Heat treatment of nitrided layer formed on X37CrMoV5-1 hot working tool steel

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Abstract. The paper presents the technology consisting of combination of the nitriding process with subsequent austenitizing at temperature above eutectoid temperature of the Fe-C system and further rapid cooling. Such treatment will cause formation of the martensite in the area of the primarily nitrided layer and the additional precipitation hardening by tempering of heat treated steel. The article shows that the heat treatment process of nitrided layer formed on X37CrMoV5-1 steel leads to strengthening of surface layer, the substrate and the core of nitrided part. Heat treatment of nitrided steel with the tempering in inert (nitrogen) or active (ammonia) atmosphere can increase the thickness of the layer formed by short-term nitriding process. After the nitriding process of X37CrMoV5-1 steel the nitrided layer had a thickness of about 160 μm, while a subsurface layer of iron nitrides had a thickness of 7 μm. After subsequent quenching and tempering processes, the nitrided layer undergoes additional diffusion and its thickness is increased to about 220 μm (inert atmosphere) or 280 μm (active atmosphere). If the tempering process is carried out in an inert atmosphere, the primarily formed layer of iron nitrides disappears. Tempering in an active atmosphere leads to forming of white layer with a thickness of 7 μm. Basic properties of nitrided layers formed in such way, like the hardness and the wear resistance, are presented.

1 Introduction

The overwhelming number of tool steels nitriding processes are long-duration processes carried out at low temperatures in the range of 500÷530°C. The reason for lower nitriding temperatures is tempering process carried-out before nitriding. This temperature of treatment is dependent on the precipitation processes occurring in these steels. For the hot work and high-speed steels tempering temperature ranges from 520 to 550°C. In order to increase the nitriding temperature, and thus producing a thicker nitrided layer in a shorter time, it would be convenient to develop nitriding process at the higher temperatures. In order to obtain good in-service properties not only of the nitrided layer, but also of the core of material, it becomes advantageous to use the heat treatment after the nitriding process (quenching and tempering) not only before the nitriding process.

Developed technology of hardening of nitrided layer, its substrate and the core of the nitrided part consists in the further soaking of workpiece at temperatures close to the austenitizing temperature and subsequent rapid cooling. Such treatment results in forming of a martensitic structure in the area of primary nitrided layer, which can be additionally hardened by aging. As a result of nitrogen migration occurring during austenitizing, the process performed in this way leads to forming in a nitrided subsurface zone of a (Fe,M)-C-N alloy with different structural features (chemical and phase composition) in comparison with the original nitrided layer. On the other hand, by choosing of an appropriate austenitizing temperature and proper cooling conditions there can also be achieved hardening of the nitrogen-free core of the material.
The already known solutions for hardening of the surface of the nitrided layer, namely, the nitrides layer substrate consist in the hardening of the diffusion layer zone. This can be achieved by rapid cooling after ferritic nitriding performed at the temperature close to eutectoid temperature of the Fe-N system (590°C), in order to achieve maximum supersaturation of a solution of Fe(N), followed by aging at temperatures of 80 ÷ 120°C, leading to strengthening of the Fe(N) solution as a result of formation of α” phase [1, 2]. This process gives visible strengthening effects in the case of carbon steels. In the case of alloyed steels such process is practically not effective because substantial impact on the strengthening of solution zone of the nitrided layer have special nitrides, mainly chromium nitrides, which are formed during the nitriding process [3, 4]. Another possible solution is the strengthening of the nitrided layer by austenitic nitriding combined with the rapid cooling [5-7]. The effect of the quenching is mainly strengthening of braunite or braunite/ferrite area by forming of nitrogen-martensite or nitrogen-carbon-martensite structure. This process can be used primarily for carbon steels, especially low carbon steels. In the case of alloy steel the process is less effective because the reduction of nitrides leads to decrease of nitrides layer hardness. Moreover, the hardness of strengthened core is reduced due to its further tempering [6]. The next solution leading to strengthening of the nitrided parts at their entire cross-section, i.e. not only in the nitrided layer, but also in the core, is combination of the nitriding with subsequent austenitizing at temperature above eutectoid temperature of the Fe-C system and further rapid cooling. Such solution is known for bearing steels [8]. On the other hand, the data on the possibility of further precipitation hardening of iron and nitrogen alloys mostly come from laboratory studies [9-14]. Due to the properties of the nitrided layer and the substrate, it is favorable to carry-out the heat treatment after the nitriding process. Improved properties of layers can be obtained by dissolving of the subsurface layer of iron nitrides and subsequent nitrogen diffusion into the substrate as a result of austenitizing, further transformation of alloyed nitrogen austenite during the processes of deep cryogenic treatment (DCT) and the precipitation of fine alloyed carbonitrides in the internal nitriding zone during tempering. However, the heat treatment of alloy steel decreases hardness of the nitride layer and reduces dispersion of nitrides and carbonitrides, so it’s advisable to use deep cryogenic treatment (after the quenching and before the tempering), which will cause grain refinement and obtaining of fine carbonitride precipitations of alloying elements. Sub-zero treatment of tools is widely used in the world, because the low temperatures technologies have a beneficial effect on the properties of heat-treated parts [15-18].

The paper presents the attempts to combine the heat treatment with DCT of nitried layer formed on X37CrMoV5-1 hot work tool steel. Analyzes include basic properties such as microstructure, hardness, hardness at the cross section and wear resistance of steel. The aim of this work is to reduce overall treatment time and to form the nitrided layer with required thickness, characterized by the high properties of the surface of the material.
2 Experimental
Research was conducted using the X37CrMoV5-1 hot work tool steel with the chemical composition given in table 1 (declared composition according to PN-EN ISO 4957:2004).

| Chemical composition of the steel used in the research. |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                | C              | Si             | Mn             | Cr             | Mo             | V              |
| Declared       | 0.33±0.41      | 0.80±1.20      | 0.25±0.50      | 4.80±5.50      | 1.10±1.50      | 0.30±0.50 max. |
| composition    |                |                |                |                |                | 0.030 max.     |
| Actual         | 0.35           | 1.29           | 0.33           | 4.91           | 1.31           | 0.29           |
| composition    |                |                |                |                |                | 0.03           |

In order to study the effect of heat treatment on the nitrided layer the samples were processed in accordance with the following schemes (figure 1). Initially hardened and tempered samples were nitrided at 580°C for 4 hours. After the nitriding samples were quenched (austenitizing temperature of 1040°C) and tempered at 550°C. The optional DCT step (at -180°C for 8 hours) was implemented in order to determine if the additional transformation of alloyed nitrogen austenite will enhance the tribological properties of the nitrided steel. Tempering was performed in two various modes, with use of inert (nitrogen) or active (ammonia) atmosphere.

![Figure 1. Block diagram of heat and thermo-chemical treatment routes.](image)

Nitriding of steel samples was carried-out in NX609 Nitrex furnace. In this furnace it is possible to perform controlled gas nitriding in a fully automatic way. Computer control ensures repeatability of process parameters, which is an important element for the proper quality of the nitrided layers. Hardening of samples was carried out in a vacuum furnace with the high pressure gas quenching using nitrogen. The tempering of the samples was carried out in the same furnace in an atmosphere of nitrogen or in a nitriding NX609 furnace in an ammonia atmosphere. Surface hardness measurements were made using Struers DuraScan-70 hardness tester under load of 0.5 kG. Hardness profiles were determined with aid of the same device. Test of resistance to wear was carried out in a 3 rollers-cone system. The wear resistance of samples was compared with samples nitrided in the conventional manner (controlled gas nitriding at 520°C for 24 hours). Test was performed with a continuous lubrication of samples using Lux-10 oil, at a constant speed of counter-specimen rotating at a rate of 526 rpm and a constant unit pressure of 100 or 400 MPa. The depth of the wear, indicating the linear wear, was determined by measurements of diameters of the ellipses formed at the surface of each of the worn out rollers. Total friction time test was 100 minutes, wear marks were measured after every 10 minutes. After each measurement the load was increased in order to achieve constant unit pressure at the worn out surface. Conical counter-specimen was made of the X153CrMoV12 steel hardened to hardness of 60 HRC and ground to a roughness Ra = 0.32 micrometers.
3 Results and discussion

After the nitriding process of steel the obtained nitrided layer had a thickness of 160 μm with a subsurface layer of iron nitrides with a thickness of 7 μm. The surface hardness was 1235 HV0.5. The microstructure observed by LM is shown in Figure 1a.

![Figure 1. Microstructure of nitrided layer on X37CrMoV5-1 steel.](image)

After subsequent quenching, deep cryogenic treatment and tempering processes (inert atmosphere) of nitrided X37CrMoV5-1 steel samples, the nitrided layer undergoes further diffusion and its thickness is increased to 225 μm (Figure 2a). There was no subsurface layer of iron nitrides and at the surface of samples was present the light area with a thickness of 60 microns from the surface. White area was soft and its hardness was 550 HV0.5. Whereas the dark layer observed under the white zone had a hardness in the range of 650 to 900 HV0.5 (Figure. 2a). After quenching, DCT and tempering in an active atmosphere of ammonia of samples, the correct surface hardness (1150 HV0.5) and high hardness of the core (640 HV0.5) was obtained, what is probably caused by the DCT process. The thickness of the subsurface layer of iron nitrides reached 7 μm, while the thickness of the nitrided layer was increased to 280 μm. It is impossible to assess the depth of diffusion zone based on the observed microstructure. Underneath the dark etched layer there is located the undisclosed by etching layer of matrix with high dispersion alloyed carbonitrides, influencing the hardness of diffusion zone. Microstructure of the nitrided layer after quenching ant tempering in an active atmosphere is shown in Figure 2b.

![Figure 2. Microstructure of nitrided layers on X37CrMoV5-1 quenched, DCT and tempered in an inert (a) or active (b) atmosphere.](image)
Figure 3 shows the distribution of hardness at a cross section of layers after nitriding or nitriding with subsequent heat treatment with tempering in an active atmosphere.

![Figure 3](image)

**Figure 3.** Comparison of hardness distribution of nitrided layer (N) with nitrided and heat treated layer (N+Q+T) or nitrided and heat treated layer with additional DCT (N+Q+DCT+T).

One can conclude that after the heat treatment of nitrided layer with properly selected parameters and use of active atmospheres during tempering (ammonia), it is possible to form in a short time a thick nitrided layer on the X37CrMoV5-1 steel (thickness up to 280 μm). The use of ammonia at a stage of tempering causes additional nitriding of the surface and forming of subsurface iron nitrides layer. Heat treatment cycle of nitrided layer, in comparison with steel simply nitrided, increases hardness of the core of material by about 100 HV (Figure 3). At the same time the use of additional operation of deep cryogenic treatment during the heat treatment cycle causes additional enhancement of the hardness level at the diffusion zone. Increased hardness is probably caused by the additional transformation of alloyed nitrogen austenite during the processes of deep cryogenic treatment and the precipitation of fine alloyed carbonitrides in the internal nitriding zone during tempering.

The results of wear resistance test in the form of diagrams of linear wear as a function of time are shown in Figures 4a (100 MPa) and 4b (400 MPa). All nitrided samples were characterized by the wear with a regular course, manifesting the occurrence of steady friction state in the entire course of wear, except running-in period.

At unit pressure of 100 MPa the lowest linear wear values in the first and last phase of test had the samples subjected to a conventional nitriding. The highest wear resistance of samples subjected to conventional nitriding is probably connected with presence of the hard compound layer at the surface of the material, influencing tribological properties of steel. Despite of the good wear properties of the surface of steel, such hard and therefore brittle layer is unfavorable from the point of view of fatigue strength of the tool made from the hot work tool steel.
Figure 4. Wear courses at 100 MPa (a) and 400 MPa (b) of samples subjected to different modes of nitriding with or without heat treatment.

Wear test performed at the unit pressure of 400 MPa demonstrated the superior tribological properties of the heat treated nitrided layers (Figure 4b). For the conventional mode of treatment (controlled gas nitriding at 520°C for 24 h) the linear wear after 100 minutes of test was 25.40 μm, while after the heat treatment or heat treatment with DCT the linear wear was about two 26% or 43% lower (18.70 μm and 14.42 μm, respectively). The nitrided layer formed in a conventional manner manifested tendency to galling, with a visible phenomenon of accelerated wear at the last stages of the test (Figure 4b). The high tribological properties of the nitrided layer subjected to heat treatment are connected with proper structure of the compounds layer on the material’s surface (Fig. 2b).

4 Conclusions
Heat treatment in an active atmosphere of nitrided X37CrMo5-1 hot work tool steel allows forming of thick nitrided layers by the short-term nitriding process. Developed technology allows to reduce the nitriding time necessary for forming the layers with a required thickness. After subsequent quenching and tempering processes the nitrided layer undergoes additional diffusion and its thickness is increased. If the tempering process is carried out in an inert atmosphere, the primarily formed layer of
iron nitrides disappears. Tempering in an active atmosphere leads to forming of white layer with a thickness of 7 μm.

Shortening of the nitriding process enables reduction of the overall duration of heat an thermochemical treatment cycle, thus affecting the cost of production process of treated parts, as well lowers the emission of the environmentally harmful gases.

Heat treatment of nitrided layers increases the hardness in the core of the tool steel. Formed layers have high resistance to wear under high loading conditions and are resistant to galling.

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