

Reference measurements in gas carburizing atmospheres: part 1

Džo Mikulović, Dragan Živanović, Florian Ehmeier

The most important parameters for the control of carburizing processes are the temperature and the C-potential of the atmosphere. Temperature is normally measured by means of thermocouples. For the control of C-potential the measurement of oxygen partial pressure of the furnace atmosphere by in-situ O₂-probes and Lambda probes (L-probes) became accepted. The thermocouples as well as the probes for measurement of residual oxygen gradually lose in accuracy. Therefore, reference measurements for adjustment of temperature and C-potential are essential for an exact control. Within this article the reasons for incorrect measurements with thermocouples and O₂-probes, respectively L-probes will be explained. The appropriate reference measurements for correction of these faults are also described. Furthermore, it is explained what has to be observed with these reference measurements and which information is given, thereby, about the furnace atmosphere, especially with the gas analysis by means of a gas analyzer. The first part for the article refers only to gas analysis as a reference measurement for C-potential. Within part 2, following later, reference measurements with a second O₂-probe or L-probe, dew point measurement and foil test will be described.

The most important parameters for the control of the carburizing process are the temperature and C-potential of the atmosphere. In order to achieve exact and reproducible results these parameters must be measured as exactly as possible. Due to aging and other potential sources of error the probes and sensors used provide inaccurate and respectively wrong data in the course of time. Thus, reference measurements are essential in order to correct the measurement result accordingly. Otherwise it is not verified that the desired results will be obtained by the control. Normally the temperature is measured by means of thermocouples. For controlling the C-potential the measurement of oxygen partial pressure of the furnace atmosphere by in-situ oxygen probes (O₂-probes) and Lambda probes (L-probes) has been established. The following article will refer to some causes of measurements error of the sensors and will focus on the potential reference measurements. Part 2 of this article will be published in a forthcoming issue.

Causes of error by the measurement of the temperature using thermocouples

Temperature measurement with thermocouples belongs to the common state-of-the-art. It must be emphasized again that thermocouples only measure temperature differences. The clamp temperature always serves as reference. Variation of the clamp temperature due to exposure of the joint to a changing environment temperature would lead to measurement errors. Different options are available to avoid this error. The two most common methods are the logging of the junction temperature – also referred to as junction compensation – or the usage of a junction thermostat to keep the temperature of the junction constant.

Regarding the temperature consistency and long-term stability of a thermocouple, the aging of the materials is of great importance. Due to the aging the thermoelectric characteristics of the thermocouples change and, therefore, the ther-

moelectric voltage/K. This is referred to as drift of the thermocouples. The drift of the thermocouples essentially depends on the following:

- The drift is temperature dependent. With the increasing approach to the fusion point the diffusion velocity of the atoms in a metal increases. Thus, very easily foreign atoms migrate into the thermocouple. Therefore, the two temperature-sensing arms are alloyed with the same foreign atoms, their thermoelectric characteristics advance and the thermo voltage decreases.
- The drift depends on the diameter of the used thermocouple wire. The smaller the ratio of the diffusion length of the diffused atoms to the total diameter of the wire, the lower the drift.
- The drift highly depends on the existing atmosphere. Strongly reducing atmospheric conditions respectively strongly oxidizing atmospheres are able to strengthen the drift substantially.

Besides the aging of the thermocouples there are also innumerable other thermal, mechanical, atmospheric, and electrical influences which complicate the exact temperature measurement. Thermocouple of type K is mostly used for temperature control. The following errors arise most frequently using this thermocouple in the carburizing atmosphere:

- Chromium depletion and green mold rot: Particularly in reducing CO- and CO₂-containing atmospheres with a complying moisture ratio and temperatures between 800°C and 1,000°C a selective oxidation of the chrome in the NiCr side can be observed. Due to the chrome extraction the thermoelectric voltage/K constantly de-

creases and a lower temperature than the actual one is indicated. The constant chrome depletion finally leads to a fracture, usually at the welded joint of the NiCr wire, if the thermocouple is not exchanged in time. The breakage shimmers light green, therefore the name green mold rot.

- K-condition:

That is the sorted or unsorted condition of the lattice elements in alloys at different temperatures. If the NiCr-Ni-thermocouple is above 600°C it always prevails an unsorted condition of the individual lattice elements in the NiCr side. During a slow cooling of the thermocouples the K-condition occurs meaning the lattice elements are sorted and additional errors of the thermoelectric voltage of approximately 3°C occur.

Regular examination of the thermocouples

The quality management according to DIN EN ISO 9000 [1] [2] demands traceability of all measuring instruments even for the temperature sensors built in a system. The term traceability means that the measured value is compared with a national normal. This traceability can be produced via a calibrated thermocouple with a valid calibration certificate. New quality standards [3] put special attention to a regular examination of the thermocouples, too.

It is possible to examine the temperature sensors in a temperature bath or a tube furnace in a metal block versus a normal thermometer. At least three check points in the application range should be examined.

In common practice in-situ-examinations of the thermocouples have been

established, thus, in the system on-site. Process controllable thermocouples possess a test channel which passes through a hole on the outside of the connection socket. The temperature examination is accomplished by a PtRh-Pt-insulated thermocouple with a valid calibration certificate directly during the process. The temperature sensor to be examined is not separated from the measuring circuit. As a result, the examination occurs for the entire measuring loop. The drift referred to the calibration measurement can be adjusted by an offset of the temperature regulator if the measured difference lies outside the tolerance. That way it is guaranteed that all conceivable errors, like linearization, compensating circuit, measuring junction temperature, and drift of the thermocouple and the controller will be considered.

Determination of the C-potential

Basically, the C-potential can be determined directly or indirectly [4]. The direct measurement methods are unsuitable for continuous measurement of the C-potential and the control based on this measurement. However, the direct methods are used to check and adjust the indirect measurement methods if necessary. **Fig. 1** indicates the various possibilities to determine the carbon level within the carburizing atmosphere.

For the control of a process, continuous measurement is essential. Dew point sensors available on the market, which could be used for continuous determination of the partial pressure of H₂O, are not robust enough for measurements in carburizing atmospheres. Therefore, they did not establish themselves in the carburizing processes. The measurement of CO₂ is done continuously with infrared sensors. This mea-

surement is frequently used as comparison measurement. The CO₂ measurement is slower compared to the O₂ measurement. In addition, the CO₂-sensor requires higher maintenance compared to the sensors for the O₂-measurement. Due to reasons mentioned for controlling the C-potential the measurement of the oxygen partial pressure of the furnace atmosphere by means of oxygen probes (O₂-probes and L-probes) prevailed. Whereas the other methods are used as comparison and reference measurements, similar to the direct methods.

Measurement uncertainties with the use of the O₂-probe

Different constructions of the O₂-probes (**Fig. 2**) and the resulting pros and cons are described in [5]. The following causes are usually responsible for the measurement uncertainties of the O₂-probes:

- 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, a temperature adulteration of the O₂-probe thermocouple also occurs.
- With the material, frame washing agent residues and covering paste enter the furnace. These chemicals evaporate in the furnace and precipitate on the outer platinum electrode. This yields to a falsified measurement and a reduced life time of the probe. To keep away the washing agent and covering paste residues from the probe element, an extended purging of the probe is necessary. One of the most known problems is the sooting of the outer electrode, particularly when the process is controlled near the soot limit. The sooting of the electrode also yields to a falsified measurement.
- Microscopic analysis shows that chromium parts of the material near the zirconia tip dissolve in the furnace after a while if chromium-nickel steels are used as protection pipe. Soot particles and oxygen cling to the porous surface. The soot on the probe causes faulty measurements. The oxygen induces increased probe reaction time and long relaxation time after probe purging.

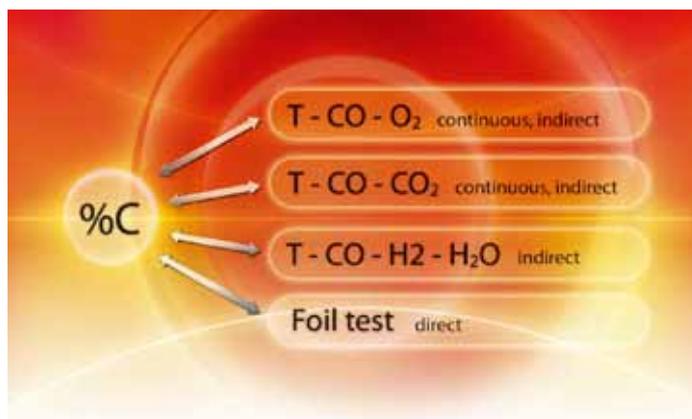


Fig. 1: Determination of carbon potential in carburizing atmosphere

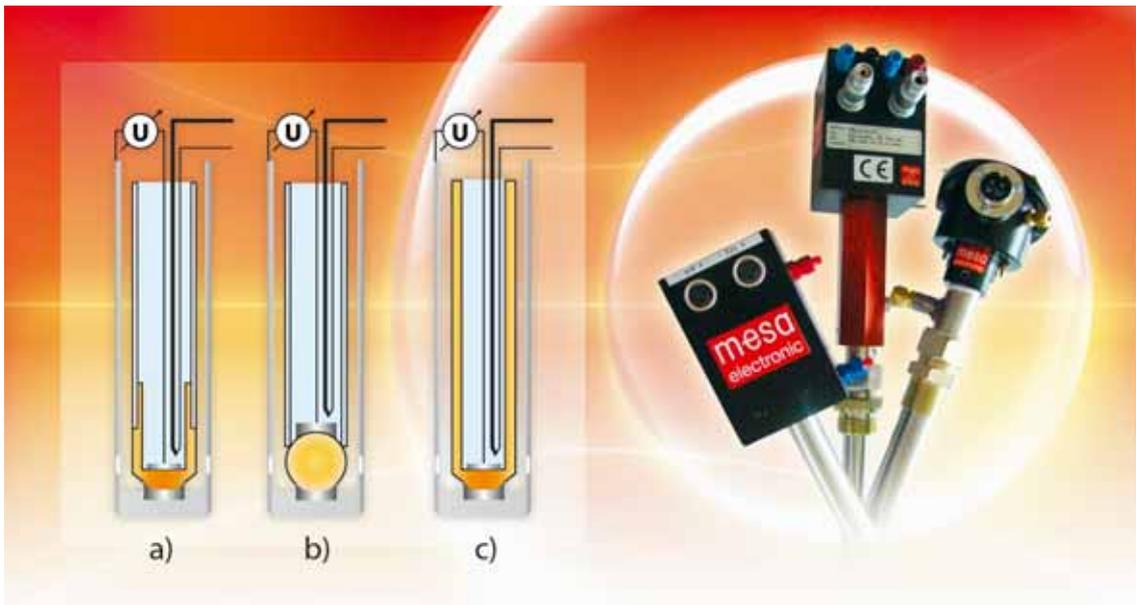


Fig. 2: Different types of O₂-probes: a) with zirconia element, b) with zirconia ball, c) with continuous zirconia pipe

Therefore, the regular examination of the O₂-probes using comparison respectively reference measurements is essential for assuring the quality of the process.

Measurement uncertainties with the use of the L-probe

The most important issue for the practical measurement of the atmosphere of a furnace using the L-probe is the correct structure and correct assembly of the gas withdrawal armature (Fig. 3) as well as the consideration of the correction factors of the C-potential calculation [5]. Due to the construction of the gas withdrawal armature the L-probe does not get in contact with the high temperature within the furnace. Additionally, the ceramic of the L-probe is not subject to variations in temperature. In comparison the O₂-probe is constantly subject to the temperature changes of the furnace atmosphere. This is a substantial reason for the long life span of the L-probe in comparison to the O₂-probe.

For an accurate calculation the control of the L-probe ceramic temperature is very important. Therewith, different perturbations such as changes of the flow rate, ambient temperature or gas composition are eliminated. The power supply NTV44P (Fig. 4) was designed by MESA Electronic GmbH company for the control of the L-probe ceramic temperature on a constant value.

Furthermore, the power supply also serves as transducer e.g. for direct transformation of L-probe signals into an O₂-probe signal. Mentioned interferences cause inaccuracies of the measurement and, thus, errors in the C-potential-calculation if the L-probe is heated only with a constant voltage occur.

Although the L-probe has a higher life span than the O₂-probe, the leakages also increase in the course of its lifetime. The material, the frame washing agent residues and covering paste evaporating into the furnace lead to a falsification of the measurement and a reduction of the life span of the probe, just like the O₂-

probes. Therefore, an examination via comparison or respectively reference measurements using the L-probe for the control of the C-potential is extremely important.

Reference measurement with CO and CO₂ measurement

For the measurement of CO and CO₂ concentration in the carburizing atmosphere solely the infrared absorption measuring has proved itself. The energy of the electromagnetic radiation is proportional to its frequency, respectively indirectly proportional to the wavelength ($E \sim \lambda^{-1}$). If the electromagnetic

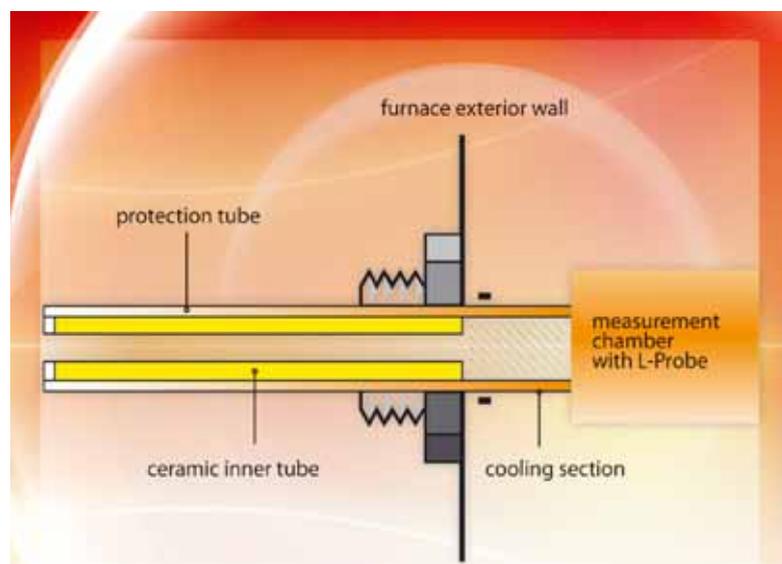


Fig. 3: Construction of the gas sampling fitting for measurement with L-probe



Fig. 4: Power supply NTV44P

radiation encounters a molecule, depending on the energy of radiation either single atoms can be split off, or vibration or rotation of the molecule is being induced (Fig. 5). In this process, the energy of radiation is being absorbed so to speak.

If the molecules are hit by an electromagnetic radiation with a wavelength in the infrared range they are being excited to oscillation. It is in the nature of the molecules that they can only vibrate at particular frequencies. So each molecule has a characteristic vibration spectrum. In other words, a molecule can only vibrate with particular energies. So if a molecule (e.g. CO₂)

encounters electromagnetic radiation of a wavelength which exactly matches the energy of one of the vibrational states of the molecule, the radiation is absorbed by the molecule and the molecule starts to vibrate with the corresponding energy. In this context we also speak of an absorption spectrum of the molecule. This property of the molecules is the basis of the infrared-absorption measurement.

Non-dispersive infrared spectroscopy (NDIR)

Fig. 6 shows a schematic design of a NDIR-sensor with dual beam method. NDIR stands for non-dispersive infrared

spectroscopy. The gas is being conducted through a measuring cuvette. An IR-source sends IR-light with a wide spectrum, i.e. with a wide wavelength range of the infrared spectrum, through the gas. Non-dispersive means that the detectors can only measure radiation with a particular wavelength.

The measurement detector detects only the spectral range in which the measurement component absorbs. If there is such a component in analyzed gas, less radiation is absorbed in the detector as in the case of absence of the component. If the radiation in the analysed gas is attenuated by other gases in other spectral ranges this does not cause an error as this radiation cannot be detected by the measuring detector.

The reference detector measures only the radiation with a particular wavelength which is not absorbed by any component of the measuring gas. In other words, it measures the fundamental intensity of the IR-source. Out of the difference of the measuring signals of the two detectors the concentration of the gas in question can be determined. The main advantage of the dual beam method is that the aging of the IR-source as well as the contamination of the optical elements are compensated. This significantly increases accuracy and longterm stability of the sensors compared to cheaper sensors which work with the single beam method.

As the infrared-absorption measurement is a concentration measuring, variations in state parameters pressure and temperature have an influence on mea-

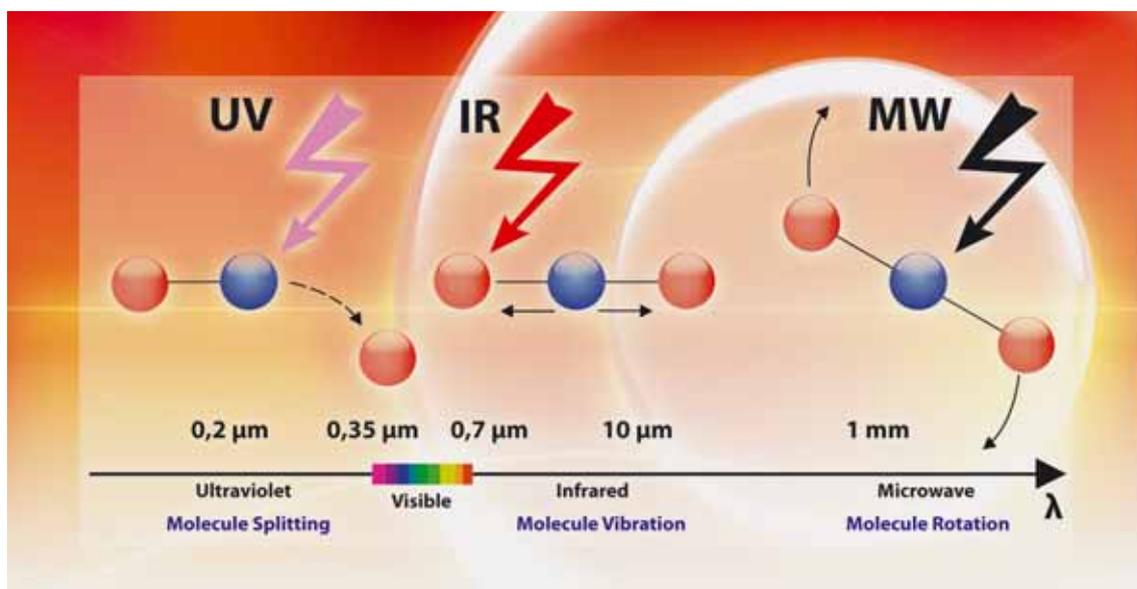


Fig. 5: Influence of electromagnetic radiation on molecules

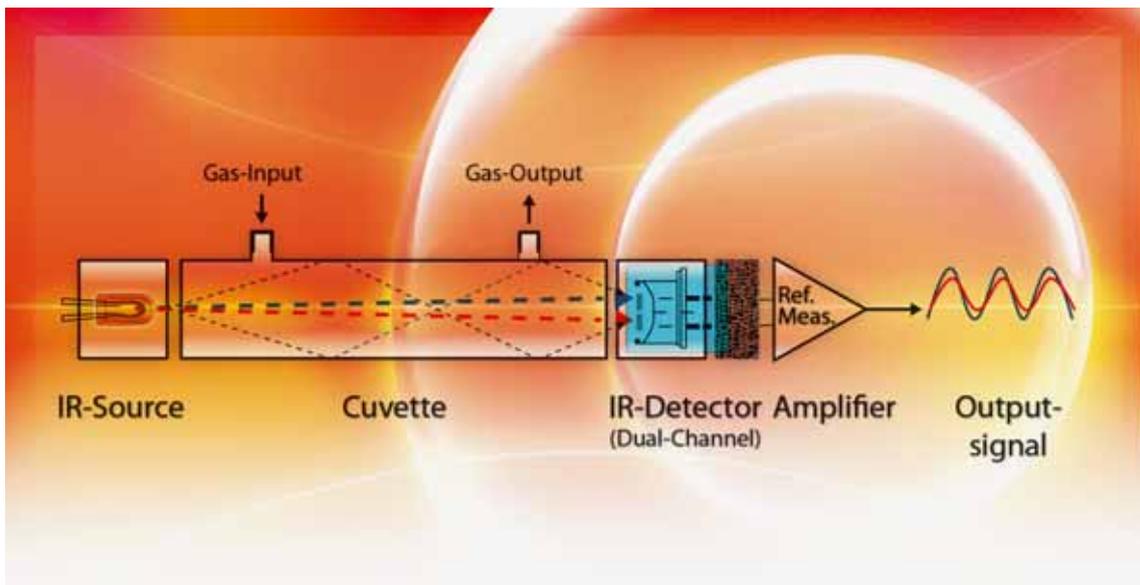


Fig. 6: Schematic construction of a NDIR-Dual wavelength sensor

surement results. A variation in the air pressure of e.g. 10 mbar is equivalent to an apparent change in concentration of 1% of the value measured, a variation in temperature of 1°C in the measuring cuvette an apparent change of 0.3%. Therefore, only sensors with pressure and temperature compensation should be used.

Reference measurements of C-potential with MGas 5.x

The device MGas 5.x (Fig. 7) can be used as a portable as well as a 19" built-in-device. It is for the measuring of

gases CO, CO₂, CH₄ and H₂. Depending on the hardware configuration (installed gas sensors) different combinations of gas measurements are possible. Apart from the direct measurement of the above mentioned gases, the C-level and dewpoint can also be determined with this device.

There are two methods for the determination of the C-potential which are implemented in MGas 5.x. The first method is based on measurement of CO, CO₂ and the process temperature. The process temperature can be measured with a thermocouple or entered as fixed value. The second method is

based on measurement of O₂, CO and the process temperature. For this method an O₂-probe or a L-probe has to be connected to MGas 5.x, however.

Beyond that the device is equipped with analog and digital in- and outputs, some of them user configurable, an USB interface with 16 MB internal data memory for recording of data, PC software for data filing and data visualization (Fig. 8), an optional MOD-Bus, Ethernet or Profibus interface and connections for an O₂-probe or a L-probe are available. Furthermore, it is possible to fix the time for automatic calibration cycles or to start calibration manually.



Fig. 7: Gas analyser MGas 5.x



Fig. 8: PC software for data storage and data visualization

A very interesting option is the integrated software for activation of a Multiplexer MUX (Fig. 9).

With the gas-multiplexer it is possible to analyze gases taken out of at most six

different sampling points online with a gas analyzer. The principal diagram of the gas flow is shown in Fig. 10. All the gas inputs are in a constant flow, not depending on the measuring point that is to be analyzed. Thus long dead times

after the switching of the gas inputs can be avoided. Calibration gases can be inserted over separate calibration inputs at the MGAs, independent of the measuring cycle. With the software integrated in the MGas 5.x for activation of



Fig. 9: Gas multiplexer MUX

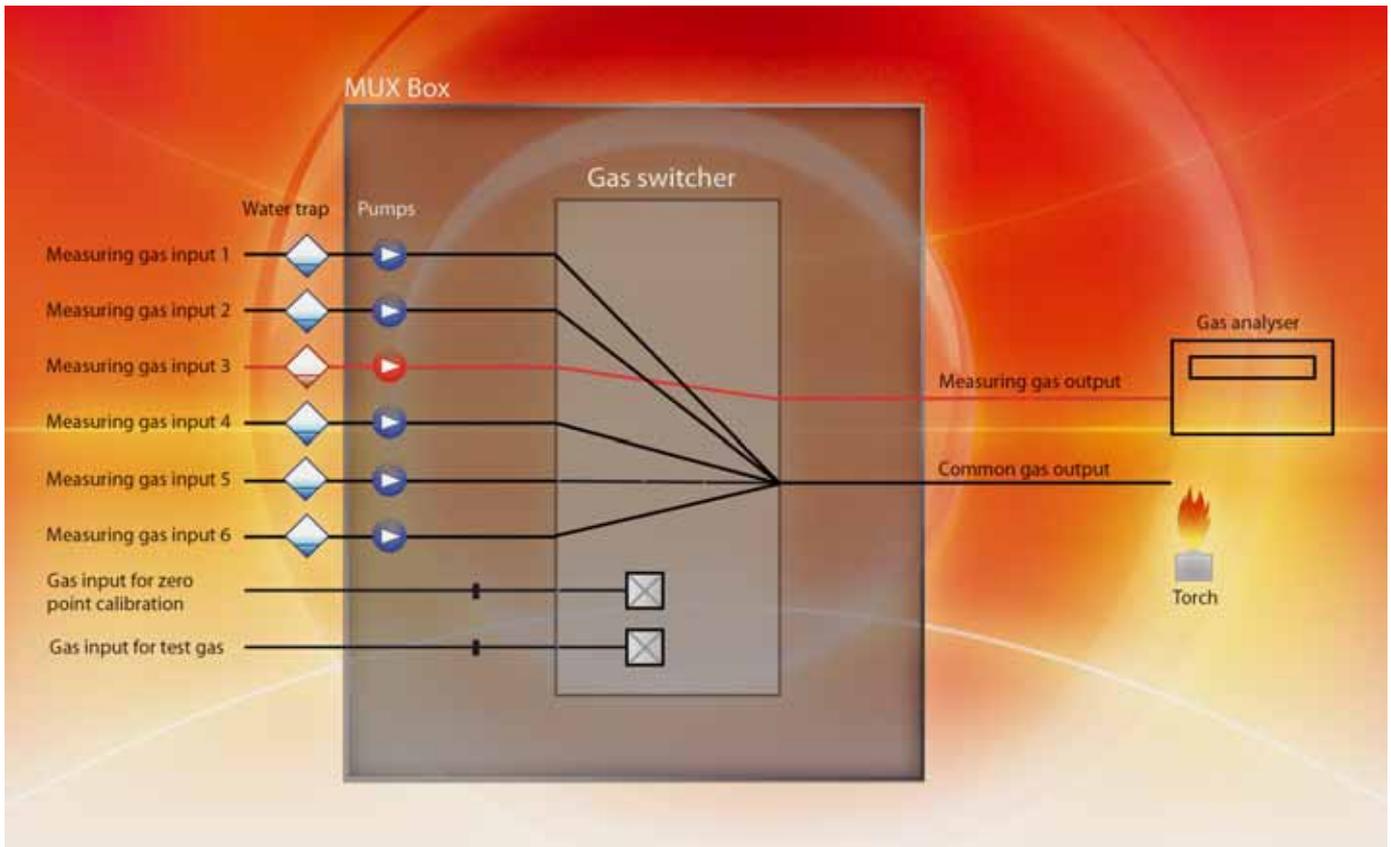


Fig. 10: Schematic presentation of the functionality of Gas-Multiplexer MUX

the gas-multiplexer MUX the operator can control all relevant parameters (e.g. switching time, duration of measurement of different channels, cycle time for automatic calibration, etc.) in a very simple way.

Influence of gas sampling, calibration and selection of CO₂ measuring range

For an exact measurement with gas analyzers we would like to especially emphasize three points:

1. Correct gas sampling

One of the most important points connected to the correct measurement of furnace atmosphere is the appropriate construction of the gas sampling fitting (Fig. 11). The construction was also especially designed for use of the fitting for foil tests. The design is similar to the one of the gas sampling fitting in Figure 3. 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 a 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. A decrease of temperature and sooting of the fitting are avoided consequently.

- A back reaction in another equilibrium state is impeded because of the sufficient thermal isolation of the gas up to the cooling section.
- The gas flow velocity is increased by reduction of the width in the ceramic tube.



Fig. 11: Gas sampling fitting

- The gas is thermally 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 back reaction in another equilibrium state is impeded therewith. Another equilibrium state of the gas would falsify the measurement of the gas components and by this also the C-potential calculation.

2. Calibration

As already mentioned in the beginning, it is in the nature of each sensor that with time it starts drifting. Therefore, a calibration of the sensors in certain intervals is most essential to get exact and reliable measuring results. For this the neutral point of the sensors is normally calibrated with nitrogen. For long online measurements it is advisable to calibrate the neutral point in regular intervals. The calibration in a second step is made with a test gas of known composition. It is recommendable to choose the composition of the gas similar to the gas composition of the furnace atmosphere. If, e.g., endogas out of methane is used as carrier gas, the composition of the test gas should be as follows: 20% CO, 0.5% CO₂, 40% H₂, 2% CH₄ and the rest N₂. The measurement uncertainty results out of the quality of the analysis of the test gas, which normally is approximately 1% of the gas level.

3. Selection of the CO₂ measurement range

The appropriate selection of the CO₂ measurement range considerably influences the accuracy of the calculation of the C-potential. Considering the relation between the C-potential, the temperature and CO₂ [4] it is evident that in the common gas carburizing atmospheres a measurement range of 0...0.5% CO₂ (percent by volume) is sufficient. With a measuring difference of 1% of the measuring value an accuracy of 0.005% CO₂ can be achieved. In an atmosphere with 20% CO at a temperature of 920°C and a C-potential of 1.10%C this would correspond to a C-potential accuracy of 0.05%C. If a CO₂-sensor with a

much larger measuring range would be used, the uncertainty in measurement and C-potential calculation would be so significant that this method would be no more suitable for reference measurement for the C-potential. If the gas analyzer should also be used for measurements in atmospheres with higher CO₂ values (e.g. hardening process) it is recommendable to use a device with two CO₂-sensors. The MGas 5.x (Fig. 7) is equipped with exactly this feature with an automatic switch of the measurement range. The device decides on basis of the measurement value which sensor should be used. If the value is in the transition range of the two sensors, the measurement is performed with both sensors and the results are rated accordingly. Thus, the accuracy of the measurement is increased additionally.

Further conclusions to be achieved by gas analysis

In practice gas analysis is not only used for reference measurement for C-potential. It also submits far-reaching information about the condition of the furnace and the furnace atmosphere. So the result of the CH₄ measurement can show if the atmosphere is in equilibrium state. If the value is too high, this is an indication for a bad gas splitting. The relation of CO and H₂ submits information about water intrusion into the furnace. These few examples show that gas analysis is most important for determination of causes of a bad gas carburizing atmosphere. Without gas analysis a quick fault clearance is almost impossible.

Gas analysis is also very helpful at the inspection of endogas generators. So from the CO and CH₄ measurements information about the condition of the retort and the catalyst can be gained. If the retort and the catalyst are in good condition, the value for CH₄ is under 1% and the value of CO should correspond approximately to the calculated values (for endogas out of methane approximately 20% and for endogas out of propane approximately 23.8%). If the value for CH₄ is above 1% and the value for CO is below the expected values, this is an indication for sooting of the catalyst, respectively for leaking in the retort. In this situation the gas analysis is an important tool for problem solution.

Conclusion

For reasons of quality management reference measurements are indispensable. In the process of gas carburizing temperature and C-potential are the most important parameters, which have to be controlled, respectively inspected in regular intervals. The reference measurement of the temperature in practise is performed as an in-situ-inspection of the thermocouples, i.e. at the plant on site. For the C-potential there are several methods which are suitable for reference measurements. The method introduced in this article, namely the gas analysis with NDIR-sensors, is also an important tool for problem solutions.

Literature

- [1] DIN EN ISO 9000, „Qualitätsmanagementsysteme – Grundlagen und Begriffe“ (ISO 9000:2005). Beuth-Verlag GmbH, Berlin, 2005
- [2] DIN EN ISO 9001, „Qualitätsmanagementsysteme – Anforderungen“ (ISO 9001:2008), Beuth-Verlag, Berlin, 2008
- [3] AIAG: CQI-9 Special Process: Heat Treat System Assessment. AIAG, 2006
- [4] AWT-Fachausschuss 5 Arbeitskreis 4 (Hrsg.): Die Prozessregelung beim Gasaufohlen und Einsatzhärten. Expert-Verlag, Renningen, 1997
- [5] Mikulović, D.; Živanović, D.; Ehmeier, F.: Carbon controlling with O₂-probe and L-probe, HEAT PROCESSING (2009), issue 3, p. 231-236 ■



Dr. Džo Mikulović

MESA Electronic GmbH,
Geretsried (Germany)
Tel.: +49 (0)8171/76 930
dmikulovic@
mesa-international.de



Dr. Dragan Živanović

Faculty of Electronic Engineering,
University of Niš (Serbia)
MESA Electronic GmbH, Niš
(Serbia)
Tel. +49 (0)80 31/9 00 57 67 50
dzivanovic@
mesa-international.com



**Dipl.-Ing (FH)
Florian Ehmeier**

MESA Electronic GmbH,
Geretsried (Germany)
Tel.: +49 (0)8171/76 930
fehmeier@
mesa-international.de