ABSTRACT: The original idea of the grain coarsening inhibition by preliminary nitriding preceding the vacuum carburizing process is a useful option of FINECARB® technology. The steel vacuum carbnitriding method based on the alternative dosing of the carbon carriers and nitrogen, and on the computer simulation of the layer growth under the conditions of unsteady concurrent diffusion of the nitrogen and carbon is presented in this paper. The application examples are also described.

1. INTRODUCTION

The advantages of vacuum carburizing process such compactness of the installation, environmental friendless, cleanness, beneficial microstructure make this process enter the industry wider and wider by installation of the single, double and multi chamber devices as well as multichamber process lines (Fig. 1) (Grafen 1999), (Heilmann 1998), (Kula 2004). These installations systematically displace conventional gas carburizing processes. Among them the advanced FineCarb® technology developed in cooperation between Seco/Warwick Ltd. and Technical University of Lodz (PL) (Kula 2000), (Kula 2004) offers the wide range of classic and less common surface hardening processes for mechanical engineering (Kula 2001). They are able to be carried out by using multipurpose vacuum furnaces equipped with high pressure gas quenching systems.

Fig. 1: Vacuum Carburizing furnaces produced by Seco/Warwick.

This generation change of one of the basic technological processes implies the necessity of urgent accommodation of the nitrocarburizing process, conventionally accompanying vacuum carburizing (applied to carbon and to low and medium alloyed steels treatment), to the conditions of vacuum technologies. Two new original steel vacuum nitrocarburizing methods based on the alternative or simultaneous dosing of the carbon carriers and nitrogen are presented in this paper. Also, the physicochemical conditions of this thermochemical vacuum process are discussed and explained on the base of theory and experimental data.

2. PHYSICOCHEMISTRY AND KINETICS OF VACUUM CARBURIZING

2.1. Synergic gas mixture for FINECARB®
The complex mixture of gases with changeable composition optimized for each new process from the point of view of treated charge, is applied as an original carburizing atmosphere in FineCarb® system. The carbon carrier in a form of preliminary mixed two undersaturated hydrocarbons (ethylene and acetylene) of specified and patented ratio is the base of the carburizing atmosphere (Kula 2002). Such prepared carbon carrier can be mixed with hydrogen or ammonia. The synergic usage of ethylene and acetylene gives advantageous effects and the final result of the treatment as a result of the synergism is powered in comparison to atmospheres based on single carbon carriers (Józwiak 2003), (Kula 2002). The gas mixture for FineCarb® ensures high level of hydrocarbons’ decomposition (70% to 90%) and consistently it causes the efficient carbon transfer to the surface of treated steel (Fig. 2).

Fig. 2: Decomposition of acetylene versus composition of carburizing atmosphere (950 °C).

The final result of its use is a reliable uniform carburizing of complicated shape workpieces (Fig. 3), especially those with narrow and deep hollows. On the other hand, high degree of hydrocarbons decomposition considerably eliminates the creation of by-products, e.g. soot and tar. The exhaust gases contain mostly hydrogen (7% ethylene, 1.5% acetylene, 91.3% hydrogen and 0.2% others) and the total consumption of carbon carrier may be reduced even twice.

Fig. 3: Machining parts after vacuum carburizing.

2.2. **Boost-diffusion model of vacuum carburizing**

The atmosphere based on the hydrocarbons as the carbon carriers is characterized by very high carbon potential. Disequilibrium nature of the vacuum carburizing imposes the division of the vacuum carburizing process into a series of phases, in this into in cycles of repeatable stages of boost and diffusion to avoid by-products creation and to reach a required carbon profile (Kula 2000), (Kula 2001), (Kula 2004). All, up to now built, industrial installations containing FineCarb® option were equipped with SimVac computer simulation software that enables to optimise the schedule of vacuum carburizing on the base of virtual analysis and complete database. For simplicity, the
algorithm of SimVac assumes that carbon transfer from carburizing medium to steel proceeds only during boost stage without any intermediate compounds (no carbon flux from atmosphere during diffusion stage – Fig. 4a). Numerous industrial verifications of SimVac software demonstrated some differences between simulation and reality. The reason of them arises probably from unsatisfactory recognition of surface phenomena during boost and diffusion stages.

Fig. 4:Carbon concentration in austenite during developing of boost and diffusion stages: (a) carburizing from hydrocarbons; (b) carburizing through carbon deposit.

2.3. Deposited carbon– the intermediate stage of carbon transfer

The SEM investigation of steel surface after initial stage of vacuum carburizing showed that quite all area of workpieces has been covered by thin film of new created compounds and some fine carbides already after several seconds of hydrocarbon gas dosing (Fig. 5).

Fig. 5: SEM image of carbon deposit. Fig. 6: Comparison of measured and calculated thickness of layer.

The TOFF SIMS analysis enabled to make the chemical identification this film as mostly containing different groups of hydrogenated carbon (Fig. 7). The creation of the intermediate compounds on the boundary between treated steel and furnace atmosphere shows the different mechanism of carbon transfer to that supposed in classic algorithms for vacuum carburizing. We call this thin film of hydrogenated carbon as the “carbon deposit”. It should be an effective source of additional carbon also during the diffusion stage (Fig. 4b). The new developed upgraded SimVac Plus software is based on the new computational algorithm that takes into account this correction factor. Thanks to the upgrading of algorithms closer to the real physical phenomena the results obtained by SimVac Plus show the satisfactory correlation with experimental (industrial) data (Fig. 6).
3. **THE BASIC PROBLEMS OF VACUUM NITROCARBURIZING**

3.1. **Physicochemistry of separate or simultaneous dosing of nitrogen and carbon carriers**

The feeding of a hot vacuum chamber with ammonia gas as the nitrogen carrier should cause new progress of chemical reactions during vacuum nitrocarburizing.

Fig. 8a: Changes of chemical compounds contents in furnace atmosphere during carbonitriding process.

Besides the basic reaction of ammonia gas dissociation that progresses catalytically on a steel charge additional unknown reactions of ammonia gas and/or hydrogen with the carbon deposit and/or the hydrocarbons gas mixture are probable under considered thermo-chemical conditions. The mass spectrometric investigation of the exhaust gases has been carried out for recognition of vacuum nitrocarburizing chemistry. The results of them are illustrated in the Fig.8a.

The ammonia gas dosing was started at 400°C. Between 400°C and 800°C, NH₃ dissociated only. Above 800°C uncommon growth of peak 28 appeared that is a superposition of nitrogen and ethylene mass. Creation of ethylene is caused by the reaction of ammonia gas and/or hydrogen with carbon deposit. However, the reactions of hydrogen and/or ammonia gas with graphite heating elements and other carbon made equipment parts are improbable. Unexpected appearing of ethylene above 800°C causes uncontrolled carburizing. That's why heating range over 800°C should...
be excluded for single dosing of ammonia gas both during heating and annealing (diffusion stages). During the boost stage simultaneous dosing of ammonia gas and hydrocarbons gas mixture causes the progress of reaction into propane synthesis. Hydrogen’s radicals play an important role in the progress of the most reaction showed on the Fig. 8b. This type of reactions differs essentially from those for classic vacuum carburizing. That fact should be taken into account during modelling and simulation of nitrocarburized cases growth and reactive gas dosing. In conclusions, the controlled dosing of ammonia gas may done only during heating of charge below 800°C (prenitriding option) or/and during boost stages (vacuum nitrocarburizing).

3.2. **Technological solutions**

3.2.1. **Prenitriding option**

The original idea of the grain growth limiting by preliminary nitriding preceding the vacuum carburizing process is a useful option of FINECARB technology (Kula 2004). This option was applied many times in practice to intensify the vacuum carburizing process, improve the microstructure of the layers as well as hardenability in the area of nitrogen penetration. This option finds a special application in vacuum carburizing with quenching in gases at elevated pressures, especially for low alloy carburizing steels generally applied in automotive industry Fig. 9.

![Diagram](image)

**Fig. 8b:** Temperature changes during carbonitriding process with possible chemical reactions.

![Graph](image)

**Fig. 9:** Vacuum treated steels: (a) after carburizing; (b) after nitrocarburizing.
3.2.2. **Boost nitrocarburizing**

The boost nitrocarburizing is especially effective to improve hardenability of low and medium carbon plain steels, however the cooling efficiency of standard multipurpose vacuum furnaces with high pressure nitrogen quenching is not enough to reach satisfactory hardness for vacuum nitrocarburized bulk parts. Today, good high pressure gas quenching results are obtainable only for thin sheet blanks (max. 2 mm thick). Vacuum installations like "seal quench " and the application of helium or hydrogen as the quenching gas medium may be the effective solution for vacuum nitrocarburizing. The combining of prenitriding option and boost nitrocarburizing is effective due to the superposition of advantages of each one and it’s often applied for thin automotive steel blanks.

3.2.3. **Less common application**

Moreover, the prenitriding option may be used for precise vacuum nitriding of machine parts and tools for machining, forging and forming (Has 1995). It is the important extending of technological abilities for multipurpose vacuum furnaces especially those in service heat treating plants.

4. **BIBLIOGRAPHIES**


