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Low-pressure ferritic nitrocarburizing: a review

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ABSTRACT

Purpose: The purpose of this article was to present in a concise and organized way the available knowledge about ferritic nitrocarburizing in low-pressure. The authors aimed to indicate the research gap, and the whole article is a starting point for further research.

Design/methodology/approach: The research method was the analysis of available literature, patent database and industry notes from manufacturers of modern furnaces.

Findings: The ferritic nitrocarburizing process has many advantages in line with the market demand and the lack of solutions. The article summarizes the knowledge in the field of the ferritic nitrocarburizing process as a systematization of knowledge and a starting point for further research.

Research limitations/implications: The information described in the article requires further laboratory research.

Practical implications: The information collected by the authors was the basis for developing the technology discussed in the LIDER/3/0025/L-12/20/NCBR/2021 project.

Originality/value: Research on this type of treatment will enable the development of technology and will meet the expectations and needs of the industry. It will also provide benefits in the form of a better understanding of the processes and the determination of the relationship between the parameters and the properties of the obtained surface layers.

Keywords: Thermo-chemical treatment, Heat treatment, Ferritic nitrocarburising, Universal furnaces

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Heat and thermo-chemical treatment of steel and semi-finished products is a significant technical process in strategic economic sectors such as automotive, aviation, machine and defence, heavy working machine production, tool industry, etc.

The international metal market increased by 7.1% per year from $3,638.17 billion in 2021 to $3,895.43 billion in 2022. The relatively low growth of such a highly profitable field was influenced by the COVID-19 pandemic and the war between Russia and Ukraine [1]. Despite this, it is an industry that generates very high profits, and the technology used is developing very much from year to year. In about 90% of the world's production volume, heat treatment is carried out in atmospheric devices, aggregates, and flow lines based on a technological concept from the turn of the 30s and 40s of the last century.

In most hardening plants operating within the structures of corporate plants, as well as in service hardening plants, the average age of technological equipment can be estimated at 15-25 years [2,3]. These are devices that are technically worn out to a large extent. Weariness contributes to the loss of competitiveness due to energy consumption of processes, lower quality, and repeatability of machining. Sometimes it even makes it impossible to continue production due to the inability to obtain environmental approvals from the Office of Technical Inspection or certificates of quality assurance systems. Therefore, the managers of these plants are faced with making a difficult and responsible decision on the costly investment in new generation technologies or the outsourcing of technological heat treatments.

The ferritic nitrocarburizing process has many advantages in line with the market demand and the lack of solutions, such as the possibility of obtaining layers in a relatively short time, characterized by high resistance to fatigue and abrasion. It also makes it possible to obtain the desired morphology of the surface layer [4-6].

This process is also a final process; after its completion, the elements do not require further heat treatment. This article describes the current state of knowledge regarding nitrocarburizing, particularly concerning ferritic nitrocarburizing as a technology with research potential.

2. Nitrocarburizing

The electrochemical and mechanical properties of metal surfaces largely determine the suitability of metals for a particular application. Modifying the steel surface by heat treatment is carried out to improve the mechanical, tribological, and anti-corrosion properties of inexpensive non-alloy steels, characterized by low corrosion resistance in various media. After appropriate thermal modifications of the surface, cheap steels can be considered a substitute for expensive alloy steels. The purpose of such surface modifications is to change the structure of the metal, taking into account the outer layer with improved properties [7,8].

Nitrocarburizing is one of the surface modification methods. Carbonitriding could be prepared in a low-temperature (450-600°C) or high-temperature (750-950°C) carbonitriding process, i.e. a diffusion process of thermo-chemical treatment [9]. The low-temperature process is also called nitrocarburation. It involves saturating the steel surface with both carbon and nitrogen at the same time [10].

The structure of the outer layer of the material obtained by nitriding depends primarily on [11-14]:

The temperature during processing;

Nitrogen activity;

Material microstructure;

The chemical composition of the material.

It was confirmed that temperature affects the hardness and thickness of the formed layer (Fig. 1). Also, such a layer applied to the previously aged steel is characterized by greater brittleness in microhardness tests compared to the layer prepared on the steel after the solution treatment process [15].

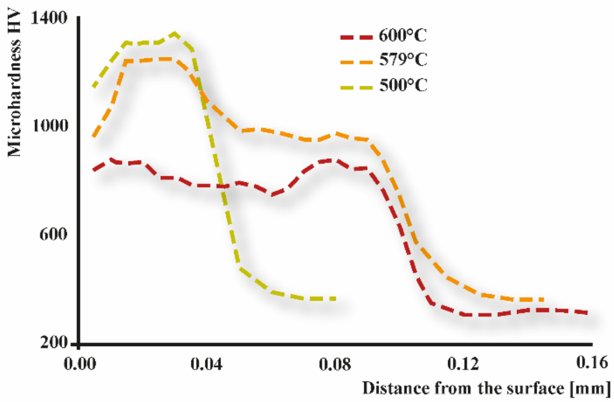

Fig. 1. Measured distribution of microhardness on the cross-section of the nitride layer at temperatures of 500, 579, and 600°C over 8 hours in solution-soaked steel (source: [15])

Publications also indicate that gas carbonitriding contributes to 5 times greater shrinkage and distortion of the material than in the case of ferritic nitrocarburizing [16]. In the same studies, the effect of gaseous ferritic nitrocarburizing together with nitrogen cooling on the dimensional parameters of the samples was also compared. The time and temperature at which the processes were carried out changed. The least significant dimensional changes were observed when cooling at 565°C for 5 hours. In addition, slight tensile stresses were revealed on the surface of the samples in the case of ferritic nitrocarburizing. In the samples subjected to carbonitriding, these stresses were compressive and correlated with the shape of the sample (rings).

The surface morphology of samples from various ferritic nitrocarburizing methods revealed that the ion ferritic nitrocarburizing procedure created a more shallow white thin coating compared to the other techniques. The thickness of the compound layer varied due to differences in the times and heat treatment temperatures [16]. These studies show that properly selected process parameters have a significant impact on various parameters of the final product.

The aforementioned components of the material affect, among others as the lifetime of the formed layer after nitrocarburizing. Thus, in the study [17], Si-Mo-Al cast iron was used for testing. It contributed to the self-sufficient growth of the diffusion layer, which resulted in the continuous oxidation of the material. Mutual strengthening of the components was possible by precipitation of aluminium nitride in acicular form and oxidation of the material containing less aluminium.

This process is widely used in the production of machine components and tools because it can achieve increased surface hardness and fatigue strength with minimal deformations [18]. Thus, the service life of nitrocarburizing machine elements is significantly extended [19-22]. Nitrocarburizing in many applications also improves corrosion resistance by creating a continuous layer on the surface of the workpiece. And this, in turn, can eliminate subsequent protective coating operations or completely avoid using anti-corrosion agents [23].

2.1. Types of nitrocarburizing

As mentioned earlier, due to the process temperatures, two main types of nitrocarburizing can be distinguished: ferritic (carried out at lower temperatures) and austenitic (also called carbonitriding).

There are various methods of carrying out the carburizing process, therefore nitrocarburizing can be additionally divided into three groups with research potential [10, 21-23]:

- Gas nitrocarburizing (which takes place in a stream of dissociated ammonia at a temperature of 500-600°C) [24-26];
- Plasma nitrocarburizing (this process, also known as ionization or fluorescent, occurs in an ionized nitrogen atmosphere; is carried out in the temperature range of 350-650°C and pressure of 1-10 hPa) [27,28];
- Nitrocarburizing in a salt bath (the details are immersed in a cyanide or cyanide-cyanate bath) [29,30].

The disadvantage of plasma nitrocarburizing is that it requires a special furnace and apparatus, which generates high costs. On the other hand, nitrocarburizing in a salt bath is associated with the use of toxic salts, mainly cyanides [31]. Therefore, nitriding in gas seems to be the most advantageous technology.

2.2. Environmental impact

Nitrocarbonitriding is often chosen to replace chrome plating for environmental reasons. Chromium waste generated by chrome plating activities pollutes the environment and endangers human health [32]. Chromium contains Hexavalent chromium, and this is a known carcinogen. During the plating process, it can be absorbed through the skin and cause liver, organ, and brain damage [33]. Ferritic nitrocarburizing is one of the surface treatment methods indicated as having the least harmful impact on the environment and human health. Strict conditions imposed on the treatment in question allowed for to reduction of the risk of toxicity to a minimum [34].

Ferritic nitriding is also used as an alternative process to solve the problems of loss of material dimensional control and distortion associated with higher temperature treatment where carburizing or austenitic nitrocarburizing is carried out [23].

2.3. Ferritic nitrocarburizing

Ferritic nitrocarburizing is a surface hardening process carried out in a gaseous environment involving the diffusion of nitrogen and carbon into the workpiece. The process temperature must be lower than the temperature at which austenite begins to form, i.e. from 723°C. It preserves core properties and good dimensional control. This process is usually carried out at temperatures between 550 and 580°C [35,36].

The researchers used an X-ray diffractometer to analyse the composition of the formed layers [15]. The tests showed that the surface layers were made of the following components: Fe_2N, Fe_3N, Fe_4N, and Cr_2N. These results were also compared with EDS and WDS results. It was concluded that in the near-surface zone, the layer was composed of nitrides ε - Fe_2N. The farther in, the layers contained more precipitates of Fe_3N and Fe_4N nitrides. In addition, in the matrix of martensite and ferrite supersaturated with nitrogen, the tests showed the presence of $(Fe,Cr)_3N$, $(Fe,Cr)_4N$, and $Fe_{2.5}N$. A simplified visualization of the detected components in the formed layers after gas nitrocarburizing is shown in Figure 2.

Ammonia is the only nitrogen supply gas in the nitrocarburizing process. Of the gases containing carbon in their structure, the following gases are most often used: carbon monoxide (IV) (CO_2), carbon monoxide (II) (CO) endogas [37], methane (CH_4) [22], propane (C_3H_8) are most often used. Controlling nitrogen and carbon concentrations that affect nitriding and carburizing potential is important to ensure the repeatability of the process [37].

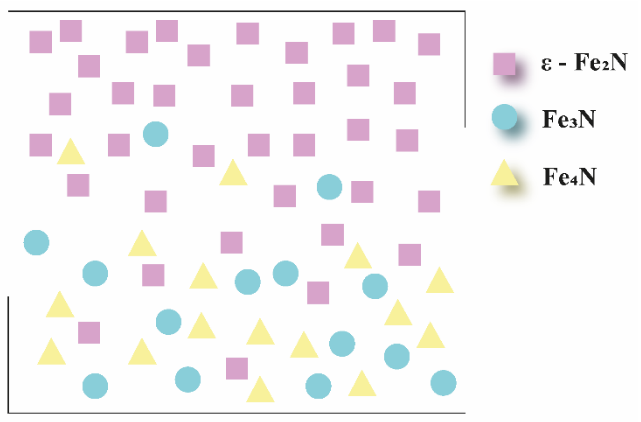

Fig. 2. Visualization of the components of the layers formed after nitrocarburizing in gas (based on [15])

The composition of the created layer in the nitrocarburizing process depends on the rate of the following processes related to the transport of nitrogen and carbon [38]:

- Typically reversible transfer from the nitrocarburizing medium to the solid surface;
- Typically reversible diffusion of a solid from the surface to the inside of the sample;
- Typically irreversible loss of nitrogen and carbon by converting them to N2 or graphite, which is impossible to recover in an iron-based solid. This process may be related to the formation of pores in the solid surface area during nitriding and the so-called metal dusting or soot formation during carburizing.

2.4. Layers of nitrocarburizing

In the case of typical ferritic nitrocarburizing, microstructural changes are obtained by changing the composition of the surface. The nucleation of iron phases on the surface depends on the competition of surface reactions. The carburizing reaction is usually much faster than the nitriding reaction. In addition, carbon has a lower solubility in ferrite than nitrogen [39-41]. For this reason, the maximum content of carbon dissolved on the surface is exceeded earlier than the solubility of nitrogen. Thus, two layers are formed [38]:

- OUTERMOST LAYER – (the so-called layer of compounds,) which is usually formed by iron carbonitrides ε (ε-$Fe_3(N,C)_{1+x}$). Sometimes also γ′ iron carbonitrides (γ′-$Fe_4(N,C)_{1-z}$) and cementite (Fe_3C) [38]. High nitriding potential appearance of iron carbonitride phase ε (after cementite nucleation) in the layer of compounds. On the other hand, high carburizing activity delays the formation of the ε phase. The result is an increase in abrasion resistance and corrosion resistance. The thickness of this layer depends on the process parameters and the type of processed material, and typically it is 2-30 µm [4,6,31,35,38];
- INTERNAL LAYER – (also called diffusion layer [38]) consists of a nitrogen-enriched ferrite matrix. The carbon enrichment in the diffusion zone is usually low. In this layer, nitrogen can be present in the following form:
  - Dissolved in the ferritic matrix (which has low nitrogen solubility – about 0.3-0.4%) [41-43];
  - Nitrides of alloying elements (e.g. CrN, AlN) [44-46];
  - Precipitated iron nitride (α″-$Fe_{16}N_2$, γ′-$Fe_4(N,C)_{1-z}$) [47-49].

The diffusion zone is responsible for the significant improvement in fatigue properties caused by compressive residual stresses [35]. In this case, the layer thickness is 0.1-0.5 mm [31].

The thickness of the formed layer of compounds depends on the process parameters such as temperature, time, and the proportion of gases used [22].

2.5. Occurring processes

Since the use of a gas mixture based on ammonia and acetylene has great research potential [13,14, 50-52], we decided to focus our further considerations in this direction, and the processes described below apply to such components.

The pyrolysis of acetylene is a complex process due to the presence of a triple bond between the nitrogen atoms. Numerous processes in the gas phase lead to a variety of products, including small molecules such as H_2, C_2H_4, the C_3H_4, as well as polycyclic aromatic hydrocarbons (PAHs), graphite and soot [53]. Heterogeneous reactions at the gas/solid interface lead to the deposition of pyrolytic carbon on the surface of the material [54]. The reactions taking place can be summarized in the following equation (1):

$$C_2H_2 \rightleftharpoons 2C + H_2 \tag{1}$$

Some hydrogen atoms combine to form a hydrogen molecule, and others combine with carbon, leading to various types of hydrocarbons, including PAHs. However, polycyclic aromatic hydrocarbons are classified as hazardous substances, causing cancerous changes in tissues and polluting the environment [55-57]. In addition, PAHs with higher molecular weights are precursors of soot, which impedes diffusion, deposits on the furnace surface, and causes damage to the pump. However, the number of PAHs and soot produced can be reduced by terminating the process promptly [53]. Reducing the formation of soot in the process can also be achieved by using a sufficiently high flow of acetylene [58]. However, it should also be emphasized that the amount of PAHs produced in the vacuum process is lower than in the traditional carbonitriding process [53]. In summary, the advantage of this process is that it is cleaner and safer than the traditional form of gas nitrocarburizing.

In [53] also, the obtained products of the pyrolysis of ammonia and acetylene were examined. According to the simulations carried out at a temperature of 127°C and a pressure of 10 mbar in the equilibrium state, it was shown that the pyrolysis products of acetylene are methane (about 75 mol%) and carbon (about 25 mol%). However, when using a temperature higher than 127°C, methane underwent pyrolysis, which resulted in the formation of carbon and hydrogen, which is presented in the following equation (2):

$$CH_4 \rightleftharpoons C + 2H_2 \tag{2}$$

But yet, when the process temperature reaches 500°C, and the pressure is equal to 10 mbar, the content of methane, hydrogen, and carbon fractions in such a system is, respectively: 0.5, 32.5, and 67 mol%. At a temperature equal to 600°C, there is no more methane in the system; also, hydrogen and carbon exist in amounts equal to 33 mol% and 67 mol% [53].

In addition, ammonia pyrolysis can be homogeneous (in the gas phase) or heterogeneous (at the interface). The performed thermodynamic analysis [53] shows that during traditional nitrocarburizing carried out at temperatures and pressures typical for this process, homogeneous ammonia pyrolysis takes place in the gas atmosphere in the furnace. Pyrolysis starts with the decomposition of ammonia, and the system becomes a mixture of acetylene, nitrogen, and hydrogen according to equation (3):

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)} \tag{3}$$

However, other studies [59,60] have shown that heterogeneous surface reactions play a significant role in the pyrolysis of ammonia and account for the majority of the reactions involved in the breakdown of ammonia. The absorbed nitrogen atoms may therefore diffuse in the solid phase φ (4) or may be desorbed (5), which is described by the equations:

$$N_{ad} \rightleftharpoons [N]_{\varphi} \tag{4}$$

$$2N_{ad} \rightleftharpoons N_2 \tag{5}$$

The thermodynamically preferred reaction is the reaction (5). However, it has been proven that below 900°C, the recombination rate of two nitrogen atoms is slow enough for nitrogen to react with metals and thus diffusion occurs [61]. According to this experimental data carried out in an industrial furnace compared with simulation results, for the process occurring at 10 atm pressure and 500°C – ammonia conversion is about 97%, and at 700°C it is close to 100% (in an infinitely long time). According to Le Chatelier's Principle (also known as the Equilibrium Law), the ammonia conversion should increase as the pressure decreases [62,63]. So, the performed simulations confirmed these considerations.

Going further, at a temperature of 570°C and a pressure of 1 atm, the conversion was 99.89%, and when the process was carried out at a pressure of 0.01 atm, it was 99.97% [53]. However, by keeping the ammonia flow high enough, such high conversions are avoided as they are not desirable in the nitrocarburizing process due to lowering the nitriding reaction potential [58].

Summing up this part, it can be assumed that the pyrolysis of acetylene and ammonia will not occur when the pressure is reduced, which allows further research in this direction.

2.6. Research achievements

The first research in the field described in chapter 2.5 was already undertaken using low-temperature vacuum carburizing in an acetylene and hydrogen atmosphere [64] and vacuum nitrocarburizing with the participation of acetylene [65,66]; however, these are different processes from low-pressure ferritic nitrocarburizing. The literature also writes separate processes that are carried out after the previous one is completed. Mentioned here are pre-carburizing, quenching heat treatment, pre-, finishing nitriding, and subsequent carburizing [67]. But, in this case, nitriding and carburizing were carried out separately at low pressure, so it is not nitrocarburizing technology. The literature also describes low-pressure nitrocarburizing processes, which use plasma, not gases [68,69]. There are also entries where you can find information on the use of unsaturated hydrocarbons, including acetylene, as a carbon source in the gaseous ferritic nitrocarburizing of iron [52]. This paper used the following mixtures for nitrocarburizing Armco iron samples: C_2H_2/NH_3, $C_2H_2/NH_3/H_2$, C_3H_6/NH_3, and $C_3H_6/NH_3/H_2$. The morphology and composition of the formed coating could be controlled by adjusting the gas atmosphere composition. And here, the mechanisms where carbon can be incorporated into the iron surface were similar to those observed in traditional gas ferritic nitrocarburizing.

For this article and project from the LIDER XII program, a detailed review of patent databases was also performed to determine whether there is industrial potential in the field.

The search revealed 27 patents (Fig. 3). Most of them, which were 9, had European status (EP2732066, EP1991038, EP3172353, EP2135967, EP2394072, EP2914756, EP1069203, EP0813059, EP1000181). 7 of them were from Poland (PL094422, PL135089, PL087466, PL108966, PL062626, PL129259, PL198128), 3 from the USA (US15318636, US10774414, US14913006), 2 from Canada (CA2474367, CA2890062) and with an international status (WO2015193295, WO2013156428). One each from China (CN104712512), Sweden (SE1550958), Brazil (BRPI0901811), and Taiwan (TWI665334). Half of them is no longer valid (expired or have been abandoned).

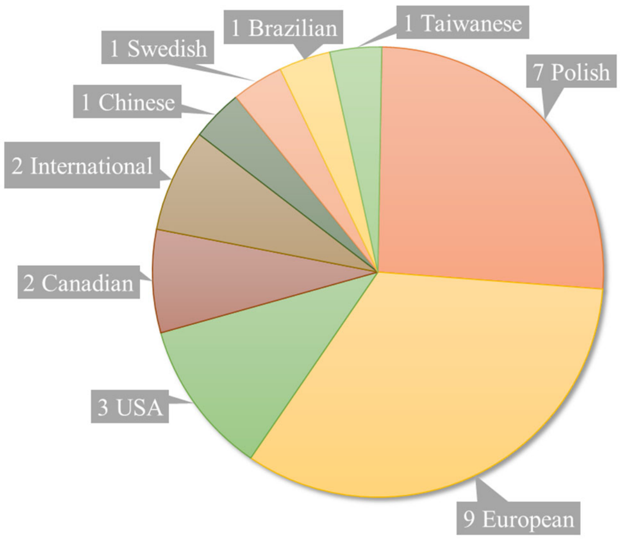

Fig. 3. The number of patents dealing with the subject of carbonitriding under low-pressure

Summing up, the collection of found articles and the patent database can be divided into four groups. The first does not apply strictly to nitrocarburizing, and this term appears only in the introduction or in the list of sources. The second group describes the properties, most often tribological, of nitrocarburized layers on various materials, where the layers were usually produced using the classic gas method. The third group describes the processes and their control, the vast majority of which are gas processes, less often implemented in salts. The fourth group is the only one that mentions reduced pressure or vacuum, but it is always associated with plasma or ion technologies. However, no mention was made of ferritic nitrocarburizing performed at reduced pressure without glow or ion assistance (in the patents and the literature). The analysed data indicate that this is a topic in which there are still research gaps with high implementation potential.

3. Conclusions

In conclusion, the article summarizes the process of ferritic nitrocarburizing in gas (mainly in low-pressure). Research on this type of treatment will allow technology development and meet the expectations and needs of the industry interested in using this technology. It will also increase the competitiveness of entities using it and expand the scope of their activities. It will also bring benefits in the form of a better understanding of the processes and determination of the relationship between the parameters and the properties of the obtained surface layers.

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