Optimised Heat Treatment in Steel Processing

More than good: harden and temper!

In the shape of Variocarb-direct, the Messer Group has developed and patented a process with which steels can be annealed more cost-effectively than before without decarburisation. Instead of using Endogas, produced in special generators or from nitrogen and liquid methanol, the annealing is carried out using nitrogen. Propane is introduced into the atmosphere of protective gas, controlled by sensors, as the reaction gas and effectively prevents decarburisation of the material. The new process produces no soot and is more efficient than conventional processes, delivering quenched and tempered steels of high quality.

The heat treatment is responsible for the useful properties of the components.
Hardening tempered steels cost-effectively and safely

How resistant to wear a component made from hardened steel is depends largely on the conditions under which it was heat treated. This specifically means the annealing and hardening stages.

During soft annealing, the material is heated slowly from 680 to 750 °C, kept at this temperature for hours and then slowly cooled again. Here, the carbon in the steel, bonded in the form Fe3C, changes from strip cementite to globular cementite and becomes easy to form and suitable for machining. Hardening follows, the steel literally becomes hard and resistant to wear. The piece is brought up to curing temperature – around 800 – 900°C - in the furnace and in doing so the bond between the iron atoms structure becomes more elastic and the crystalline structure of the metal is transformed: from the body-centred cubic ferrite lattice into a face-centred cubic gamma iron lattice. The steel is then quenched, that is, abruptly cooled like a boiled egg, which causes another change in the crystalline structure. After quenching, the lattice is distorted and the structure – called martensite – is very hard, brittle and susceptible to breaking. In order to reduce the prevailing tension in a controlled way, the hardened steel, depending on its type and required strength properties, is tempered by warming it to 150 – 500°C. The temperature is maintained until slackens sufficiently and the steel loses its brittleness. The annealed steel now has the desired toughness and practical hardness.

Ensuring the resistance to wear of hardened steels.

During heat treatment, the steel is given the required characteristics. However, whether or not it still has sufficient resistance to wear at a later stage depends to a large degree on whether attempts at keeping away the oxygen (which could be present in the proverbial “hot phase” of the heat treatment in the hardening furnace) from the metal have succeeded and the oxidation process on the surface of the metal prevented. How the oxygen enters the furnace, whether as a component of the air or in the form of a metal oxide or as a result of impurities on the material is of little importance. What is important is that the products resulting from the reaction, water and carbon dioxide, are quickly removed, otherwise they could react with the carbon dissolved in the allow. (Equations 1 and 2). Even small amounts of water and carbon dioxide are sufficient to partly remove the carbon which is in the steel and to damage the edges of the piece.

![Fig. 1: Measurement and control system for the dosing of nitrogen and propane](image)

\[
\begin{align*}
C_{\text{removed}} + H_2O & \rightarrow CO + H_2 \quad (1) \\
C_{\text{removed}} + CO_2 & \rightarrow 2 CO \quad (2)
\end{align*}
\]
It has been shown that no costly technical equipment using gas generators is needed in order to allow austenisation (800 – 900 °C) to take place in a carbon-neutral atmosphere. With Variocarb-direct, the Messer Group has developed and patented a process in which a controlled nitrogen/hydrocarbon (propane) mixture is introduced directly into the hot furnace, thus effectively preventing the decarburisation of the steel. The reaction to bind the carbon dioxide and water using propane runs as follows:

\[
\begin{align*}
3 \text{CO}_2 + C_3\text{H}_8 & \rightarrow 6 \text{CO} + 4 \text{H}_2 \\
3 \text{H}_2\text{O} + C_3\text{H}_8 & \rightarrow 3 \text{CO} + 7 \text{H}_2
\end{align*}
\]

**Easy to handle, reliable result**

An oxygen probe measures the degree of conversion from moisture and carbon dioxide to hydrogen and carbon monoxide. If necessary, propane will be dosed into the hot furnace automatically in adequate quantity. Thanks to a standardised measuring and dosing technique, the decarburisation of the piece can be effectively prevented. Over time, the quantity of propane necessary reduces and less is fed into the furnace.

\[\text{C}_3\text{H}_8 \rightarrow \text{CH}_4 + 2 \text{C} + 2 \text{H}_2\] (5)

The controlled voltage (millivolt) of the oxygen probe is calculated empirically and the value entered in the process programme. Which set point is optimal for the hardening process depends on many specific parameters.

On the basis of the number of installations carried out for customers and the experience gained, a new installation with nitrogen and propane can be quickly implemented.

The Variocarb-direct process has been used over many years to harden (without decarburising) numerous products from different types of steel with varying degrees of carbon content in a variety of furnaces e.g. roller hearth furnaces, continuous tube or conveyor as soon as retort furnaces.

**Fig. 2:** Thermal cracking of propane

**Fig. 3:** Working range of the probe voltage

**Fig. 4:** Continuously conveyor furnace from Aichelin

**Fig. 5:** Annealed bearing rings of 100 Cr6 steel
**Examples of Annealed Parts:**

- Bearing components
- Chain plates
- Screws
- Industrial needles
- Springs
- Saw blades

It is also possible to use on-site nitrogen, which is produced by means of membrane or adsorption technic. The residue oxygen from this nitrogen reacts very easily with propane (equation 6) to the required components of carbon monoxide, hydrogen and methane.

\[
\begin{align*}
&\text{(O}_2 + 99 \text{ N}_2)_{\text{On-site}} + \text{C}_3\text{H}_8 
\hspace{1cm} \rightarrow \\
&2 \text{ CO} + 2 \text{ H}_2 + \text{CH}_4 + 99 \text{ N}_2
\end{align*}
\]

Equation 6

Upwards of a temperature of about 600 °C, propane begins to dissociate into reactive radicals; they attack oxygen, convert it quickly and completely and render it harmless.

**Reports from practice**

**The task**

In a cooperation between a screw manufacturer and the Messer Group, the Variocarb-direct process was to be introduced into a 500 kg continuous conveyor furnace. There were several aspects which had to be looked at closely:

- Aim: annealing of screws without decarburisation.
- Simulation of on-site nitrogen and optimal premixing of gases as well as injection of the mixture into the furnace.
- Handling of the new gas process and calculation of the quantities of gas in order to prevent decarburisation and the creation of soot.
- Burning off the weakly combustible nitrogen/propane waste gas by suitable discharging of the gas.
- Reduction of operating costs by replacing methanol by on-site nitrogen and the advantages connected with this, such as:
  - Reduction of quantities stored and reduction in use of methanol
  - Reduction of CO₂ emissions
  - Reduction of energy for heating (cracking energy from methanol)

**Implementation**

Various quantities of air and propane were dosed into the amount of nitrogen required. Injection was conducted in such a way that the individual components were mixed intensively even before entering the furnace.

The homogenous gas mixtures were introduced into the furnace by two lances, installed above the drop shaft. For the purposes of measurement, gas could be taken from one of the lances and the oxygen content of the fresh gases.

![Fig 6: Individual hardening of small parts in the shaker hearth furnace](image)

The oxygen content determined was between 0.5 and 1.0% by volume. The propane gas requirement was adjusted to the oxygen concentration.

The sample gas for the analysis of the atmosphere in the furnace was taken from about 1m in front of the drop shaft. The gas components H₂, CO, CH₄, CO₂, H₂O and O₂ were measured and recorded. The carbon level of the atmosphere in the furnace was controlled by the existing oxygen probe and the computer. About 300 litres of propane per hour were injected at a constant rate. For all trials, the furnace temperature was 900 °C. The screws were mainly composed of 19 MnB₄ alloy. During the hardening trials, screws were taken out at intervals and examined metallographically.
Table 1 shows the comparison between the optimised and the previously used quantities of gas.

**Results**

All screws which were hardened in a simulation involving on-site nitrogen and propane in the continuous conveyor furnace demonstrated no differences in quality; they are comparable to screws which have been treated using nitrogen and methanol. The strength properties required as well as the surface carbon content corresponded to the norm and oxides were not found. Practical tests bear out the value of the Variocarb-direct process: methanol can be substituted by nitrogen and propane.

**Savings**

Due to the changeover to a comparatively cheap nitrogen/propane gas mixtures with a monthly production time of 720 hours, around 5760 l of methanol can be saved. This is substituted by 10,800 m³ of nitrogen and 215 m³ of propane. The saving and the investment for a new methanol tank lead to a considerable reduction in costs and increase in productivity.

**Conclusion:**

With sufficiently high temperatures such as are used when hardening steel, no expensive engineering is necessary to produce a carbon-neutral atmosphere in the furnace. In fact, the Variocarb-direct process patented by the Messer Group and based on the use of nitrogen-propane mixtures is sufficient. The requirements-based adaption of the measuring and control system makes it possible to dose the propane gas optimally. The replacement of Endogas results in a cost saving, the amount of which can vary from case to case.

Technical advice on and implementation of direct gas injection is undertaken with the support of the Messer Group GmbH.

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<table>
<thead>
<tr>
<th>Continuous furnace</th>
<th>N₂-Demand m³/h</th>
<th>Methanol l/h</th>
<th>Cracked gas m³/h</th>
<th>Total flow rate m³/h</th>
<th>Propane l/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>2 mal 8</td>
<td>2 mal 4</td>
<td>14</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>On-site-N₂</td>
<td>2 mal 15</td>
<td>0</td>
<td>0</td>
<td>30</td>
<td>300</td>
</tr>
</tbody>
</table>

*Table 1: Quantities of gas used before and after changing over to nitrogen and propane*
You work in industry as an applications expert and have specific questions on this article?

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