High Temperature Low Pressure Carburizing with Prenitriding Process – The Economic Option for Vacuum Carburizing

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ABSTRACT

The original idea of grain growth limitation by preliminary nitriding preceding low pressure carburizing (LPC) is presented as a useful option for the FineCarb® technology. This new process called PreNitLPC® enables high temperature carburizing up to 1050°C for a variety of common carburizing steels without any adverse effects on both microstructural or performance. The shortening of carburizing time may result in a decrease in manufacturing costs as well as energy consumption from 5-50% depending on the case depth. This has been confirmed on the basis of several pilot industrial installations.

The metallurgical background of PreNitLPC® has been discussed at the microstructural level. The mechanism of nanonitrides precipitation has been found as the effective way for intensive nucleation of austenite grains and for inhibition of grain boundary movement at significantly high temperatures. The results of comparative investigations of fatigue and impact strength as well as pitting resistance for traditional endothermic gas carburizing (ENDO), standard LPC and PreNitLPC® are presented. They confirm the efficiency of the pre-nitriding option in grain growth limitation for plain carbon and low alloying steels enabling high mechanical properties to be achieved in machine parts hardened using PreNitLPC®.

The problem of increased carburizing temperature on heat treatment distortion is also discussed. The results of comparative geometrical measurements show the possibility to keep the distortion level from the high temperature carburizing similar to that for traditional ENDO carburizing, although this requires additional optimization of the PreNitLPC® parameters.

Keywords: vacuum carburizing, case hardening, costs assessment, fatigue strength
1. INTRODUCTION
Thermal and thermochemical processing are significant capital-intensive factors in the production process of machine parts and tools; therefore, it is important in terms of the competitive advantage and profitability of the metal industry in the global market environment to make this processing as economical as possible. Now that the competition is fierce, high product quality must be accompanied by low prices. For a novel technological solution to be adopted for a commercial application, it must not be worse than previously applied solutions in terms of quality, but it must also provide an opportunity to create an economic advantage.

High-temperature vacuum carburizing with pre-nitriding - PreNitLPC® - is a technology which meets these requirements. The typical process temperatures in traditional carburizing is 920°C, but temperatures as high as 1050°C can be only applied in vacuum carburizing furnaces [1]. An increase in carburizing process temperature from 920°C to 1,000°C can reduce the duration of the carburizing process, reducing the cost of treatment. However, this is associated with the risk of rapid austenite grain growth. To prevent this, a novel technology of nitriding-supported vacuum carburising - PreNitLPC® - has been developed. The processing involves feeding ammonia into the preliminary phase of the process - during the pre-carburising heating. This results in an absence of grain growth in the carburized layers even when the process temperature is higher than traditional process temperatures. Nitrogen enters the surface layers of the steel to form nitrides and/or carbonitrides, which block austenite grain growth during the carburising phase [2,3].

2. CARBURIZING TRIAL
Two low-pressure carburizing processes, conventional low-pressure (LPC) and low-pressure carburizing with pre-nitriding (PreNitLPC®), have been conducted at 920°C and 1000°C in order to compare the structure and properties of the surface layers obtained from these two treatments. Conventional gas carburising (ENDO) at 920°C has also been used to provide a standard benchmark for the two low pressure processes.

The carburising process was conducted in an acetylene - ethylene - hydrogen atmosphere. Nitrogen for the pre-nitriding process was obtained by dissociation of ammonia. The dosing parameters of the carburising atmosphere were selected in accordance with the relevant patent [4], and those of ammonia in accordance with another patent [3]. Ammonia was fed within the temperatures range from 400°C to 700°C during the heating stage of the charge for carburising for a period of 60 min. Two kinds of steel were carburised - typical carburising grades 16MnCr5 and 17CrNi6-6. The process parameters are shown in table 1. Samples for metallographic tests had a diameter of 25 mm and a thickness of 10 mm. Samples for mechanical testing had shape and dimensions according to the standards used in such measurements.

For process control purposes, carbon distribution in the steel surface layer was determined after carburizing via gradual removal of surface layers. Carbon content in the layers was determined by IR (infrared) absorption with a Leco CS200 analyzer. The results are shown in Figure 1.

In the next stage of the research, microstructures obtained at different temperatures were compared in regard to
Table 1. Carburising process parameters.

<table>
<thead>
<tr>
<th>Type of carburising</th>
<th>ENDO</th>
<th>LPC</th>
<th>PreNit LPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process temperature</td>
<td>920°C</td>
<td>920°C</td>
<td>1,000°C</td>
</tr>
<tr>
<td>Ammonia dosing</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>temperature range</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carburizing time</td>
<td>2h47min</td>
<td>23min</td>
<td>11min</td>
</tr>
<tr>
<td>Diffusion time</td>
<td>-</td>
<td>1h 52min</td>
<td>43min</td>
</tr>
<tr>
<td>Gas carburizing</td>
<td>endothermic gas</td>
<td>C₂H₂ + C₂H₄ + H₂</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>1,100 hPa</td>
<td>Carb:300-800 Pa</td>
<td>Diff.: 10Pa</td>
</tr>
<tr>
<td>Layer thickness (0.4%C)</td>
<td></td>
<td>0.6 mm</td>
<td></td>
</tr>
<tr>
<td>Surface concentration</td>
<td></td>
<td>0.75%C</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Carbon profile in the surface layer of 16MnCr5 steel following low-pressure carburising and ENDO at 920°C and following low-pressure carburising with pre-nitriding at the temperature of 1,000°C.

the austenite grain size (Figure 2). The samples were etched by aqueous solution of picric acid, at 70°C. The grain size was estimated by a planimetric method, according to ISO 643: 2003.

Figure 3 shows that grains in the carburized layer are much smaller after the PreNitLPC® processes. Even grains produced by carburising at a temperature of 1,000°C are smaller than those
obtained by carburising at 920°C without pre-nitriding.

The effect of the process temperatures on the core grain size was examined in the LPC processes conducted at 920°C and in PreNitLPC® processes at 1,000°C. As expected, the grains in the core of 16MnCr5 steel carburised by the PreNitLPC® technology at 1,000°C are larger than in the LPC process at 920°C (Figure 2 and 4). Therefore, it can be concluded that the small size of grains in the surface layer is caused by the presence of nitrogen fed during the heating stage. The differences in the grain size at 920°C obtained for different technologies are the result of measurement experimental errors.

In conclusion, raising the temperatures of low-pressure carburizing treatment can significantly reduce the process duration, while at the same time eliminating excessive grain growth in the steel surface layer (Table 1).

3. EVALUATION OF THE STRENGTH PROPERTIES

The most important feature concerning the potential application of the PreNitLPC® technology is the evaluation of the mechanical properties.

Comparison of the results of hardness distribution in the surface layer of 16MnCr5 steel shows that increasing the carburizing process temperature in the PreNitLPC® technology does not result in a decrease of the hardness as compared to low-pressure carburising alone. The hardness distributions obtained from the two processes are similar (Figure 5).

A series of tests were also conducted to determine the fatigue bending strength using the resonance method. The measurement relies on the implementation of the resonance frequency of vibration on the sample. Sample fatigue failure is detected by the change of sample vibration frequency. The tests were done according to ASTM E 606-04.
Figure 3. Microstructure of the surface layer of 16MnCr5 steel following low-pressure carburising at 920°C (a) and following low-pressure carburising with pre-nitriding at 1,000°C (b).

Figure 4. Microstructure of 16MnCr5 steel core following low-pressure carburising at 920°C (a) and following low-pressure carburising with pre-nitriding at 1,000°C (b).

Figure 5. Comparison of 16MnCr5 steel hardness following low-pressure carburising and ENDO at 920°C and low-pressure carburising with pre-nitriding at 1,000°C.
The results, shown in Figure 6, were used to plot Wöhler’s curves for limited and unlimited fatigue strength for samples following the LPC process at a temperature of 920°C and following the PreNitLPC® process conducted at a temperature of 1,000°C. A comparison of the values shows that the fatigue bending strength of 16MnCr5 steel is higher following the PreNitLPC® process.

Contact fatigue tests (pitting resistance) were performed using a modified apparatus with four-node friction cone-balls under a load of 392.4 N according to PN-76/C-04147. The values of contact fatigue strength obtained for 16MnCr5 steel in each variant of carburising (Table 1) are comparable and close to $1.6 \times 10^6$ cycles.

**Figure 6.** Comparison of unlimited fatigue bending strength for 16MnCr5 steel after different surface treatments.

### 4. Generation of Carburising Atmosphere

A competitive edge for surface processing, both on local and global markets, may be created by reducing operating costs for vacuum machines and equipment and by reducing the duration of processes. However, relatively high costs are still incurred as a result of having to use carbonaceous gases, especially ethylene ($C_2H_4$). The average price of ethylene ($C_2H_4$) on the European market is approximately six times higher than that of acetylene and hydrogen. The problem is especially significant in the countries where there are problems with ethylene supply, e.g. in India. This considerably limits the possibility of application of vacuum technologies in less industrialised countries and makes them more costly. Therefore, there is a strong need to produce a carburizing mixture with set parameters in regard to an additional reduction of the cost of the process of low-pressure carburising.

To this end, a working atmosphere generator has been developed in which hydrogen and acetylene ($C_2H_2$), as well as a palladium regiospecific catalyst deposited on Al$_2$O$_3$, is used to produce a carburising mixture with the following composition 40%$C_2H_2$, 40%$C_2H_4$ and 20%$H_2$. Due to
appropriately selected process parameters, it is possible to hydrogenate acetylene to ethylene without formation of ethane, which could change the carbon potential of the processing atmosphere. Moreover, it is possible to eliminate formation of oligomeric compounds on the catalyst surface, which effectively limits deactivation of its active sites. This prevents a decrease in the process efficiency, which is close to 55%, over time. In the next stage, in order to obtain a carburizing mixture of the desired composition, i.e. 40% C₂H₂, 40% C₂H₄ and 20%H₂, C₂H₄ has to be diluted at the appropriate ratio with C₂H₂ and H₂. Then, the carburising gas mixture can be sent to the reaction chamber and the low-pressure carburising then be conducted.

It is also important that an on-line production of a mixture of carbonaceous gases is possible in the “Boost” and “Diffusion” system, for the full range of possible flow rates and times of each “Boost” stage. It also enables optimisation of the process cost in terms of elimination of an additional buffer tank where an excess amount of mixture is stored.

Figure 7. An example of change of the carburising mixture, produced: “on line” for the low-pressure process in the “Boost” and “Diffusion” options.

5. ECONOMICS OF THE PROCESS

In 1999 a research plan was developed at ASM International, where priority aspects were identified for the improvement of thermal processes. These included economic aspects, such as: reducing the process duration, reducing the production cost, reducing energy consumption, etc. [5]. In general high-temperature low-pressure carburising with pre-nitriding - PreNitLPC®, meets those objectives.

A breakdown of costs reveals the economic advantage of the PreNitLPC® technology as shown in Table 2 for layers
up to 5 mm thick. The low-pressure technology is already more cost-effective for a 0.4 mm layer. An analysis of the unit cost shows that the PreNitLPC® technology is cheaper by 4% to 29% when the thickest layers were obtained.

Currently, the low-pressure processes account for approx. 15% of the carburising market [6]. It is estimated that the level will have increased to about 35% by 2020 [7].

Table 2 reveals not only lower unit costs but also the potential for generation of higher profit despite lower prices resulting from the lower unit cost (assuming the same 20% margin). Implementation of the new technology of high-temperature carburising with pre-nitriding makes it possible to generate from 6% to as much as 75% higher profit as compared to the conventional technology, depending on the layer thickness.

<table>
<thead>
<tr>
<th>Estimated Carburizing Depth (ECD) [mm]</th>
<th>ENDO 920°C</th>
<th>ENDO 980°C</th>
<th>PreNitLPC® 1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Profit [%]</td>
<td>Unit cost [%]</td>
<td>Profit [%]</td>
</tr>
<tr>
<td>0.4</td>
<td>100</td>
<td>100</td>
<td>X</td>
</tr>
<tr>
<td>0.6</td>
<td>100</td>
<td>100</td>
<td>X</td>
</tr>
<tr>
<td>0.9</td>
<td>100</td>
<td>100</td>
<td>X</td>
</tr>
<tr>
<td>1.2</td>
<td>100</td>
<td>100</td>
<td>X</td>
</tr>
<tr>
<td>2.0</td>
<td>X</td>
<td>X</td>
<td>100</td>
</tr>
<tr>
<td>3.0</td>
<td>X</td>
<td>X</td>
<td>100</td>
</tr>
<tr>
<td>5.0</td>
<td>X</td>
<td>X</td>
<td>100</td>
</tr>
</tbody>
</table>

6. SUMMARY

The mechanical properties such as pitting resistance and hardness of layers produced in the PreNitLPC® technology are comparable to those achieved in the LPC process. Feeding nitrogen during the heating phase makes it possible to achieve higher fatigue bending strength. Investigation of the grain size shows that raising the temperature of the PreNitLPC® process by nearly 100°C still results in smaller grains than in the traditional LPC process.

The PreNitLPC® technology can be applied at much higher temperatures as compared to LPC or conventional technologies, without reduction in properties. Due to the temperature increase, the process duration needed to achieve the desired layer thickness can be considerably reduced. This has a positive effect on the PreNitLPC® process economy and provides huge application opportunities for mass production.

The possibility of producing a three-component carburising atmosphere without having to use expensive ethylene, which is not easily available, increases the application potential of the technology and improves its economical aspect.
REFERENCES


