

Carbon controlling with O₂-probe and L-probe

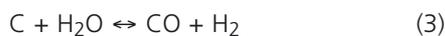
Džo Mikulović, Dragan Živanović, Florian Ehmeier

Gas carburizing still plays an important role in heat treatment. Temperature and carbon potential (C-Potential) of the atmosphere are the essential parameters for the process control. Till this day there is no direct measurement method for C-Potential which could be used for online process control. The measurement of the oxygen partial pressure in the furnace atmosphere is the most used indirect method for the control of the C-Potential. There are different types of oxygen probes. In this article the essential differences in construction will be discussed as well as their advantages and disadvantages.

Nowadays, the process of gas carburizing is well understood [1]. The most important parameter beside temperature is the carbon potential (C-Potential). The C-Potential of a furnace atmosphere is defined as the carbon content (expressed in weight percent) of unalloyed austenite which is in equilibrium with the corresponding atmosphere. An atmosphere with e.g. 0.7% C-Potential would be in equilibrium with an austenite with 0.7% C. An austenite with more than 0.7% C would be decarburized up to 0.7% C whereas an austenite with lower C content would be carburized up to this value. It should be also mentioned that the C-Potential of a certain atmosphere depends on temperature. In order to get a definite carburization depth in the parts, C-potential of the furnace atmosphere has to be measured and controlled during the heat treatment process.

Indirect determination of the C-Potential

Basically, the C-Potential can be determined directly or indirectly. The direct measurement methods are not suitable for a continuous measurement of C-Potential and a control based on this measurement. However, the direct methods are used to check and to adjust the indirect measurement methods if necessary. Following equations are the basis for the indirect determination of the C-Potential:



These reactions take place in the furnace atmosphere as well as on the surface of the work pieces. It follows from these reactions that the CO gives off the carbon and O₂, CO₂ and H₂O absorbs it. If the C-Potential of the atmosphere is higher than the carbon content on the surface of the work pieces, CO transfers the carbon to the work pieces whereas

O₂, CO₂ and H₂O detract the carbon from the furnace atmosphere. If the C-Potential is lower than the carbon content on the surface of the work pieces, CO transfers the carbon to the atmosphere whereas O₂, CO₂ and H₂O detract the carbon from the work pieces. In both cases these reactions cause an equalization of the carbon content on the surface of the work pieces and the C-Potential of the atmosphere.

For the calculation of the C-Potential also the activity becomes important. The activity depends on temperature and content of carbon which is dissolved in austenite. For a given temperature each C-Potential equates to a certain value of the activity $a_c(\% \text{C}, T)$. The reactions (1)-(3) can be linked to the activity via following equations:

$$\frac{1}{K^{\text{O}_2}} \cdot \frac{p(\text{CO})}{\sqrt{p(\text{O}_2)}} = a_c(\% \text{C}, T) \quad (4)$$

$$\frac{1}{K^{\text{CO}_2}} \cdot \frac{p^2(\text{CO})}{\sqrt{p(\text{CO}_2)}} = a_c(\% \text{C}, T) \quad (5)$$

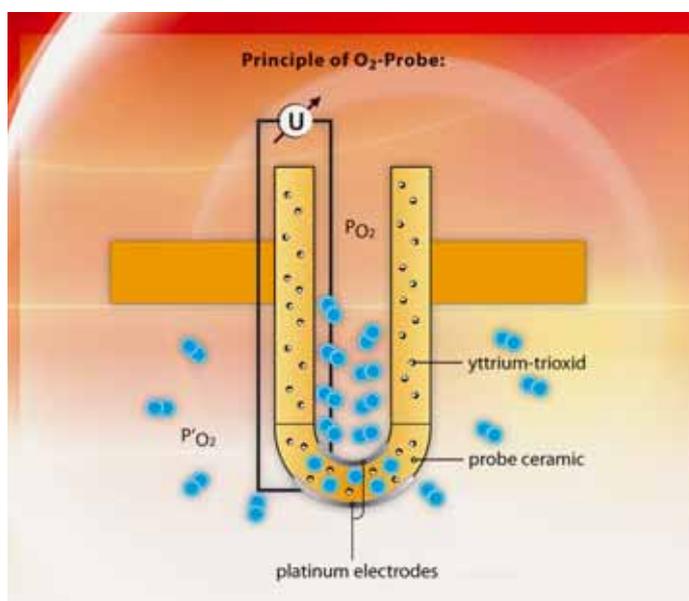


Fig. 1: Principal construction of an O₂-Probe

$$\frac{1}{K_{H_2O}} \cdot \frac{p(CO) \cdot p(H_2)}{p(H_2O)} = a_c (\%C, T) \quad (6)$$

The equilibrium constants of equations (1)-(3) - K_{O_2} , K_{CO_2} and K_{H_2O} - are functions of temperature. These functions are well known in literature. Therefore, in order to calculate the C-Potential it is enough to measure the temperature and the partial pressures appearing in one of the equations (4)-(6). In certain atmospheres, e.g. endogas or mixtures of nitrogen and methanol, the partial pressures $p(CO)$ and $p(H_2)$ are much higher than the partial pressures $p(O_2)$, $p(CO_2)$ and $p(H_2O)$. When the C-Potential is changing, the partial pressures $p(CO)$ and $p(H_2)$ vary percental only a little compared with the percental variation of $p(O_2)$, $p(CO_2)$ and $p(H_2O)$. This is the reason why for the calculation and control of the C-Potential in most cases the partial pressures $p(CO)$ and $p(H_2)$ are assumed to be constant and only the partial pressure or volume contentment of O_2 , CO_2 or H_2O is measured.

For the control of a process continuous measurement is essential. On the market available dew point sensors, which could be used for continuous determination of the partial pressure of H_2O , are not robust enough for measurements in carburizing atmospheres. Therefore they didn't establish oneself in carburizing processes. The measurement of CO_2 is done continuously with infrared sensors. This measurement is frequently used as a comparison measurement. The CO_2 measurement is slowly compared with the O_2 measurement. In addition, the CO_2 sensor has

higher maintenance requirements because of the drift of zero point. Therefore, the zero point has to be corrected daily with nitrogen if the CO_2 measurement is used for C-Potential control. These are the main reasons why the measurement of oxygen partial pressure with the oxygen probe (O_2 -Probe) has become widely accepted for the control of C-Potential.

Construction and functionality of the O_2 -Probe

Fig. 1 shows the principal construction of the O_2 -Probe. The measuring cell of a O_2 -Probe consists of an one-sided closed probe ceramic. The material is zirconium dioxide dotted with e.g. yttrium trioxide. These intentionally implemented lattice defects enable the needful oxygen ions conductivity. Furthermore, these defects also stabilize the ceramic against thermal and mechanical stress. The ceramic is connected with platinum inside and outside. These are the electrodes of the measuring cell. On the inside of the probe reference gas is provided, mostly air with the known 20,9% O_2 . The outside is exposed to the furnace atmosphere. The O_2 -Probe is applicable for measurements in furnace only at temperatures above 700°C since the oxygen ions conductivity is temperature dependent.

At the inside platinum electrode oxygen is reduced to oxygen ions. These ions move via ceramic defects to the outer electrode in order to compensate the low oxygen concentration there. The accumulation of electric charges results in a voltage (Nernst equation)

$$U = 0.0496 \cdot T \cdot \log \left(\frac{p(O_2)}{0.209} \right) \text{ mV}, \quad (7)$$

which can be measured between the electrodes. The voltage increases when the oxygen content in measuring gas decreases. In the process of carburizing this imply the following: higher voltage corresponds to a higher C-Potential, contrariwise lower voltage corresponds to a lower C-Potential.

Nowadays, there are mostly three different models of O_2 -Probes on the market (**Fig. 2**):

- The first model has an one-sided closed zirconia element which is glued or welded to a ceramic pipe made from alumina. Apart from that the probe works as described, reference air inside, furnace gas outside, oxygen ions movement through the ceramic.
- The second model has a zirconia ball.
- The third model has a continuous, closed and dense zirconia pipe.

Probes with a zirconia element or ball are mostly cheaper than the probes with continuous zirconia pipe, but on the other hand these probes have lower leak tightness. This results from the difference of the extension coefficients of the two different ceramics. Due to different extension coefficients fine hair cracks arise at the contact point of the two ceramics. Through these hair cracks the furnace atmosphere ingress into the inside of the probe ceramics and modifies the reference air. The probe voltage decrease and the calculated C-Potential is lower than the actual value in furnace. This error can be minimized by increasing the flow rate of the reference air.

For calculation of the C-Potential via O_2 measurement and the equation of chemical equilibrium, the temperature is important twofold:

- Firstly, the temperature is needed for the determination of the O_2 content (see equation (7)).
- Secondly, the temperature is needed to determine the equilibrium condition from which the C-Potential is calculated (see equation (4)).

Therefore, more often than not the probe temperature in furnace atmosphere is measured with a thermo couple which is fitted inside the probe ceramic.



Fig. 2: Different types of O_2 -Probes

It is recommendable to use probes with thermocouples of type S or without thermocouple. In this case a separate furnace thermocouple which is mounted close to probe has to be used for the calculation of the C-Potential. There are also low cost probes – mainly with zirconia element or ball – equipped with thermocouple of type K. Because of the ceramic design it is possible to use only thinly thermocouples. Trough ceramic leakages furnace atmosphere reaches the thermocouple. This gives rise to lower accuracy and a reduced lifetime. For this reason probes with thermocouple K are only conditionally recommendable.

Uncertainty of measurement of the O₂-Probe in the field

When handling the O₂-Probe in the field following points should receive attention:

- The O₂-Probe is exposed to mechanical and thermal stress. Since the ceramic is not break-proof the probe is imperiled accordingly. Particularly the unbalance of circulating fans can decrease the probe life time. Therefore, mounting of the probe near such equipment should be avoided. Furthermore, due to thermal sensitivity the exchange of the O₂-Probe under process conditions takes a long time.
- Probe leakages increase in the course of time. The increase of the porous area and hair cracks in the ceramic lead to a growing flow rate of reference air. Aside from the already described adulteration of probe voltage also a temperature adulteration of the O₂-Probe thermocouple occurs.
- With the Material and the frames washing agent residues and covering paste enter the furnace. These chemicals evaporate in the furnace and precipitate on the outer platinum electrode. This yields a falsified measurement and a reduced life time of the probe. To keep away the washing agent and covering pasta residues from the probe element, an extended purging of the probe is necessary. One of the most known problems is sooting of the outer electrode, particularly when the process is controlled near to the soot limit. The sooting of the electrode yields a falsified measurement too. In this case the only

Fig. 3: L-Probe



help is a cyclic probe purging with air. Attention! The valve for air purging has to be mounted near the probe. Long pipes produce long dwell time after the purging. The valve must close well and should not jam.

- At temperatures above 1100°C the electron conduction in the zirconia is growing highly and cannot be neglected anymore [2][3]. Decarburizing processes at high temperatures, e.g. decarburizing of cast iron, can be controlled with the oxygen probe if and only if the electron conduction effect is compensated.
- If chromium-nickel steels are used as protection pipe, it can be detected with the microscopes that near the zirconia tip after a while chromium parts of the material dissolve away in the furnace. Soot particles and oxygen cling to the porous surface. The soot on the probe cause faulty measurements. The oxygen induces increased probe reaction time and long relaxation time after probe purging.

Construction and functionality of the L-Probe

Due to the above mentioned troubles attempts were made to place a smaller oxygen measurement cell outside the furnace. The use of oxygen conductive solid electrolytes, e.g. zirconia ceramic, for combustion control in the automotive industry has led to miniaturized oxygen probes, namely the Lambda probe (L-Probe) (Fig. 3). Because of a large production quantity a robust and economically priced sensor is available today.

The functionality of the L-Probe and O₂-Probe is basically the same. However, there is an essential difference in construction and measuring setup. The form of the L-Probe is similar to the O₂-Probe, namely a one-sided closed pipe (Fig. 4). The ceramic is also the same. The probe ceramic surface is covered with a micro porous platinum layer inside and outside. These two platinum layers are the electrodes of the measuring cell. The outside platinum layer is

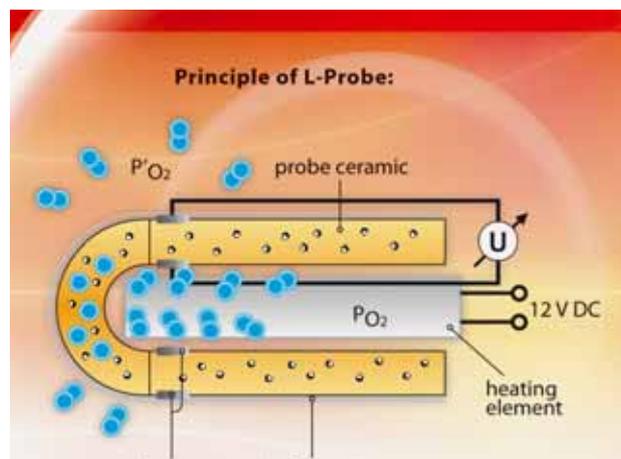


Fig. 4: Construction of the L-Probe

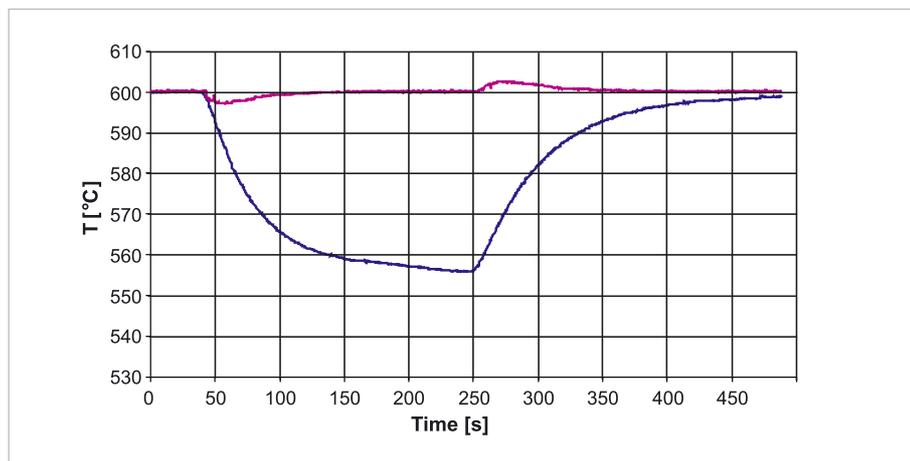


Fig. 5: Temperature profile of a temperature controlled L-Probe and a uncontrolled L-Probe by change of process conditions. Purple: temperature controlled L-Probe; Blue

protected with a highly porous ceramic layer. In order to enable the oxygen ions movement through the ceramic, inside the L-Probe a nickel heating element heats the ceramic. A rapid heating of the probe is possible because of the PTC-characteristic.

Specifics of L-Probe

There are few points which should be considered for an accurate handling of the L-Probe. If one arranges measurements with L-Probes in air, a voltage between -8...-15 mV instead of 0 mV is indicated. The reason for this is an eternal thermo couple effect. Each L-probe is heated different because of minor differences of the heating elements. For the heating of the probes a voltage of 12 V is provided and the temperature of the ceramic takes on values between 500...600°C. In order to have an accurate oxygen measurement and an accurate C-Potential calculation based on

this measurement, the abovementioned characteristics have to be incorporated in the calculation in form of correction factors.

For an accurate calculation the control of the L-probe ceramic temperature is very important. Therewith, different perturbations such as changing of the flow rate, ambient temperature or gas composition are eliminated. **Fig. 5** shows the temperature profile of a controlled and an uncontrolled L-Probe by equal changes of process conditions. In this test the modification of gas composition and flow rate has effectuate a temperature change of about 40°C of the uncontrolled probe. In contrast, the temperature of the controlled probe has changed hardly and the adjustment to the primary value happened after a short time.

The Power supply NTV44P (**Fig. 6**) was designed by MESA Electronic GmbH company for the control of the L-probe



Fig. 6: Power Supply NTV44P

ceramic temperature on a constant value. Using this power supply flow rates higher than 50 l/h are now also possible. Thereby, the dead time (time which the furnace gas needs to pass the probe) can be reduced enormous. For a gas sampling pipe with nominal length of 720 mm and a gas flow rate of 20 l/h the dead time is 17 seconds. It decreases to less than 6 seconds if the flow rate is 60 l/h. Both times are harmless in the process of carburizing. Furthermore, the working temperature is reached much faster if the L-probe ceramic temperature is controlled instead of heating the L-probe with constant voltage.

It should be also noted that for certain oxygen partial pressure in furnace the O₂-Probe and the L-Probe give different voltages. To control the C-Potential with the L-Probe you need either a controller which can calculate and control the C-Potential using the L-Probe voltage and correction factors (**Fig. 7**) or a measurement transducer which is able to do the same calculation or to transform the L-Probe signal to the O₂-Probe signal (**Fig. 8**). One of the many options of the power supply NTV44P is the transformation of the L-Probe signal to the O₂-Probe signal also.

Gas sampling fitting with L-Probe for C-Potential control

One of the most important points connected to the correct handling of the L-Probe by measurements of furnace atmosphere, is the appropriate construction of the gas sampling fitting (**Fig. 9**). The fitting is constructed such that it can be mounted without mechanical work in the entry of an O₂-Probe. A ceramic pipe guides the furnace gas up to the outer furnace wall. On the steel protection pipe of the gas sampling fitting a mark shows the end of the inner ceramic tube. The remaining part of the steel protection pipe serves as cooling section. By this construction the following is achieved:

- The hot reactive gas and the steel parts of the gas sampling fitting are not in contact. Temperature decresies and with it sooting of the fitting is avoided.
- A back reaction in another equilibrium state is impeded because of the sufficient thermal isolation of the gas up to the cooling section.



Fig. 7: Carbon controller for L-Probe



Fig. 8: Measurement transducer for L-Probe

- Besides, the gas flow velocity is increased by reduction of the width in the ceramic tube.
- The gas is thermal isolated up to the furnace outer wall only.
- At the furnace outer wall the flow velocity is reduced severely because of the larger width.
- When the gas leaves the furnace isolation and enters the cooling section, a fast cooling and with it a refreezing of the gas components occurs. A beck reaction in another equilibrium state is impeded therewith. Another equilibrium state of the gas would falsify the C-Potential calculation and produce sooting of the sampling pipe.

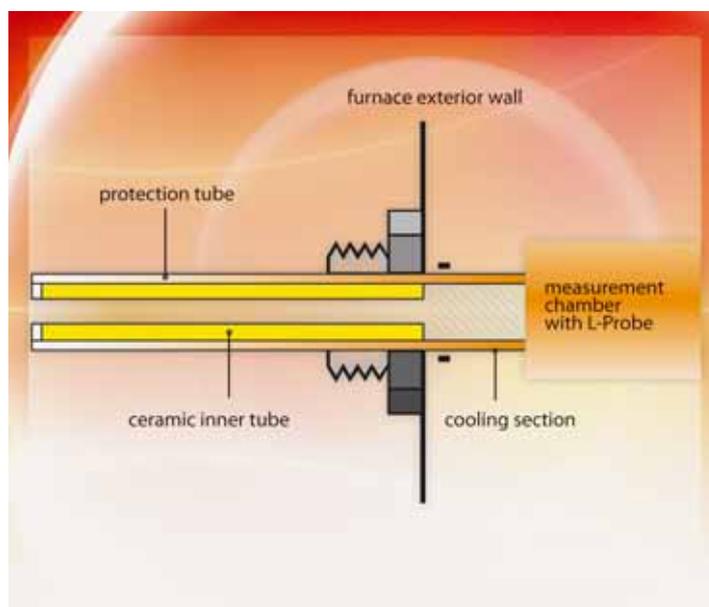


Fig. 9: Construction of the gas sampling fitting

The measurement with the L-Probe takes place outside the furnace. The inside temperature of the most L-Probes is between 550...600°C. These temperatures are still high enough to sustain the oxygen ions conductivity of the zirconia. In contrast to the O₂-Probe a lower temperature is sufficient. This is a result of the difference in the construction. The temperature in the measurement chamber is such low that the back reactions of the measuring gas are excluded.

Advantages of the L-Probe

Both probes, O₂-Probe and L-Probe, qualify very well for the control of the carburizing process. In addition, compared to the O₂-Probe the L-Probe possesses some noteworthy advantages:

- The L-Probe is very robust and was designed for operating conditions as changing temperatures and mechanical impacts, e.g. the exhaust pipe in cars. The L-Probe is insensible to mechanical vibrations. Therefore, it can be mounted closer to the fans than the O₂-Probe.
- Since the L-Probe is outside the furnace it can be replaced during the process in only few minutes.
- Contrary to the O₂-Probe, the L-Probe can be used in processes with temperatures up to 1600°C without a signal falsification. However, for these kind of processes the cooling section has to be designed properly.
- Because of the design of the gas sampling fitting, the L-Probe is not in

contact with the high temperature of the furnace. Moreover, contrary to the O₂-Probe the ceramic of the L-Probe is not affected from the temperature variation of the furnace. These are the essential reasons for the higher life time of the L-Probe compared with the O₂-Probe. From the experiences made with the L-Probe applications in carburizing processes during the last 20 years, it can be said that the life time of the L-Probe is twice as much compared with the O₂-Probe in the same process. In processes, in which the O₂-Probe is exposed to a highly thermal stress, the lifetime of the L-Probe attains a multiple of the O₂-Probe life time.

- One important advantage of the L-Probe is the price for the initial purchase as well as for the repeat order. The initial price of the L-Probe is little higher than the price for a O₂-Probe when a O₂-Probe has to be replaced by the L-Probe and the existing controller is unable to calculate the C-Potential from the L-Probe voltage. In this case a measurement transducer or the power supply NTV44P with the

option of signal transformation has to be purchased additionally. However, taking into account the longer life time and lower follow-up costs for the replacement and the repairing of the L-Probe respectively, a return of investment is achieved after the first breakdown of the O₂-Probe.

Conclusion

The experiences made by handling with the L-Probes in the last 20 years show that these probes are very well qualified for the control of C-Potential. The same can be said for the O₂-Probes. There are pros and cons for both probes. The evident benefits of the L-Probe are the lower price and a higher life time. Consequently, cost saving without loss of quality is achieved using the L-Probe.

Literature

- [1] AWT-Fachausschuss 5 Arbeitskreis 4 (Hrsg.): Die Prozessregelung beim Gasaugkohlen und Einsatzhärten. Expert Verlag, Renningen, 1997
- [2] Schmalzried, H.: Über Zirkonoxid als Elektrolyt für elektrochemische Untersuchungen bei höheren Temperaturen. Z. Elektrochem. Ber. Bunsenges. Physik. Chemie. 66 (1962) 7, S. 572

- [3] Schmalzried, H.: Ionen- und Elektronenleitung in binären Oxiden und Ihre Untersuchung mittels EMK-Messungen. Z. Phys. Chem. N.F. 38 (1963), S. 87



Dr. Džo Mikulović
 MESA Electronic GmbH,
 Geretsried
 Tel.: +49 (0) 8171-76930
 dmikulovic@
 mesa-international.de



Dr. Dragan Živanović
 Fakultät für Elektrotechnik,
 Universität Niš, Serbien
 MESA Electronic GmbH, Niš,
 Serbien
 Tel.: + 381 (0) 8031-
 900576760
 dzivanovic@
 mesa-international.com



Dipl.-Ing (FH) Florian Ehmeier
 MESA Electronic GmbH,
 Geretsried
 Tel.: +49 (0) 8171-76930
 fehmeier@
 mesa-international.de

KNOWLEDGE for the FUTURE

Handbook of Burner Technology for Industrial Furnaces

The demands made on the energy-efficiency and pollutant emissions of industrial furnaces are rising continuously and have high priority in view of the latest increases in energy prices and of the discussion of climate change for which CO₂ emissions are at least partly responsible. Great importance is now attached to increasing energy-efficiency in a large range of industrial sectors, including the steel industry and companies operating heat-treatment installations. This work is intended to provide support for those persons responsible for the clean and efficient heating of industrial furnaces.

The book discusses the present-day state of technological development in a practically orientated manner. The reader is provided with a detailed view of all relevant principles, terms and processes in industrial combustion technology, and thus with important aids for his or her daily work. This compact-format book, with its plethora

of information, is an indispensable reference source for all persons who are professionally involved in any way at all with the heating and combustion-systems of industrial furnaces.

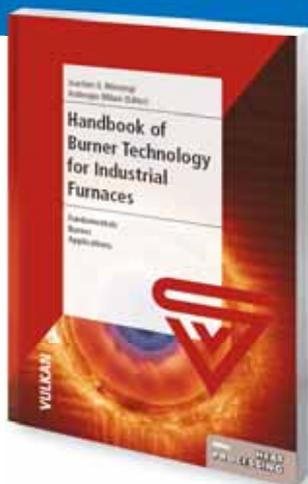
Selected topics:
 Combustion theory, Fluid mechanics, Heat transfer, Combustion technology, Computer simulation, Pollutant reduction, Heat exchangers, Indust-

rial burners (types and applications), Standards and legal requirements, Thermodynamic tables and terms, etc.



Vulkan-Verlag
www.vulkan-verlag.de

Order now by fax: +49 / 201 / 820 02-34 or send in a letter



Editors: Ambrogio Milani, Joachim Wünnig
 2009, 218 pages, hardcover, € 90.00
 ISBN 978-3-8027-2950-8

Yes, please send me

___ Cop. Handbook of Burner Technology for Industrial Furnaces

Editors: Ambrogio Milani, Joachim Wünnig

Vulkan Verlag GmbH
Versandbuchhandlung
Postfach 10 39 62
45039 Essen
Germany

Please note: According to German law this request may be withdrawn within 14 days after order date in writing at Vulkan Verlag GmbH, Versandbuchhandlung, Postfach 10 39 62, 45039 Essen, Germany. In order to accomplish your request and for communication purposes your personal data are being recorded and stored. It is approved that this data may also be used in commercial ways by mail, telephone, fax or email. This approval may be withdrawn at any time.

Company/Institution _____

First name, Surname of recipient (department or person) _____

Street/P.O. Box No. _____

Country Postcode Town _____

Phone _____ Fax _____

E-Mail _____

Branch/Profession _____

X Date, Signature _____