ADAPTATION OF THE PIT FURNACE FOR THE NEW AND THE SHORTER NITROCARBURIZING METHOD IN $\text{NH}_3 + \text{CO}_2$ MIXTURE

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Abstract

Usually, the process of nitrocarburizing takes up from 30 to even 100 hours, depending on the depth of the hardened layer. However, despite their great duration, these processes are inevitable during the production of some steels (particularly tool steels), since their surface hardness usually is not satisfying enough. Nitrocarburizing is carried out in order to increase the hardness at the surface while maintaining sufficient toughness at the inside. One of the continuous goals for researchers is to find new methods of nitrocarburizing which will be shorter and faster, but which will simultaneously keep the quality of the process on the high level. Aim of this paper is to present the adaptation of the old nitrocarburizing system to a new shorter method of nitrocarburizing in $\text{NH}_3 + \text{CO}_2$ mixture (ammonia plus carbon dioxide). The whole process is described in detail and the three different steels were exposed to a process and their hardness was examined to see if there is any decrease in the hardness due to a shorter time.

Keywords: Pit furnace; Shorter nitrocarburizing method; Ammonia; Carbon dioxide.

1. Introduction

Some types of steel (like tool steels, for example, [1]) have to be case-hardened in order to obtain the best performances. Case-hardening is the process where the surface of a product is hardened, while inside of the product and its core remains softer and tougher. The thin layer of hardened metal on the surface is usually called the case [2]. This is particularly important for steel products with low carbon content since their hardenability is pretty poor. Processes of case-hardening involve infusing additional harder material (mostly carbon or nitrogen) into the surface layer [3].

One of the most popular case-hardening processes lately is the process of nitrocarburizing, which simultaneously enriches the surface of the product with carbon and nitrogen. The main advantage of this process is the lower temperature on which it is implemented [4]. These temperatures are usually under the $600\text{ }^\circ\text{C}$ (always under the austenitizing temperature A_1). This is important since it ensures there are no any microstructural changes at the inside of the product being case-hardened, which is kept with almost intact toughness. On the other side, the surface is hardened and consequently, it becomes more resistant to wear. That is why these processes are significant for the tool steels since they enable the tool to be unlikely to wear, but at the same time, they have sufficient toughness to withstand impacts during the operational work [5].

The more resistant surface is the result mostly of the nitrides formed with the iron (Fe_2N , Fe_4N) or with the other alloying elements (AlN , CrN , etc.), which decrease a chance of surface reacting with some of the elements from the products being machined (basically, they reduce sticking and adhesive wear). Besides nitrides, another product of these processes are carbides (compounds with carbon). Even if a greater amount of carbon has some negative consequences, its optimal range at the surface also helps to increase hardness and wear-resistance, since it reduce abrasive wear [6]. Lower temperatures additionally decrease the danger of deforming the product, which is another important advantage of nitrocarburizing. Even the corrosion resistance is getting better, thanks to improved nitrogen amount [7]. Aim of this study is to find out is it possible to adapt conventional nitrocarburizing system to a new shorter method and to see if this process can bring some improvements (money savings or better mechanical properties).

2. Problems and current situation

Ordinary nitriding and the nitrocarburizing process is basically straight-forward. Ammonia (NH_3) dissociates at the temperature range from 490-550 °C, which usually takes 30 to 100 hours, depends on the necessary depth of the hardened layer (case). Nitrogen can diffuse at the product's surface only in its atomic state, which means the only amount of ammonia which dissociates directly at the surface is usable. Products of ammonia decomposing are nitrogen and hydrogen, and another problem is the tendency of these both elements to create a new molecule, thus making another dissociation products unusable for case-hardening [8]. Since a lot of ammonia is lost in these processes, it is an additional disadvantage. Also, conventional nitriding processes can lead to a formation of a thin white layer, which is extremely hard but also highly brittle and it has to be removed before the use of the product. Despite their advantages (great case depths and increased hardness in the diffusion zone), conventional nitriding and nitrocarburizing processes are used less and less nowadays.

Modern processes whose application has increased lately are usually called short-term nitrocarburizing or soft nitrocarburizing. There are some variations and different methods, but all of them share the main important characteristic – they do not last more than 7-8 hours (with the heating and cooling included). They can be done in different mediums like solid (powder), liquid (salt bath), gas (gas mixtures) or ionized gas. Different physical laws are used in different processes to enable the more intensive process of diffusing carbon and nitrogen at the surface layer. Most known processes are patented by the companies which invented them and they are called according to them, such as TENIFER® [9] and NITEMPER® [10].

The choice between different processes is made according to the requirements. For example, if a product is going to be heavily loaded, then some processes which produce deeper case are necessary. If deformations of the product are not allowed during the process, then some of the processes with lower cooling speed is preferable. The case is usually divided into two zones: the compound zone and the diffusion zone. These two zones have to satisfy the necessary requirements for successful nitrocarburizing [11].

3. Experimental work

To conduct the experiment, the process of nitrocarburizing has to be chosen first. Existing equipment (pit furnaces Degussa GRSU 110/250 and GRSU 80/140) is suitable for the conventional longlasting nitriding processes, but in order to shorten the process and enable some money savings, an idea was to adapt it to modern nitrocarburizing process. The process was chosen based on the research [12], where Fe-C-N ternary diagram is shown (Fig. 1.)

Fig. 1. Ternary Fe-C-N diagram

Gas mixture of ammonia (NH_3) and carbon dioxide (CO_2) is chosen in order to enable the diffusion of the nitrogen and the carbon. In addition, carbon dioxide serves as a catalyzator which fastens the diffusion of the nitrogen. Temperature of the process was set at the 560-570 °C, to reduce the chance of forming the brittle white layer at the surface. The theoretical basis for this idea is great resolvent power of ϵ phase (marked with red lines on Fig. 1.), which can dissolve excess of carbon content (and it can also dissolve some other detrimental elements).

Existing equipment only had to be upgraded in order to introduce carbon dioxide in the process (additional 4 gas bottles). This was also the main limitation in this study, since any additional improvements were not desirable (an idea was not to create totally new equipment at this stage of the research, but to adapt an old one with minor changes). If results are acceptable with this approach, then it would mean planning of another improvements is justified. Three different steel grades were chosen for this experiment: low-alloyed S355J2 (1.0577), stainless steel 42CrMo5-6 (1.7233) and hot-work tool steel X38CrMoV51 (1.2343).

NH_3 flow was 5 l/min for the first half an hour (from 500-560 °C), while CO_2 flow was 0.5 l/min. For the rest of the process (3.5 hours), NH_3 flow was 33.3 l/min and CO_2 flow was 3.3 l/min. Temperature and the flow were chosen according to the literature and suggestions, while other parameters were empirically established and they are shown in Fig. 2. From point 1 to point 2 there is only heating, from point 2 (500 °C) to point 3 (560 °C) there is lower gas flow, from point 3 to point 4 there is working gas flow and from point 4 to point 5 there is cooling.

Fig. 2. Chart diagram for a nitrocarburizing process

After the process of nitrocarburizing, specimens were first conducted to hardness testing. Also, their microstructure was observed (pictures were obtained using an optical microscope) and the dimension of the compound zone and diffusion zone were examined (pictures were obtained using a scanning electron microscope).

4. Results and discussion

Fig. 3. shows the diagram of hardness distribution for three different steel grades.

Fig. 3. Hardness distribution after the nitrocarburizing process

It can be seen that higher hardness is obtained when the grades are higher alloyed. On the other hand, hardness drops steeper at the same grades (it is distributed more uniformly in depth when the grade is lower alloyed). However, hardness obtained for every particular grade is still satisfying.

Fig. 4. shows microstructures of 42CrMo5-6 (a) and X38CrMoV51 (b) steel grades. Compound zone of S355J2 contains ϵ phase and it is homogenous. Beneath it, there is a diffusion zone with mixed ferrite-perlite grains and needle-shaped grains of nitrides (probably Fe_4N). 42CrMo5-6 also has a homogenous compound zone, but its thickness is much less uniformly distributed, probably due to poor surface finish prior to the nitrocarburizing (higher surface roughness). Diffusion zone contains ferrite-bainite grains, but some nitrides are present also. The microstructure of the X38CrMoV51 is similar as of the 42CrMo5-6, but it contains martensite-bainite grains.

Fig. 4. Microstructures of 42CrMo5-6 (a) and (b) X38CrMoV51 steel grades

The scanning electron microscope was used primarily to measure the dimensions of the compound zones and Fig. 5. shows the example of measuring these dimensions for the S355J2 grade.

Depth of the compound zone for the S355J2 grade ranges from 4.8-9.6 μm , and depth of the diffusion zone ranges from 336-360 μm . For the two other grades, both compound zone and diffusion zone are shallower (compound zone ranges from 3.6-4.3 μm and diffusion zone is about 240 μm deep for the grade 42CrMo5-6, while for the X38CrMoV51 compound zone ranges from 2.4-4.8 μm and the diffusion zone is 290 μm deep). Reason for it could be lower alloy content of the S355J2 grade, which enables nitrogen and carbon to enter deeper into the product surface.

Fig. 5. Depth of the compound zone on the surface of S355J2 steel grade product

5. Conclusions and suggestions for future researches

After considering the problems (which were the initiators for this research), and after the hardness testing and microstructure observations, some conclusions could be drawn as follows:

- it is possible to adapt the conventional nitriding system to a new shorter method of nitrocarburizing with some minor changes – this means that the first problem is solved and other improvements could be done in future;
- this new method enables case-hardening of different steel grades (from lower alloyed to higher alloyed) – this means that this new method is not limited to particular steel;
- process duration could be reduced for even 6-7 times compared with the conventional processes (4 hours of active nitrocarburizing instead of 30) – this is the most significant improvement in this research since it can be used in scientific purposes as the basis for new researches, but also in the professional work due to its possibility to save money in the daily application;
- carbon dioxide could be used as carbon supplier for the process (which was expected), but also as catalizator which fastens the whole process (this was not expected, but it is a positive consequence);
- this process enables the formation of homogenous compound zones.

However, there are still some issues and challenges to be resolved, which could help to improve this process and enable its application more commercially:

- additional testing of chemical composition could be done in order to find out which nitrides are needle-shaped grains formed in all three grades (if it is Fe_4N , it could cause a significant deterioration in toughness properties, annulling the whole purpose of case-hardening) – this should definitely be the basis for the next research since it is important to prove are there any detrimental phases;
- other improvements for the equipment could also be planned since these results have shown a positive outcome with only minor changes;
- some automation of the process could be useful since the whole regulation during this process was done by the human, which means some future researches should be interdisciplinary and include scientists from other branches (automation and electrical engineering, for example).

6. Literature

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