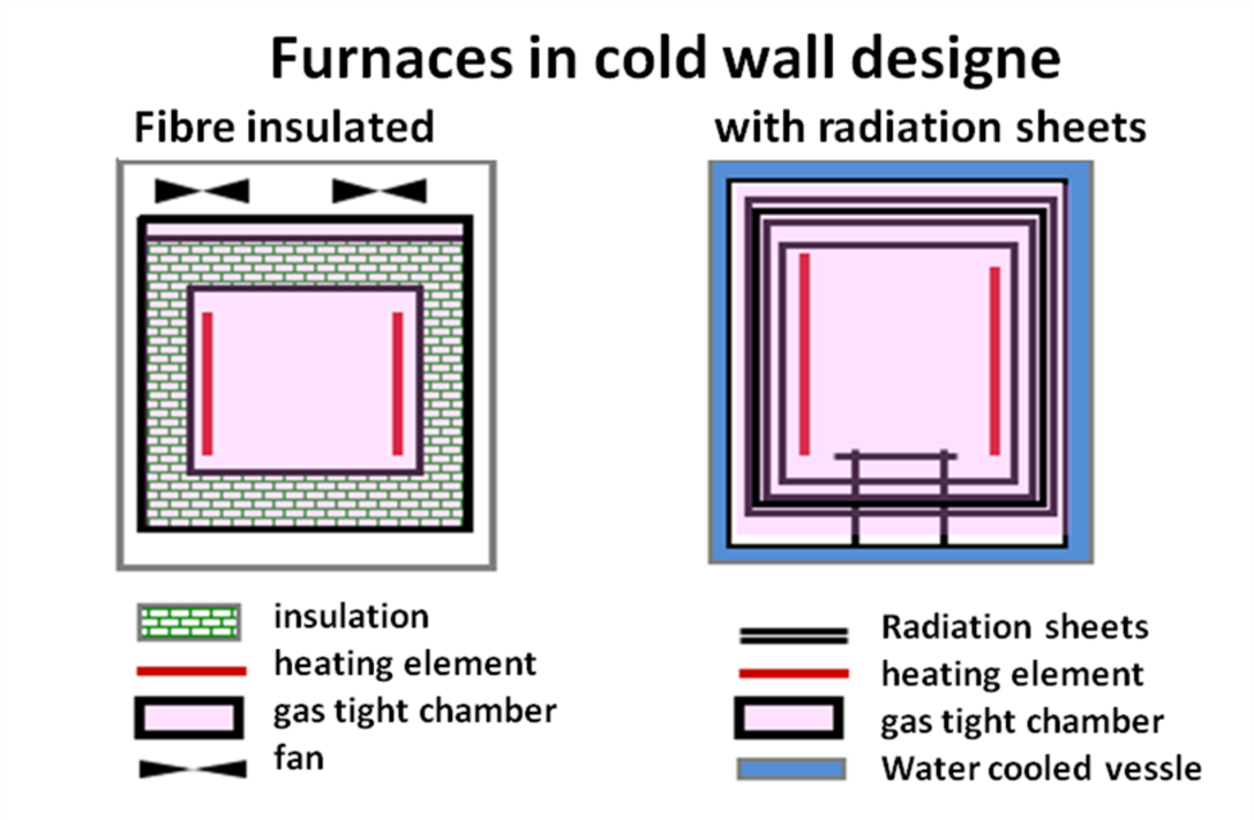
Control unit

The design of the control unit, particularly the positioning of the thermocouples in hot wall furnaces, requires some preparatory thoughts which consider the temperature – time regime of the process. LINN HIGHT THERM uses as standard program controller SE-402 from the manufacturer Stange (picture 4), which is distinguished by its very easy handling. The SE-402 can store 25 programs with up to 50 steps. Thermo couples can be used for precise control or data acquisition are directly connected to the device. From a PC with installed process leading system the controller can be controlled via an RS 422 interface. On the PC all the relevant data can be to archived or processed.

Picture controller
Program controller SE-402

One practicable solution is to place the measuring point into a welded-in tube in the protective gas chamber. Thereby it can be easily changed from the outside and is not exposed to the furnace atmosphere. This is important when using Pt-PtRh thermo couples with hydrogen operation. This couple is connected to the controller. A safety controller supervises the temperature in the void between the heater and the protective gas chamber. This assures that the protective gas muffle remains undamaged during fast heating – up cycles and/or heavy charges.
An additional flexible thermocouple in the furnace chamber, which is connected to a display and/or a temperature recorder, in many cases is reasonable, as it is able to measure the real temperature on the charge and protocol it.
The thermo couple is placed inside the chamber. It reacts when starting heating, depending on charge and muffle, more or less slow. Especially when heating fast and dwell times at low temperatures an "overshooting" of the furnace may occur. The heat first has to flow through the muffle, during this time the furnaces is continued to be operated at full power, as a result the furnace machine is overheating.
Although the heating is switched off the temperature in the chamber keeps increasing. The effect can be avoided by choosing a slow heating rate in the beginning and the choice of a suitable PID control parameter. Placing the thermo couple outside of the protection chamber enables a linear heating without overshooting, however it must first be detected how big the temperature difference between furnace and protection chamber is. With the help of a modern difference controller, which uses the inner elements as guidance and the outside element as actuating variable with an adjusted offset, this problem can be solved.

2. The cold wall principle



Picture 5: Design of cold wall furnaces with fibre insulation or radiation screens

Heater and insulation are situated in a gas- / vacuum tight chamber (picture 5) in a cold wall furnace. This means that the sealing chamber wall is not at furnace temperature. No special requirements for the material have to be taken in account with regard to the heat and temperature stability, yet mostly stainless steel is used in order to prevent corrosions. Furnaces being operated under over pressure must therefore be constructed according to that technology. High-pressure sintering furnaces (picture 6) are needed for producing non-porous powder metallurgical parts and ceramics. Under pure oxygen atmosphere up to pressures of 1000 bar is used for high temperature superconductor research as well as for the heat treatment of rubies in order to improve their colour. If requested e.g. for ultra high vacuum furnaces or to avoid contamination in the nuclear field the material can be electropolished. In contrast to that insulation and heating conductors are exposed to the furnace atmosphere and temperature, this has to be considered when choosing the material and can lead to different furnace concepts depending on type and charge and heat treatment processes.

Picture 6: High pressure furnace up to 1000 °C. Operation under pure oxygen up to 100 bar. Heated with molybdenum-disilicide. For development of High-Temperature Superconductiv materials (HTSC).

Heating conductor materials

Established heating conductor materials for protection gas furnaces are the same as for the hot wall furnaces iron-chrome-alumina alloys, molybdenum-disilicide, molybdenum, Wolfram and graphite. In special cases due to the chemical behaviour, Tantal heaters are used. The max. temperature that can be applied in different gases are in the table below. For combined protection gas/air operation only FeCrAl- alloys and $MoSi_2$ are suitable. The classical cold wall design with radiation plates made of the same material as the heaters can be realised with $MoSi_2$, as no thin-walled plates are manufactured of $MoSi_2$.

Atmosphere	Chem. formula	APM (A1) FeCrAl	Kanthal Super 1700/1800/1900	Molybden Mo	Tungsten W	Graphit C
air	$N_2, O_2,$ Ar	1400 °C	1700/1800/1850°C	400°C	500°C	400°C
oxigen	O_2	1300 °C	1700/1800/1850°C	<400°C	<500°C	*<400°C*
nitrogen	N_2	1200 °C	1600/1700/1800°C	~ 1480°C	~ 1480°C	1700°C
argon	Ar	1400 °C	1600/1700/1800°C	2000°C	3000°C	3000°C
amonia	NH_3	1200 °C	<1400°C	1100°C	<1480°C	*<1700°C*
Hydrogene dry Dew point -60°C	H_2	1400 °C	1150/1150/1150°C	1800°C DP< -28°C	3000°C	1700°C (2400°C)
Hydrogen wet Dew point +20°C	H_2	1400 °C	1450/1450/1450°C	<1400°C	<1350°C	
water vapor	H_2O	*1200 °C*	*1600/1700/1800°C*	*700*	700°C	
Exogas 10%CO_2, 5%CO,15%H_2		1150 °C	1600/1700/1700°C	<1200°C (CO_2)	900°C	
Endogas 40%H_2,20%CO		1050 °C	1400/1450/1450°C	<1400°C (CO)	900°C	2500°C
Vacuum < 10-3mbar		1150 °C	1150/1150/1150°C s.Dia	1500°C	2200°C	2200°C

Tab. 1 Max. heating element temperature

Picture 7 Cold wall furnace KKV 140/270/2000 up to 2200 °C.
Toploader with tungsten mesh heater, turbomolecular pump up to 10^{-5} mbar, gas supply and burning device for hydrogen.

2a. Furnaces with radiation screen insulation

Cold wall furnaces with radiation screens (picture 7) are applied as high vacuum furnaces up to 10^{-7} mbar, vacuum hardening furnaces with quick gas chilling, for heat treatment and sintering of sensitive alloys, e.g. with niobium- or chrome shares, and for active brazing.

Furnace chamber

The furnace chamber consists of stainless steel and generally needs water cooling. This can be designed as double jacket or with a welded cooling coil. Attention has to be paid to the double jacket that a directed water flow is ensured, that there are no points in the flow shadow or no formation of dead rooms, in which gas bubbles can accumulate. Especially the latter can lead to a destruction of the vessel due to over heating. When using a cooling coil ensure sufficient heat change-over and complete cooling of the whole vessel, especially in the door area.

Temperature measuring and control

A measuring up to max. approx. 2100 °C can be done by Wolfram-Rhenium-thermocouples. At higher temperatures a pyrometer is required. A combination of both measuring methods is reasonable. The furnace can also be exactly controlled in the lower temperature area with a thermo couple. A simple pyrometer only works from approx. 800 °C. In the overlapping range of thermocouple and pyrometer measuring range the adjustment of the pyrometer can be controlled. (Emission factor, geometrical order). At higher temperatures the thermo couple is retracted to the insulation. It is strongly recommended to install a temperature limiter with additional pyrometer.

Insulation

The poor efficiency of the radiation insulation leads to a higher energy consumption. A furnace with Wolfram mesh heater with diameter 200 mm and height 350 mm, temperature up to 2000 °C and 5 radiation sheets requires a connection power of approx. 36 kW under vacuum operation, a higher power at argon atmosphere of approx. 6 %, nitrogen atmosphere of approx. 8 % and operation under hydrogen atmosphere of approx. 50 % can be expected. The number of radiation sheets is matched to the max. temperature of the furnace. Common are 6 -9 screens in the temperature range from 1600 – 2800 °C. The heat loss at vacuum can be calculated roughly with the following formula for small distance between the shrouds.

$$E = \sigma * \frac{(T_i^4 - T_a^4)}{\left(\frac{1}{\varepsilon_i} + \frac{1}{\varepsilon_a} - 1\right) + n * \frac{2}{\varepsilon_s}}$$

E:	losses	[W/m²]
σ :	Stefan-Boltzmann-parameter	[$5,67 \times 10^{-8}$ W/m²]
T_i:	furnace temperature	[K]
T_a:	housing temperature	[K]
n:	number of shrouds	

ε_i: emission factor heaters; ε_a: emission factor housing, ε_s: emission factor radiation screen

The distance between the single screens can be very small for a vacuum furnace. Under gas atmosphere the insulation effect can be optimized by variation of distances, bigger to the outside and smaller towards the inside. The distance is chosen that large heat losses by conductance are minimize, however small enough that no convection of the gas atmosphere can be formed.
The screens in the very inner are mostly manufactured of the same material as the heaters. From the in- to the outside a change to materials more moderate in price can be made, for instance Wolfram-Molybdenum-Inconel-Stainless steel.
The radiation screen packets having a poor insulation effect in contrast to fibre material, though have advantages regarding achieving high cooling speeds. This is supported by low specific heat of the materials applied (Mo: 0.251 J/(g K) at a specific weight of 22 g/cm³ in comparison to steel 0.449 J/(g K) bei 7.8 g/cm³).

Heating:

The most established heat conductor materials are molybdenum to approx. 1600 °C and Wolfram up to 2400 °C. For operation at higher temperatures a strongly shortened life time can be expected (the exhaust rate of Mo at 1800 °C is 3 x 10^{-2} mg/(cm² h)). Wolfram only reaches that exhaust rate at 2400 °C.
The heating elements can be produced of sheets being non-perforated, perforated or strips (picture 9) of wire or mesh texture (picture 8). Sheets are especially used for Mo-heaters, canvas for Wolfram. Due to the low resistance of the heating elements, very high heating currents which can amount to some 1000 A are necessary.

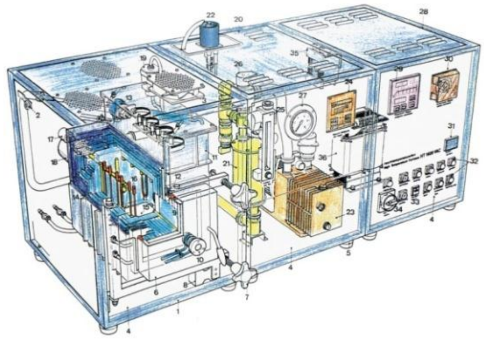
Pictrue 8 Wolfram – Maschenheizer
T_{max} 2300 °C mit Strahlungsschirmen
tungsten – mesh heater with radiation screens for T_{max} 2300 °C.

Picture. 9 Wolfram – Bandheizer
T_{max} 3000 °C mit Strahlungsschirmen und Chargentisch.
tungsten – strip heater with radiation screens and working plate for T_{max} 3000 °C

2b. Furnaces with fibre or stone insulation

If the requirements of vacuum and dew point of the furnace atmosphere are not too high (vacuum up to max. 10^{-2} to 10^{-3} mbar) ceramic fibre, graphite felt (up to 10^{-4} mbar, with pumps of a very high capacity up to 10^{-5}mbar) or a brickwork (pictures 11-12) can be utilized as insulation.
Common are ceramic fibre materials to 1800 °C, as they are utilized for furnaces operated on air. If reducing gases, especially with hydrogen at temperatures above 1600 °C are applied, a special high-quality fibre material with low SiO_2 content and a higher Al_2O_3 content has to be used. Conventional fibre material would be decomposed quickly due to reduction reactions. In the case of the furnace being operated above 1700 °C under hydrogen, e.g. nuclear industry, the very inner insulation layer is substituted by brickwork with hollow corundum bricks, thereby longer life under extreme conditions is ensured. Graphite felt insulation is available in qualities which in combination with graphite heaters allow furnace temperatures to above 2800 °C. But then the vaporisation rate of carbon will be extremely high. The efficiency of the insulation, in contact with the working gas, is strongly influenced by its heat conductance. This amounts up to 7-fold of air at hydrogen and helium depending on the temperature. This has to be considered when constructing insulation and heaters.

Picture 11
HT 1400 GT Vac Protective gas/vacuum furnace up to 1400°C with 3 – zone heating.



Picture 12.
Drawing of HT 1600VAC with gas supply and burning device for hydrogen operation.

A compromise between low energy consumption and still tolerable cooling speed has to be found when constructing the insulation. The reason for that is that protection gas furnaces let themselves open only at relatively low temperatures, due to the heat conductor material and combustibles, and cooling of the chambers with protection gas is really expensive (gas consumption) or with gas re-cooling too complex. Moreover the operator shall not be put in danger due to hot furnace housing.
It has been approved to turn the back to the strict cold wall principle and to surround the gas tight furnace chamber on the outside with two housings. The thickness of the insulation is chosen so that the inner housing reaches a max. temperature of 200 °C. This heat is quickly conducted by ventilators, which blow air through the interspaces to the outer housing. In this way cooling times of approx. 1 h from 1400 °C to 600 °C can be achieved, at the same time the surface temperature of the furnace remains at max. 40 °C above the ambient air temperature.
The advantage of this furnace principle is a lower capacity requirement by the factor 5 in comparison with a cold wall furnace with radiation sheets and the possibility to change during temperatures over 1400 °C from oxidizing to reducing atmosphere with $MoSi_2$ heaters during a furnace operation. The downside thereby is the limitation of vacuum and dew point. The increased surface of the ceramic fibre is responsible for that. Especially nothing that ceramic fibres are strongly hygroscopic. When opening the furnace the humidity of the ambient air appears as thin water layer on the fibre surface and during the next heating it is released progressing from the inside to the outside again. This is the reason why furnaces should not be kept open for a long time, as otherwise significant water quantities can condense. When restarting the furnace this can be noted by a clearly reduced heating speed as well as a poorer end vacuum and a higher dew point.

B. Safety technology

All safety technical systems have to be designed with redundancy.

The dangers posed by utilization of protection gases can be intoxication, suffocation, deflagration and explosion.

Suffocation

When using neutral gases such as nitrogen or argon at usual flushing quantity and good chamber ventilation no threatening concentration of gas can arise, even if the exhaust gas is directly led into the chamber. It has to be noted, that argon (1,784 kg/m³) is considerably heavier than air and nitrogen slightly lighter. This can lead to problems in poorly ventilated rooms in case of argon. Carbon dioxide (1,977 kg/m³) basically should be led to the outside via a fan. A general rule is that rooms with protection gas use have to be well ventilated. Furnace manufacturer and end customer should therefore design a common room air concept.

Intoxication
Especially mixtures of exo- and endogases, which contain carbon monoxide (CO) are dangerous when used in protection gas furnaces. The MAK-value (maximum work station concentration) for CO has low value of 30 ppm by law. Especially dangerous is the CO as it is odourless and even at low concentrations in the breath during longer exposures it is concentrated strongly in the blood, due to its high affinity to haemoglobin (red blood colorant).

Amonia (MAK: 20 ppm) can be detected in low concentrations due to its penetrative smell.

Deflagration-; explosion danger
Gases can be divided into • oxidizing – exotherm: air, water vapour, carbon dioxide • neutral: nitrogen, argon, helium, • reducing – endotherm; hydrogen, carbon monoxide, methane, ammonia and so on. Mixtures of hydrogen and nitrogen with H_2 content < 5 vol.-% are reducing but not flammable. From the safety side they can be treated like neutral gases.

Explosion limits of different gases at 20°C und 1013 mbar

Gas	Chem. formular	Specific weight (-) < air (+) > air	Lower Explosion-limit 20°C,1013mbar	Upper Explosions-limit 20°C,1013mar	ignition Tempert.	danger explosiv (Ex) poison (G) suffocation(E)
ammonia	NH_3	0.72 kg/m³ (-)	15%	27%	690°C	Ex,G,E
hydrogen	H_2	0.084 kg/m³(-)	4%	74%	570°C	Ex,E
methan	CH_4	0.671 kg/m³(-)	5%	15%	580°C	Ex,E
carbonmonoxid	CO	1.17kg/m³ (-)	12.5%	74%	630°C	Ex,G,E
propan	C_3H_8	1.88 kg/m³ (+)	2.2%	9.5%	480°C	Ex,E
Endogas 1 C_3H_8	31% H_2, 23%CO 46% N_2	0.89 kg/m³ (-)	7%	72%	560°C	Ex,G,E
Endogas 21 CH_4	40% H_2, 23%CO 37% N_2	0.79 kg/m³ (-)	7%	72%	560°C	Ex,G,E
Exogas	14% H_2, 7%CO 5% CO_2,	1.12 kg/m³ (-)	17%	72%	560°C	Ex,G,E
Cracked amonia	25%N_2, 75% H_2,	0.38 kg/m³ (-)	3%	72%	530°C	Ex,,E

Tab. 2 Explosionsgrenzen und Zündtemperatur von Gasen bei 20°C und 1013 mbar
Explosion limits and ignition temperature for different gases at 20°C and 1013 mbar

In order to fill a furnace chamber with flammable gases, no oxygen shall be contained. There are three different methods for that:

1. slow insertion of fuel gas over 750 °C
2. free-flushing with inert gas
3. evacuating, subsequently filling with protection gas

1. Initiating of fuel gases
This method is the most economical one, but has two crucial disadvantages:
Normally it can only be applied for continuous furnaces or furnaces with sluices; otherwise the combustible has to be heaten up to at least 750 °C in the air.
In the combustion chamber the burning temperature of 750 °C shall not be exceeded. In the case that an unfavorable volume relation from the cold to the hot area exists, e.g. if the heat insulation is situated inside the protection gas chamber or for conituous furnaces in whose outlet often has a cooling section, it may be flushed free separately with neutral gas. The filling process is finished as soon as the gases led out of the furnace are flammable. Before opening the furnace this procedure has to be repeated, this time with air. The problems are the same as mentioned above. Additionally the furnace should still be filled with air for a longer time, to enable the gas venting out from the insulation.

2. Free flushing with inert gas
This is the most wide spread method. Before initiating the fuel gases the furnace is brought to a value of < 1 vol.-% by flushing with nitrogen or argon.

Calculation of the remaining gas content in dependence on the concentration of Ko at the beginning and the flush factor S=V/Vo:

$$K = Ko * e^{-V/Vo} = Ko * e^{-s}$$

Vo = Chamber volume
Vs = flush gas volume
Ko = concentration at the beginning
K = end concentration

In case that a flush gas flow Vs(t)is given, the necessary flushing time for reaching 1 vol.-% remaining oxygen content: $t = -\frac{Vo}{Vs(t)} * ln\ [\frac{0{,}01}{0{,}21}] = 3 * \frac{Vo}{Vs(t)}$

Theoretically a furnace with 1 m³ inner volume V_o (this does not correspond to the usable chamber but the total volume inclusive insulation at the hot wall or shroud area respectively of the cold wall furnace) has to be purged with 3 m³ purging gas V. This corresponds to a purging factor of 3. Due to safety reasons (death corners, insulation) it is worked with purging factor 5, hence a slight over pressure in the furnace has to be paid attention to. The inlet point of the feeding gas has to be selected or designed so that the complete furnace chamber and also pre-connected and downstream components (tubes, bubbler, condensation traps) are flushed.
At the end of an operation the procedure has to be repeated in order to flush the furnace free. Thereby pay attention to the content of the flammable gas now 100 vol.-% and not 21 vol.-% (oxygen content of air). The flushing factor should hence by increased to approx. 6,5.

In order to monitor the procedure and design it absolutely safe, the following equipment, surveillance functions respectively are to be integrated into the gas unit:

a. Monitoring of purging time, purge gas flow and purg gas stock (in case of bottles). By inductive monitoring of a minimal gas flow (G_{min}) in the flow measuring device and a minimal flushing time (S_{min}) a sufficient purging can be guaranteed via in advance set values (S_{min} x G_{min} > 5 x Volume) in the control unit. The purge gas stock is controlled by the bottle pressure, which has to be 12 times the amount of the chamber volume in order to being able to purge the furnace free after the treatment with protection gas.
b. Measuring of the oxygen content in the furnace (nominal value < 1 vol.-%) also detects appearing leaks or stronger oxygen gas release.
c. By a stop valve in the gas outlet a slight over pressure of approx. 5-50 mbar in the furnace is generated, which avoids air entering the chamber.
d. The protection gas flow is also monitored, for example during cooling the protection gas flow stops, an under pressure in the chamber occurs which can lead to implosion or suction of air into the chamber. In both cases flammable gas mixtures could develope.
e. Locking of doors from the initiating of the protection gas until the stopping of the purging procedure.
f. Gas sensors at potentially endangered points (door sealing, gas unit, chamber ceiling).
g. Provide emergency water supply in case of breakdown of the cooling water, to prevent overheated seals.

Purging factor	Oxygen content (%)	vacuum (mbar)
0	21	1031
1	7.7	378
2	2.8	137
3*	1	45*
4	0.38	18
5	0.14	6.9
6	0.05	2.4
7	0.019	1
8	0.0007	3×10^{-1}
9	0.0025	1×10^{-1}
10	0.0009	5×10^{-2}
16	0.000006	3×10^{-4}

Tab. 3 Restsauerstoffgehalt in Abhängigkeit vom Spülfaktor oder Vakuum das einen vergleichbaren Sauerstoffpartialdruck erzeugt.
Residual oxygen content depending of purging volume and comparable vacuum with same oxygen level

3. Evacuating and subsequent filling with protection gas

This technique can be applied for furnaces which are also designed for vacuum operation apart from the protection gas operation, for example if the furnace process requires a combined gas/vacuum treatment or highly pure atmosphere (partial pressure $O_2 < 10^{-6}$ mbar). Flammable mixtures are already avoided by the pre-evacuation of the furnace to 45 mbar. In practice it is mostly evacuated up to the 10^{-1} mbar range, which can still be reached easily and quick with a one stage rotary vane pump. For additional safety the pump is switched off and the pressure increase is registrated (automatic leak test): Should this value be over the preset

value, leaks in the system can be expected, and those have to be fixed before initiating the protection gases. For unloading the furnace has to be flushed free with inert gas, as described above. In single cases a repeated evacuation is also possible, the gas ballast inlet of the vacuum pump must than be connected to the inert gas. The conveyance-mass of the pump must be throttled so far that it is possible to burn off gases without any problem.
The pre-evacuation of the furnace chamber is recommended for the treatment of bulky goods or wire wrapped on coils, as the cavities can only be flushed with much time and gas consumption.

Nowadays, electrical heated protection gas and vacuum furnaces are utilized in the temperature range from 100 °C to 3000 °C. The application spectrum ranges from drying in the semi conductor industry to the production of special graphite. Between that, are the broad working fields of heat treatment of copper wire, other non-ferrous heavy metal, stainless steel and platinum - and refractory materials. For production of fluorescent substance, nanopowder, hyperpure silicon, non-oxide ceramics and plenty of chemical processes protection gas furnaces are indispensable.
This is the reason why protection gas- and vacuum furnaces are a key technology of our era, even if it is little known.

Roland Waitz
geb 12.5.1958.
1978-1984 Studium der Geophysik an der Ludwig-Maximilians-Universität München.
1985 Diplomarbeit Geophysik Gravimetrie.
1986-1987 Voruntersuchungen zur Kontinentalen Tiefbohrung (KTB). Magnetik und Radiometrie.
Seit 1987 bei der Firma Linn High Therm, Eschenfelden als Vertriebsingenieur tätig.

Roland Waitz
born 12.5.1958.
1978-1984 studies at the Ludwig-Maximilians-University Munich, subject Geophysics.
1985 dissertation on Geophysics Gravimetry.
1986-1987 Magnetic and radiometric survey at the location of the Continental Deep Drilling Project.
Since 1987 sales engineer at Linn High Therm.

Dr.-Ing. Peter Wübben
geb. 14.10.1956
1976 - 1982 Studium Brennstoffingenieurwesen an der RWTH Aachen
1983 - 1987 Doktorand bei der Bergbauforschung Essen
1987 Promotion an der Universität Essen
1987 - 1995 Anwendungsingenieur, Techn. Leiter, Niederlassungsleiter bei Airoil Flaregas

1995 - 1998 Abteilungsleiter bei Wistra Thermoprozesstechnik
1998 - 2010 Spezialist für Sonderanlagen bei Elino Industrie-Ofenbau
seit 2010 Techn. Leiter bei Linn High Therm

Dr.-Ing. Peter Wübben
born 14.10.1956
1976 - 1982 Studies of Combustion and Fuel Engineering RWTH Aachen
1983 - 1987 Doctoral thesis at Bergbauforschung Essen
1987 Promotion at University Essen
1987 - 1995 Application engineer, Technical Manager, Office Manager Airoil Flaregas
1995 - 1998 Section manager at Wistra Thermoprozesstechnik
1998 - 2010 Specialist for special furnace plants at Elino Industrie-Ofenbau
Since 2010 technical manager at Linn High Therm