

KARBONITRIDACE V PLYNU V PRAXI

GAS NITROCARBURIZING IN PRAXIS

Petr Brejša, Ing., Bodycote HT s.r.o., Křížová 1018, 15021 Praha 5,
petr.brejsa@bodycte.com

Pavel Ryvola, Ing., Bodycote HT s.r.o., Křížová 1018, 15021 Praha 5,
pavel.ryvola@bodycte.com

Jiří Stanislav, Ing., CSc., Bodycote HT s.r.o., Tanvaldská 345, 43611 Liberec,
jiri.stanislav@bodycote.com

ABSTRACT

Nitrocarburizing is a low temperature process for surface modification. The result of process is a compound layer covered by oxides Fe_3O_4 . The main quality is a high corrosion resistance, for automotive industry up to 260 h. Bodycote in Prague is working on this application since the ninetieth on ZEZ pit furnaces, then on chamber nitriders DAC 8GR. In the last years Bodycote has rebuilt pit furnaces and equipped them by new control system for nitrogen potential regulation and for gases through hydrogen probe. In the article are described some of problem linked to this equipment and technology application

1. Equipment for nitrocarburizing

Gas nitrocarburizing in commercial heat treatment plant Bodycote HT s.r.o., Prague has been operating since the second half of the 1990s. The first experience was gained with the RSHZM pit nitriding furnace with a gas-tight muffle. This device, see Fig. 1, was manufactured in the mid-1980s by a factory for electrothermal equipment at the Prague ZEZ. For both nitrocarburizing and nitriding processes, the original furnace muffle was provided with enamel on the inner surface and an oil-sealed outlet with burning of the outgoing furnace atmosphere.

The atmosphere was created in the furnace by feeding ammonia and endogas in a constant ratio of 1: 1. Nitrogen was used for the initial and final purge. The atmosphere was unregulated, its flow rates were determined according to experience by the type of material being processed and the total batch surface. A perchlor washer, which was originally part of the Ipsen line, was used to wash the carbonitrided parts prior to the process. This washing machine was taken out of service at the end of the 1990s and replaced by a modernized alkaline water washing machine with two washing stages, which was used until the middle of this year. The 1st stage of this washing was carried out by flooding and swirling, followed by draining and the 2nd stage by intensive spraying and subsequent drying.



Obr.č. 1 – Šachtová pece RSHZM

After mastering the nitrocarburizing process, customer demand for this technology increased over time, and a decision was made to increase process capacity. Therefore, the Ipsen DAC 8GR chamber furnace was purchased in 2002, which was and is used only for nitrocarburizing processes. The nitrocarburizing was performed on this furnace, followed by oxidation, first using nitrogen protoxide, later by adding water. As the requirements for the quality of nitrocarburized layers also increased with the capacity requirements, a decision was made in 2004 and in 2005 the RSHZM pit furnaces were modernized. This modernization was gradual, at first one and then in 2006 at the second furnace. The modernization of RSHZM pit furnaces was carried out as a supplier and consisted of:

- 1) complete refurbishment of the muffle cover, inlets and outlets of gases and atmosphere, efficient and powerful fan
- 2) updated gas control system including mass flow meters for ammonia and carbon dioxide
- 3) installation of a fully programmable controller/recorder Stange SE-607, including a hydrogen probe for nitriding number control
- 4) water dosing installation for the final oxidation of the nitrocarburized layer

Furnaces are equipped with automatic recording of process parameters, the possibility of their printing, including the possibility of long-term archiving and fast retrieval of older data.

As the existing washing machine did not meet the increased capacity of the furnaces and its capacities will be used by the extended hardening line, a new modern 3-chamber alkaline washing machine with 2 rinsing stages was purchased. In the first chamber, the batch including the baskets is washed intensively with an air-swirling bath of concentrated detergent with the support of ultrasonic radiators. In the second chamber, the batch is sprayed with water with a very low detergent concentration and in the third chamber is dried. This washing machine has been in operation since mid-August 2008 and practical experience is being gained with it. The dimensions of the washing machine enable the washing of batches of nitrocarburizing parts, both for pit furnaces and for DAC chamber furnaces.

2. Nitrocarburized layers

The layers formed by the nitrocarburizing process consist of three basic interlayers.

- From the diffusion layer forming the transition to the substrate. The thickness of this layer is usually 0.1 to 1 mm depending on the type of process and application. It consists of precipitated (carbo) nitrides and a solid solution of nitrogen dissolved in iron α with increased hardness and fatigue limit
- From a compact layer consisting of ϵ - and γ' - (carbo) nitrides. The thickness of this layer is usually 5 to 30 μm .
- From the surface layer of oxides with a thickness of 0.5 to 3 μm , consisting of iron oxides type Fe_3O_4

The compact layer tends to have high hardness and high wear resistance, especially when composed predominantly of ϵ -nitrides. Under special conditions, the oxide layer acts as a passivation of the compact layer and as a corrosion protection. Achieving a high nitrogen content in the layer with a sufficient carbon content has proven to be crucial for this property. Since this concentration is directly affected by the process parameters, the process of carbonitriding followed by oxidation becomes very demanding in terms of controlling these parameters. This process is registered with Bodycote under the trademark Corr-I-dur®.

The corrosion resistance of the layer thus formed can reach up to 400 hours under test conditions according to DIN 50021-SS (ASTM B 117-73). The usual requirement for the automotive industry is then 260 hours under conditions

Mass-% NaCl	Temperature	PH-value
50 \pm 5 g/l	35 \pm 2°C	6,5-7,2

3. Nitrocarburizing of different steel grades

In gaseous environments, carbon steels, low-alloy, free-cutting with lead, gray and ductile iron can be nitrocarburized. Steels with a high Cr content < 8%, intended for die casting molds, hot forming tools, can only be processed under strictly defined conditions. Steels with Cr > 8%, ie ledeburitic steels, austenitic steels with a high Ni content can be nitrocarburized in the gas only under special surface activation conditions before the process itself. In these cases, nitrocarburizing in gas cannot compete with nitrocarburizing in liquid or plasma, and in austenitic steels with the Kolsterising® process. These processes provide much more reproducible and uniform results.

Examples of steels, layers and their achieved parameters thickness / hardness:

11523 (S355J2), 12050 (C45), 14220 (16MnCr5), 15142 (42CrMo4) – compound layer 10 to 23 μm , max. 30% porosity

42CrMo4 – compound layer 10 μm , oxide layer of 2 μm , corrosion resistance min. 250 h

9SMnPb28k – compound layer 25 – 35 μm

11SMnPb30 – compound layer min. 10 μm , oxide layer 2 μm , corrosion resistance min. 48 h, surface hardness min 300HV_{0,3}

42CrMoS4 – compound layer 5 - 20 μm , oxide layer 3 - 5 μm , diffusion layer 0,2 – 0,3 mm, surface hardness 500-700HV₅

Ck75 – compound layer 5 - 20 μm , surface hardness 600-700HV_{0,2}

C35, C45 – compound layer min. 10 μm

9SMnPb28K – compound layer min. 10 μm , oxide layer not defined, requested black surface

3.1. What should be the customer's requirements regarding the quality of the nitrocarburized layer?

- **compound layer thickness**, diffusion (nitriding) layer and tolerances, compound layer thickness is from 3 to 40 μm , usual tolerance is 50% of the required maximum compound layer
- **Hardness measured by HV_{0,1} až HV₅**
- **Porosity** - in some applications metallographic inspection of the porosity of the upper part of the compound layer is required, porosity should be inspected only in the polished unetched state
- **Surface oxidation** is provided for higher corrosion resistance
- **Corrosion resistance** – is required in a number of applications in the range of 48 to 240 h, it is performed by testing in neutral salt spray according to the corresponding ASTM or DIN standards
- **Surface roughness** - usually deteriorates slightly, it can be improved by subsequent polishing, tumbling, etc.
- **Increase in dimensions** - it is typical for this technology of chemical-thermal treatment and ranges according to the achieved thickness of the compound layer from 0.01 to 0.04 mm
- **Conservation** - is carried out only at the customer's request, usually by immersion or spraying with an water emulsion, which after drying creates a permanent non-stick preservative surface
- **Chemical composition of the layer** - no one has yet required to determine the nitrogen content in the layer

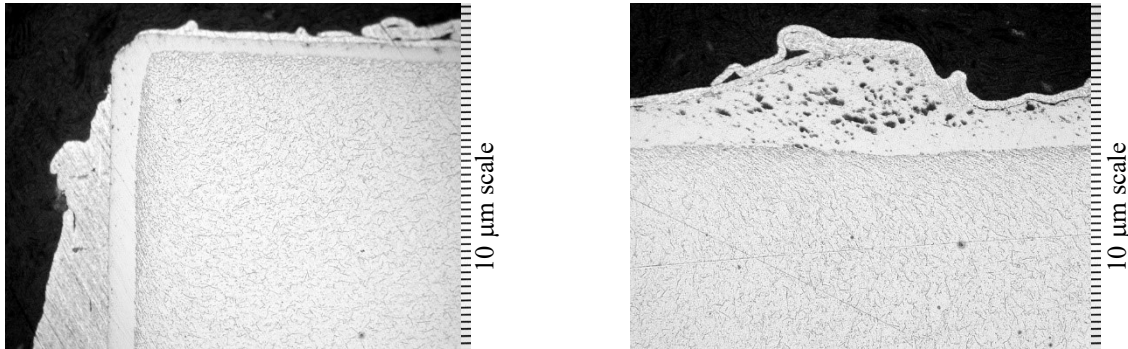
3.2. What should be the goods from the customer intended for nitrocarburizing in gas?

From the point of view of nitrocarburizing, it is necessary that the customer of the heat treater, which wants to have its parts nitrocarburized, adheres to certain rules and procedures, as the previous processing will affect the result of the nitrocarburizing process. The following conditions are important:

Surface cleanliness, grease, corrosion, conservation, spontaneous passivation, surface stresses after machining, forming and cutting (intensive deformations and local stresses), stability of parameters, regularity of deliveries. The customer may negatively affect the result of nitrocarburizing by an untested change in his technology, a change in the method of washing and conservation, a change in the supplier of input material, etc.

4. PRACTICAL EXAMPLES

Different layer thickness on one part - example of precise sheet metal cutting, structural steel with higher yield strength etc.

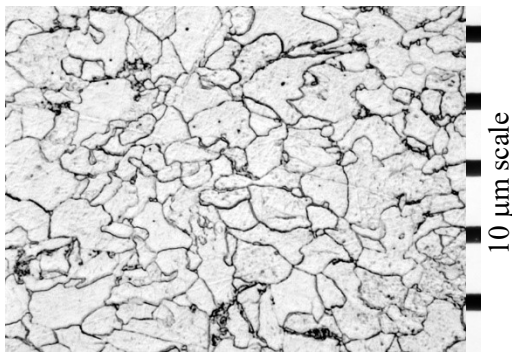


Fluctuating thickness and hardness - cast iron has graphitic structures in the vicinity of these structures the surface hardness fluctuates considerably, only the maximum measured hardness values are considered

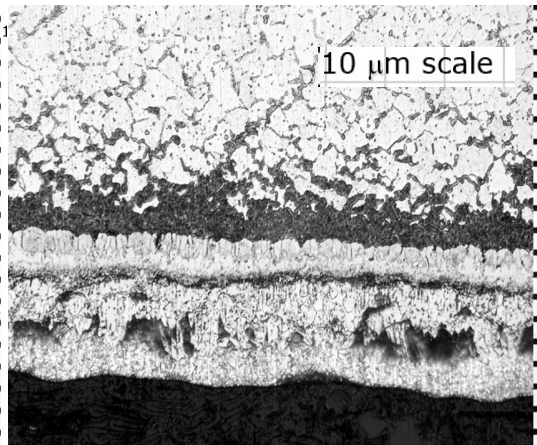
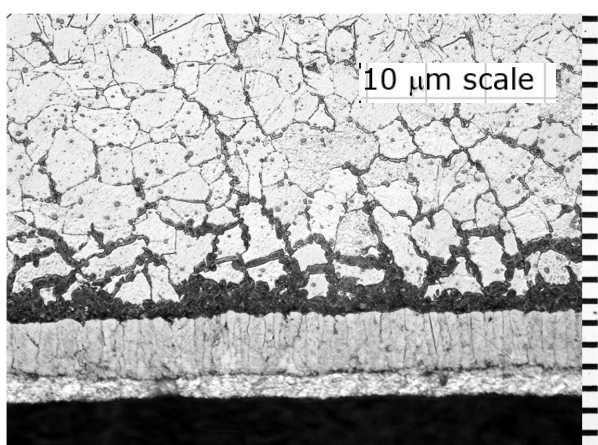
Surface hardness measurement - best performed on a layer cleaned (locally ground) with a rubber grinding wheel (mixture of rubber and glass abrasive)

Pre-oxidation with air - used to activate the surface and even the results of the oxidation bilayer process is observable usually when using pre-oxidation above 350 °C and times longer than 2 hours

Embrittlement, loss of toughness - structural steel with a higher yield strength, on the left picture the envelopes along the grain boundaries, the part became brittle after nitrocarburizing, on the right the part could be bent and had a tough fracture in the core



Nitrocarburizing of lead-containing steels, with improved machining properties, these steels show an unusually large dispersion in the achieved thicknesses during carbonitriding in gas



5. Future in gas nitrocarburizing

Nitrocarburizing in gas has its future and applications between salt and plasma processes. Each of these processes has its advantages and disadvantages. The advantages of the gas process are, in particular, the mass production of parts in bulk batches and the possibility of achieving uniform layers in parts with complicated shapes. There is no need to get rid of residual salts after the process and there is no need to use auxiliary electrodes.

One of the disadvantages is the need for a sufficiently active surface before the process, and this can usually only be achieved with non-alloy or low-alloy steels. Other disadvantages are the higher energy intensity and low efficiency of the use of gases containing N and C. Nevertheless, it can be expected that for a long time this chemical-thermal treatment technology will find its place on the heat treatment market and will be included in the offers of commercial heat treatment plants