Reference measurements in gas carburizing atmospheres: part

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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 O_2-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. In the first part of this article [1] the reasons for incorrect measurements with thermocouples and O_2-probes, respectively L-probes have been explained. The appropriate reference measurements with calibrated thermo couple and gas analysis for correction of these faults were also described. Furthermore, it was 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. Within part 2, following now, following additional reference measurements for C-potential will be presented: reference measurement with a second O_2-probe or L-probe, dew point measurement and foil test. The advantages and disadvantages of theses reference measurements will be also discussed.

The most important parameters for the control of the carburizing process are temperature and carbon potential (C-potential) of the atmosphere. To achieve accurate and reproducible results these parameters must be measured as accurately as possible. Due to aging and other possible sources of error the thermocouples and O_2-probes as well as L-probes used for this purpose, over time, provide inaccurate or false readings [1]. Therefore, reference measurements are essential in order to correct the results accordingly. Otherwise there is no guarantee that by controlling the desired results will be achieved.

As described in the first part of the article [1] the reference measurement for the temperature occurs via a test thermocouple. To determine the C-potential in the carburizing atmosphere several indirect and direct ways are available (**Fig. 1**). In carburizing atmospheres, using endothermic or nitrogen/methanol as carrier gas, CO and H_2 values are nearly constant. Therefore, in practice, to determine the C potential often only O_2, CO_2 or the dew point is measured and the values for CO and H_2 are assumed to be constant.

For controlling purposes the measurement of the oxygen partial pressure via O_2-probe or L-probe has prevailed. The reference measurement via gas analysis (CO and CO_2 measurement via a gas analyzer) was described in part 1 of the article [1]. Below the indirect reference measurements of the C-level using a second O_2-probe or L-probe and via dew point measurement are described. Advantages and disadvantages of some measurement methods for the direct determination of the C-potential are also discussed.

Reference measurement of the C-potential with a second O_2-probe or L-probe

The construction and operating mode of the O_2-probes as well as L-probes were described in detail in [2]. The reference measurement with these probes, as well as the reference measurement using CO and CO_2 gas analysis, has the advantage of allowing the measurement to be performed continuously. Using a C-potential controller which has the option to work with two probes and compare them, the failure probability of the C-potential control system can be reduced enormously. In this context we speak about redundancy. In technology this term commonly indicates the additional presence of functionally equal or comparable components of a technical system when they are not

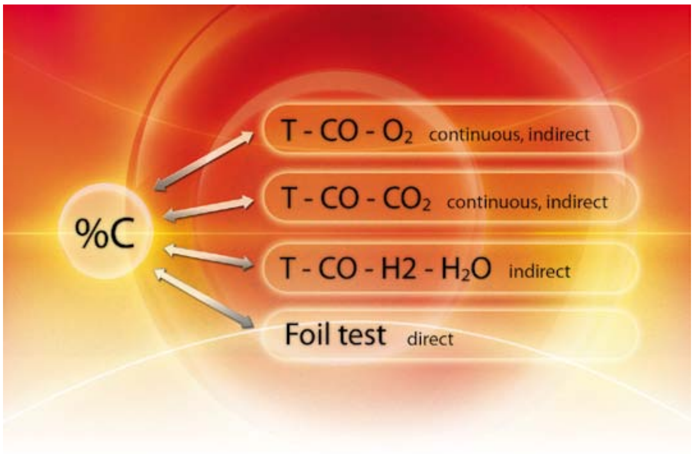

Fig. 1: Determination of carbon potential in carburizing atmosphere

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C-Meßstellenvergl.
O2-Son L-Son2
-----,- 1204,4 mV L-S
1167,9 1167,4 mV O2S
39E-22 40E-22 O2 Vol
 0,082  0,083 %CO2
   1,25   1,24 %C
   1,20   1,20 %Ckorr
     94     94 %aktiv
regelt
```

```
Sondenvergleich
(nur falls 2 Sonden)
Warnung ab C-Pegel-
Differenz von:
0,30%C
Führende Sonde:
Sonde 1
Verzögerung:
180 Sekunden
```

Fig. 2: C-Potential controller Carbomat-M: a) Comparison of two parallel working probes; b) Setting menu for probe switching parameters

needed in the normal case of a trouble-free operation.

The C-potential controller Carbomat-M holds the option to work with two probes in comparison (**Fig. 2**). One probe known as the leading probe is used for calculation of the C-level, the second probe works as comparison probe. In case of failure the Carbomat-M switches from the leading probe to the comparison probe and keeps calculating with the values of that probe. This avoids that the C-potential control and data recording will be interrupted especially if the probe fails during a current process. Murphys Law („Whatever can go wrong, will go wrong" or for our purpose more appropriate formulation "If something can go wrong in different ways, it will always go wrong in the way which will cause the most damage") [3] says that the failure of the probe will occur exactly at the time when the most damage can be caused. This damage can be prevented by using this redundant system.

A short sample calculation will show how the failure probability of the C-potential control is reduced if a redundant system made of two parallel working probes is used. To eliminate systematic errors it is important to use probes of various types, e.g. an O_2-probe and L-probe. Due to the fact that the probes are essentially different in construction the process and unit related interference influences have a different impact on the probes. In such case the failure of the probes can be viewed independently from each other which is very important regarding the calculation. Assuming that within a corresponding time period the first probe has a failure probability of 30 % P(probe1) = 0.3 and the second probe a failure probability of 20 % P(probe2) = 0.2 the probability of both probes failing simultaneously is calculated as product of individual probabilities. The result of the considered case is as follows:

$$
\begin{aligned}
&P(\text{probe1} \cap \text{probe2}) \\
&= P(\text{probe1}) \cdot P(\text{probe2}) \qquad (1) \\
&= 0.3 \cdot 0.2 = 0.06
\end{aligned}
$$

The failure probability for a system made of two probes is reduced to 6 % for the corresponding time period meaning an enormous reduction of the failure probability of the system.

Reference measurement of C-potential by measuring of dew point

For the determination of the C-potential from the H_2O-content of furnace atmosphere the dew point is measured. The dew point or dew point temperature defines the temperature at which condensation of the water just starts. **Fig. 3** shows the saturated vapour pressure line out of the phase diagram for water for the temperature range from -30 °C to +20 °C. The line which was determined experimentally represents the relationship between dew point and partial pressure and accordingly the proportion of water in an atmosphere. Knowing the dew point temperature of a furnace atmosphere, one can read the partial pressure from the diagram and thus determine the C-potential. In an atmosphere with a dew point of, e.g. +10 °C, the partial pressure of the water is 12.27 mbar. Using the Magnus formula [4], which for the first time was established in 1844 by Heinrich Gustav Magnus empirically and only supplemented by more accurate values since then, the partial pressure of water in a furnace atmosphere can be calculated from the dew point. For dew point temperatures ≥ 0 °C the formula is

$$
\begin{aligned}
&p(H_2O) = \\
&6.112\,\text{mbar} \cdot \exp\left(\frac{17.62 \cdot T}{243.12\,°\text{C} + T}\right), \qquad (2)
\end{aligned}
$$

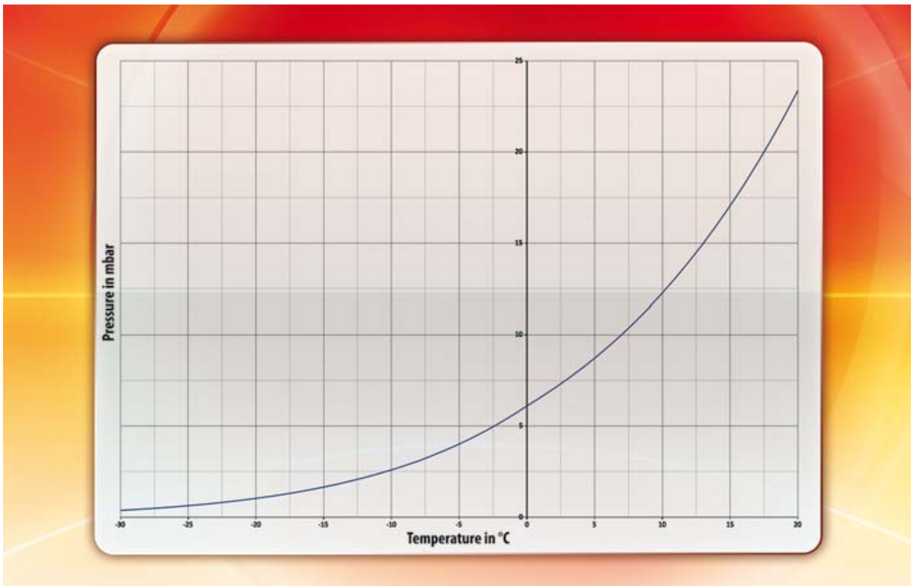


Fig. 3: Saturated vapor pressure curve for H_2O

and for dew point temperatures < 0 °C and > -65 °C

$$p(H_2O) = 6.112\,\text{mbar} \cdot \exp\left(\frac{22.46 \cdot T}{272.62\,°C + T}\right). \qquad (3)$$

T is the dew point temperature in °C.

The dew point sensors on the market with which the partial pressure of H_2O can be determined continuously are not robust enough for the carburizing atmosphere and could not establish themselves. For dew point measuring the so-called mirror dew point measurement devices are used. The schematic design of these devices is shown in **Fig. 4**. The furnace gas is passed through a measuring chamber on the surface of a mirror. The mirror is cooled with a thermoelectric Peltier element until dew shows on the mirror surface. By use of a temperature sensor the temperature of the mirror surface can be detected. As soon as condensation starts the temperature of the mirror is read out directly. This is the dew point temperature.

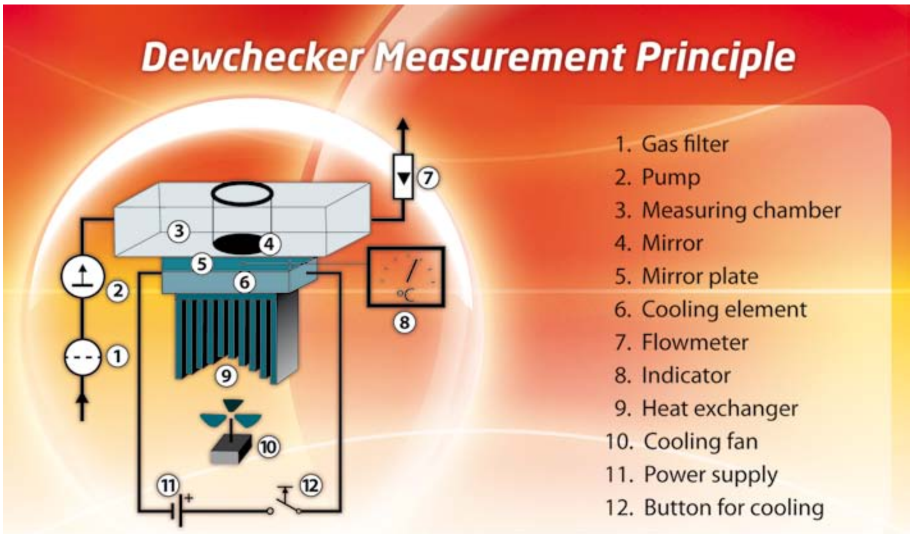


Fig. 4: Schematic construction of a mirror dew point measuring system

The mirror dew point checker Dewchecker 1.1. (**Fig. 5**) is characterized mainly by the fact that the temperature of the mirror can be adjusted permanently to a constant value. For this purpose the required mirror temperature is defined as a fixed set point. The electronics then controls the Peltier element so that the predetermined set point temperature of the mirror is kept. This allows an accurate approximation to the dew point and thus a very accurate measurement of dew point independent of the operator. For an accurate dew point measurement with mirror dew point measurement devices the following points have to be observed:

- The gas sampling fitting in this case plays an equally important role as for a gas analysis with a gas analyzer and therefore has to be constructed as described already in the first part of the article [1].
- If the dew point of the gas to be measured is higher than the ambient temperature or higher than any part of the sample gas extraction system, it will lead to premature condensation. This is particularly the case when the sample gas supply lines come in contact with cold parts (e.g. water pipes) or are placed near open windows or on cold walls. Premature condensation in the measuring chamber system of the dew point measuring device can also occur when the device is brought from a cold to a warmer room and if the dew point of the gas to be measured is above the temperature of the device parts which are in contact with the gas.

  Remedy:

  If condensate has formed within the measuring gas extraction system the suction hose should be detached from the gas sampling point. Then air should be sucked through the device with the installed pump until pipes, filter and measuring chamber are dry again. The check whether the system is dry is assuaged when the dew point of the ambient air is measured before the measurements of the furnace atmosphere with the device are started. By occasional measurements of the ambient air dew point it can be controlled if the dew point is still constant after the measurement and the measuring system has remained dry.
- The devices should be maintained and calibrated regularly. For calibration of the entire measurement system different dew points are generated by use of a controlled climatic chamber. The measurement is then performed with the device to be calibrated and with a with a precision dew point hygrometer. From the comparison of the measured values then a corresponding correction is made so that the readings are within tolerance.

Direct determination of the C-potential

The methods for direct measurement of C-potential include measurements using pure iron wire and pure iron foil. In the measurement with pure iron wire,

Fig. 5: Dewchecker 1.1 (Prototype)

Fig. 6: Foiltester FPG 1.0 with terminals T200 and T300

the wire is exposed to the carburizing atmosphere to be determined. Then, with a resistance meter the resistance and by that the difference in resistance is measured. From the change in electrical resistance the C-potential of the atmosphere is determined.

When measuring is done with an approx. 0.05 mm thick pure iron foil, the foil is exposed for 10 to 15 min. to the furnace atmosphere to be determined. Due to the necessary balance the duration of measurement depends on temperature and C-potential of furnace atmosphere.

Subsequently, the carbon content of the foil is determined. For this there are various methods [4-6]:

Glow discharge spectroscopy (GDOS): This is the most accurate method. With the GDOS it is possible to measure the depth profile of carbon in the foil. When using this method, so to speak, the carbon content in the core of the foil is used as a measure of the C-potential. All error conditions such as contamination or surface oxidation of the foil which would lead to errors in other methods of measurement do not matter in GDOS. Despite of the high accuracy this method is far too complicated and too expensive to determine only the carbon content in foils with it.

Combustion process: The combustion process for determining the carbon content in foil is widespread today. The foil is heated in a small pot with about 1 g of tungsten granulate. In a high-frequency furnace the material burns under pure oxygen. With suitable filters all oxides except carbon dioxide are filtered out. Then, the CO_2 content is measured with an IR absorption meter. The CO_2 content determined in this way is a measure for the carbon content of the foil or accordingly the C-potential of the furnace atmosphere. In comparison with eddy current measuring and weighing of the foil, this method is very expensive and time consuming. In addition, the calibration effort in this process is considerably high and requires a high skill of the operator.

Eddy current method: With this method the differences in the electromagnetic properties of the foil caused by the different carbon content are analyzed by an eddy current measurement. The advantage in comparison to the foil weight measurement is that you do not have to deal with the foil carefully because dirt and impurities do not affect the result.

Compared to weight measurement the eddy current measurement, however, has significant disadvantages. The electromagnetic properties analyzed here are not only depending on the carbon content of the foil, but also on other parameters, such as lattice structure and particle size. These parameters depend again on how quickly and how much the foil cools down. It is very difficult to eliminate these error sources in practice. Another major drawback is that for calibration of the instrument a second measurement procedure, usually foil combustion or weight measurement must be available. If one of those procedures is already used, however, it is uneconomical to purchase an additional device that has no significant advantages.

Gravimetric method: Weighing with a precision scale is certainly the easiest and cheapest method for determining the carbon content in pure iron foils. The weight of the foil before and after it is exposed to the furnace atmosphere is measured. From these two weight measurements and the carbon content of

Fig. 7: Accessories for foiltester FPG 1.0

the foil before it was exposed to the furnace atmosphere, the weight percentage of carbon is calculated as follows:

$$\%C = 100 - \frac{m_0}{m} \cdot \left(100 + \%C_0\right), \qquad (4)$$

m_0 is the weight of the foil before it is exposed to the furnace atmosphere, m the weight of the foil after it is exposed to the furnace atmosphere and % C_0 the basic carbon content before the foil is exposed to the furnace atmosphere. The weight fraction of carbon calculated with formula (4) corresponds to the C-potential of the furnace atmosphere according to DIN 17014. When the gravimetric method is used it has to be ensured that errors due to impurities in the form of soot, grease or fingerprints are avoided. In addition all forms of oxidation during removal of the foil have to be prevented, as oxide layers lead to a distortion of the result.

Direct measurement of C-potential with foil tester type FPG 1.0

The foil tester type FPG 1.0 (**Fig. 6**) is a precision scale for gravimetric determination of carbon content in thin iron foils. The weight is measured with a tension strip bedded moving coil mechanism. The C-potential can be measured with an accuracy of ± 0.01 % C.

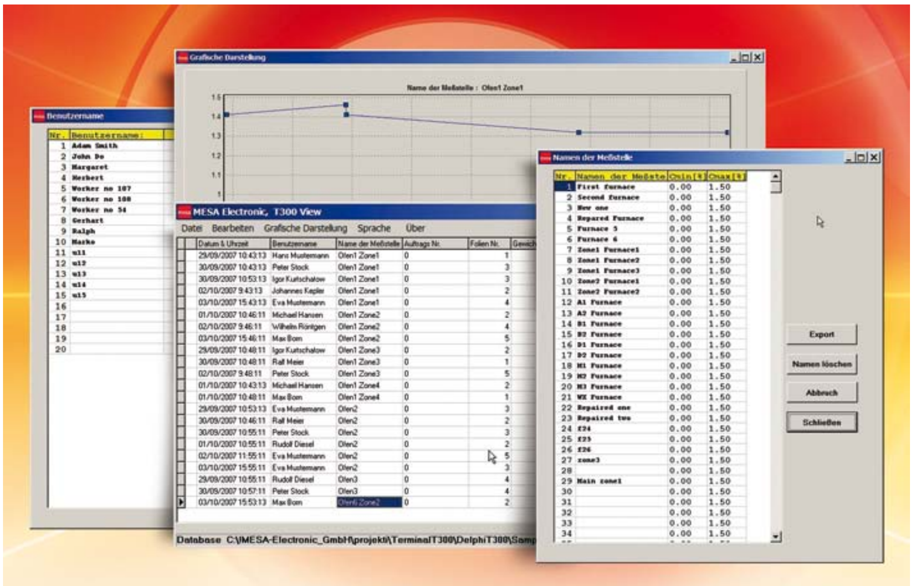
To ensure high measurement accuracy over a longer period of time the foil tester needs to be calibrated with a 95 mg test weight every time when it is turned on. The foils used for measurement have a weight of about 97 mg. This allows measurements at the calibration point which leads to high accuracy. Furthermore each measurement cycle performs seven measurements. The maximum and the minimum measured values are ignored and the average value is calculated out of the five remaining measurements.

As already mentioned it is very important for an accurate weight measurement that the foil is free of contaminants such as grease or fingerprints. For that reason each foil tester contains miscellaneous accessories (**Fig. 7**), which are required to prepare the foils. The foil has to be wrapped around the attached wooden stick and afterwards inserted into a plastic bottle filled with acetone for cleaning. For measuring it has to be removed with anti-magnetic tweezers and dried with a heat gun or hair dryer. The foil should not be touched with the hands thereafter.

A special feature of the device is the easy manual operation with the terminals T200 or T300. The display of the operation terminals show each step in plain text and thus a correct handling of the device is ensured. With the operating terminal T300 and the corresponding PC software „T300 View" (**Fig. 8**) usernames and names for the foil samples can be added and managed. With an USB flash drive all data can be transferred to a PC and analyzed and archived with the software.

Foil sample and two-point correction

The direct determination of the C-potential with a foil tester is often used to correct the C-potential, which is calculated with an O_2-probe or L-probe. Most C-potential controllers allow an offset or in other words a correction of the C-potential in one operating point. This correction is adequate for processes with a constant C-potential and a constant temperature. For carburizing processes where temperature and C-potential are changed such corrections are not sufficient.



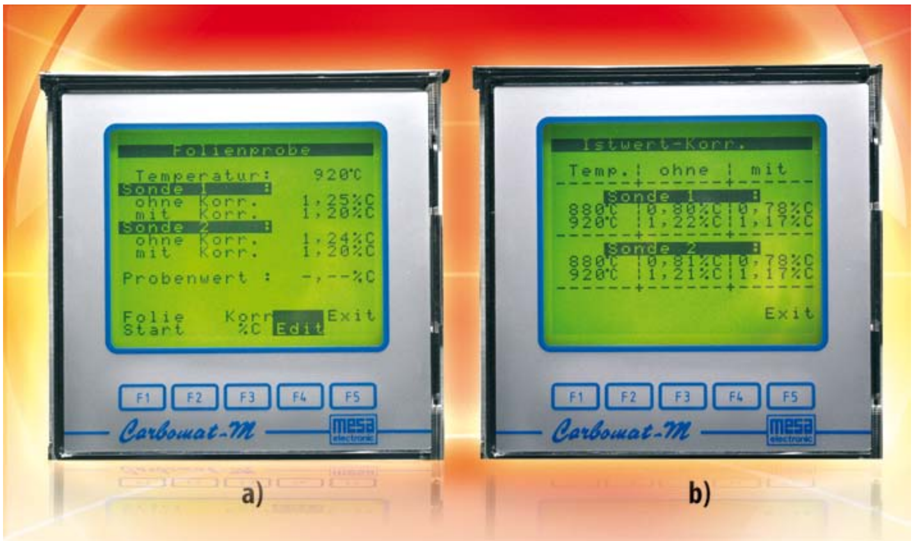
Nr.	Benutzername:
1	Adam Smith
2	John Do
3	Margaret
4	Herbert
5	Worker no 107
6	Worker no 108
7	Worker no 54
8	Gerhart
9	Ralph
10	Marko
11	w11
12	w12
13	w13
14	w14
15	w15
16	
17	
18	
19	
20	

Datum & Uhrzeit	Benutzername	Name der Meßstelle	Auftrags Nr.	Folien Nr.	Gewich
29/09/2007 10:43:13	Hans Mustermann	Ofen1 Zone1	0	1	
30/09/2007 10:43:13	Peter Stock	Ofen1 Zone1	0	3	
30/09/2007 10:53:13	Igor Kurtschatow	Ofen1 Zone1	0	3	
02/10/2007 9:43:13	Johannes Kepler	Ofen1 Zone1	0	2	
03/10/2007 15:43:13	Eva Mustermann	Ofen1 Zone1	0	4	
01/10/2007 10:46:11	Michael Hansen	Ofen1 Zone2	0	2	
02/10/2007 9:46:11	Wilhelm Röntgen	Ofen1 Zone2	0	4	
03/10/2007 15:46:11	Max Born	Ofen1 Zone2	0	5	
29/09/2007 10:48:11	Igor Kurtschatow	Ofen1 Zone3	0	2	
30/09/2007 10:48:11	Ralf Meier	Ofen1 Zone3	0	1	
02/10/2007 9:48:11	Peter Stock	Ofen1 Zone3	0	5	
01/10/2007 10:43:13	Michael Hansen	Ofen1 Zone4	0	2	
01/10/2007 10:48:11	Max Born	Ofen1 Zone4	0	1	
29/09/2007 10:53:13	Eva Mustermann	Ofen2	0	3	
30/09/2007 10:46:11	Ralf Meier	Ofen2	0	2	
30/09/2007 10:55:11	Peter Stock	Ofen2	0	3	
01/10/2007 10:55:11	Rudolf Diesel	Ofen2	0	2	
02/10/2007 11:55:11	Eva Mustermann	Ofen2	0	5	
03/10/2007 15:55:11	Eva Mustermann	Ofen2	0	3	
29/09/2007 10:55:11	Rudolf Diesel	Ofen3	0	4	
30/09/2007 10:57:11	Peter Stock	Ofen3	0	4	
03/10/2007 15:53:13	Max Born	Ofen6 Zone2	0	2	

Database C:\MESA-Electronic_GmbH\projekt\TerminalT300\DelphiT300\Samp

Nr.	Namen der Meßste	Cmin[%]	Cmax[%]
1	First furnace	0.00	1.50
2	Second furnace	0.00	1.50
3	New one	0.00	1.50
4	Repared Furnace	0.00	1.50
5	Furnace 5	0.00	1.50
6	Furnace 6	0.00	1.50
7	Zone1 Furnace1	0.00	1.50
8	Zone1 Furnace2	0.00	1.50
9	Zone1 Furnace3	0.00	1.50
10	Zone2 Furnace1	0.00	1.50
11	Zone2 Furnace2	0.00	1.50
12	A1 Furnace	0.00	1.50
13	A2 Furnace	0.00	1.50
14	B1 Furnace	0.00	1.50
15	B2 Furnace	0.00	1.50
16	D1 Furnace	0.00	1.50
17	D2 Furnace	0.00	1.50
18	H1 Furnace	0.00	1.50
19	H2 Furnace	0.00	1.50
20	H3 Furnace	0.00	1.50
21	WX Furnace	0.00	1.50
22	Repaired one	0.00	1.50
23	Repaired two	0.00	1.50
24	f24	0.00	1.50
25	f25	0.00	1.50
26	f26	0.00	1.50
27	zone3	0.00	1.50
28		0.00	1.50
29	Main zone1	0.00	1.50
30		0.00	1.50
31		0.00	1.50
32		0.00	1.50
33		0.00	1.50
34		0.00	1.50

Fig. 8: Software "T300 View"



```
Folienprobe

Temperatur:       920°C
Sonde 1          :
 ohne Korr.      1,25%C
 mit  Korr.      1,20%C
Sonde 2          :
 ohne Korr.      1,24%C
 mit  Korr.      1,20%C

Probenwert :     -,--%C

Folie     Korr      Exit
Start      %C  Edit
```

```
Istwert-Korr.

Temp. | ohne   | mit
------+--------+-------
   Sonde 1          :
880°C |0,80%C |0,78%C
920°C |1,22%C |1,17%C
------+--------+-------
   Sonde 2          :
880°C |0,81%C |0,78%C
920°C |1,21%C |1,17%C
------+--------+-------

                  Exit
```

Fig. 9: C-Potential controller Carbomat-M: a) Menu for C-potential correction with foil test; b) Menu with values for two point correction

The inaccuracy of O_2-probe measurements is usually caused by fine hairline cracks in the ceramic of the probe. The extent of the cracks depends on the temperature. Therefore the measurement errors with the probe are different at various temperatures. If the C-potential is corrected at a high temperature, e. g. at 920 °C and a C-potential of 1.2 % C the measuring results with the probe and thus also the control near to these values are very accurate. If, however, the temperature and the C-potential are lowered the value becomes inaccurate because of the different behaviour of the probe and the correction made.

With the C-potential controllers Carbomat-M (**Fig. 9**) and Carbo-M it is easy to achieve a correction in two points with the foil test. If the temperatures at which the corrections with the foil sample are made differ by more than 30 °C the controllers handle these values as corrections in two different points. Otherwise the values of the first correction are overwritten with the values of the second correction. It is recommended to perform the foil sample at a carburizing temperature of about 920 °C and 1.2 % C and at a hardening temperature of about 880 °C and 0.80 % C. The intermediate values are then automatically interpolated. This results in a very accurate C-potential measurement and control in the entire working range.

Conclusion

For quality assurance reference measurements are essential. In the process of gas carburizing the temperature and the C-potential are the key parameters that have to be monitored and reviewed regularly. The reference measurement of temperature is carried out in practice by an in-situ verification of the thermocouples, which means in the plant on site. For the C-potential there are several methods suitable as reference measurement.

The presented method in the first part of the article, the gas analysis by NDIR sensors, is furthermore an additional tool for solving of various problems. The reference measurement with a second O_2-probe or L-probe provides the advantage that with appropriate controllers the process can be controlled without any interruption with the second probe automatically if the first probe fails. The mirror dew point measurement instrument is not only suitable for C-potential reference measurement. With this device also the dew point of an endogas generator can be determined which can be used as reference measurement for the dew point control system of the generator.

Among the methods used for direct determination of the C-potential in particular the gravimetric method has to be emphasized. The weight measurement with a foil scale is easy to perform and very economical. For these reasons the weight measurement is preferred in practice compared to the other direct methods.

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