

## THE APPLICATION OF DEEP CRYOGENIC TREATMENT TO IMPROVE THE PROPERTIES OF NITRIDED LAYERS FORMED ON X153CrMoV12 STEEL

Deep cryogenic treatment (DCT) is gaining popularity as a treatment used to modify structures obtained during heat or thermo-chemical treatment. The article presents the influence of DCT, carried out during heat treatment before and after gas nitriding processes, on the formation of gas nitrided layers on X153CrMoV12 steel.

It was found that the use of DCT between quenching and tempering performed prior to gas nitriding processes, increases the hardness, thickness and wear resistance of the nitrided layers. At the same time, if we apply cryogenic treatment during post-heat treatment of nitrided layers, we also get very high wear resistance and increased thickness of nitrided layers, in comparison with conventional gas nitriding of X153CrMoV12 steel. In this case, DCT significantly increases also the hardness of the core by the transformation of retained austenite and the precipitation of fine carbides of alloying elements.

*Keywords:* gas nitriding, nitride layers, cryogenic treatment, heat treatment, tribology, corrosion resistance, X153CrMoV12 steel

### 1. Introduction

The first reports on the impact of DCT for wear resistance of tool steels appeared in the 1950s [1]. The precursor of this technology is R. F. Barron, who published comparative results of wear resistance tests for various steel grades subjected to sub-zero treatment at temperatures of  $-84^{\circ}\text{C}$  and  $-190^{\circ}\text{C}$  [2]. These studies indicated a significant increase in wear resistance of various steel grades as a result of their cryogenic treatment. Since then, there have been many publications on the effect of DCT on the performance of steel, but there is still a lack of widely accepted explanation of its impact mechanisms, which can cause a significant increase in resistance to wear. The effect of DCT on martensitic transformation, stress relaxation and dimensional stability of steel, in principle is the same as in case of conventional sub-zero treatment. In some the efficiency of such process may be higher due to lower temperature of the process. A well-documented mechanism of the impact of DCT on steel, other than the transformation of retained austenite into martensite, is the precipitation of fine-dispersed carbides. Available data on this topic relate mainly to tool steels [2-10].

The interesting issues reported in the literature are trials on combining DCT with nitriding of tool steels, mainly high-speed steels [11,12]. It has been found that cryogenic treatment before the nitriding process, carried out between quenching and tempering, increases the surface hardness and enhances the wear resistance, as compared to regular nitriding. It was found that

combining of heat treatment involving DCT and with subsequent nitriding leads to the increase in the thickness and hardness of the diffusion layer. The additional precipitation processes of fine-dispersed carbides, whose nucleation occurs during DCT [10], can contribute to increased wear resistance and changes in hardness distribution in these layers. The use of DCT in a route of heat treatment and nitriding requires at least a cursory analysis of the equilibrium diagram [13]. In the Fe-N system, only two phases are stable, which constitute boundary solutions on the *bcc* and *fcc* iron networks. Metastable phases, on the other hand, are nitrides and nitrogen martensite, which is formed from nitrogen austenite in an identical process to the carbon martensite transformed from carbon austenite. Nitrogen austenite is an ordered solution of nitrogen atoms in octahedral hatches of the *fcc* network [14-16]. Depending on the cooling rate, nitrogen austenite may be a subject to eutectoidal decay or martensitic transformation. Similar to an increase in the carbon content in the carbon austenite, an increase in nitrogen content lowers the  $M_s$  temperature, which makes it possible to maintain this structure after quenching if the nitrogen concentration exceeds 8.2% at. The supersaturated nitrogen austenite or aged nitrogen martensite can be transformed into a metastable intermediate  $\text{Fe}_{16}\text{N}_2$  ( $\alpha''$ ) phase with an orderly distributed nitrogen atoms. This phase occurs up to  $300^{\circ}\text{C}$  and is always supersaturated with respect to ferrite and nitrogen martensite [13, 17]. The  $\alpha''$ -phase structure is considered as the  $\text{Fe}_4\text{N}$  phase ( $\gamma'$ ) subnet deformed as a result of the removal of nitrogen atoms from certain positions.

\* INSTITUTE OF PRECISION MECHANICS, 3 DUCHNICKA STR., 01-796 WARSAW, POLAND

\*\* WARSAW UNIVERSITY OF TECHNOLOGY, FACULTY OF MATERIALS SCIENCE, 141 WOLOSKA STR., 02-507 WARSAW, POLAND

# Corresponding author: piotr.wach@imp.edu.pl

For this reason, the phase  $\alpha''$  is considered as the intermediate phase between nitrogen martensite and  $\text{Fe}_4\text{N}$  nitride.

There are no reports in the literature regarding the heat treatment of nitrided layers in combination with deep cryogenic treatment. This work aims to show the effect of DCT on the structure and properties of nitrided layers formed on X153CrMoV12 steel. DCT is applied during the heat treatment performed prior to nitriding processes and during post-heat treatment of nitrided layers.

## 2. Experimental

Research was conducted using the X153CrMoV12 cold work tool steel, with the chemical composition given in table 1 (declared composition according to EN ISO 4957:1999).

TABLE 1

Chemical composition of X153CrMoV12 steel

	C	Mn	Si	Cr	Mo	V	P	S
EN ISO 4957:1999	1,45-1,60	0,20-0,60	0,10-0,60	11,0-13,0	0,70-1,00	0,70-1,00	max. 0,03	max. 0,035
Actual composition	1,55	0,32	0,30	11,2	0,70	0,70	0,01	0,007

The heat treatment of the samples before and after the nitriding process was carried out in the vacuum furnace equipped with high pressure gas quenching. The deep cryogenic treatment process was carried out in the industrial sub-zero processor. The nitriding of steel samples was carried-out in the NX609 controlled gas nitriding furnace. In such furnace it is possible to perform the controlled gas nitriding in a fully automatic way. Computer control ensures the repeatability of process parameters, which is an important element for the proper quality of nitrided layers.

Heat treatment and nitriding processes of 153XCrMoV12 steel samples were made according to variants I-III shown in Fig. 1. The samples were subjected to heat and thermo-chemical treatments in the normalized condition (normalized by the steel producer).

The gas nitriding processes were carried out at various temperatures and times. The choice of parameters depended on the modes. In mode I, a temperature of 530°C and nitriding atmosphere of 50%  $\text{NH}_3$ -50%  $\text{NH}_3$ diss were used to produce nitrided layers consisting of a thin surface layer of iron nitrides and a deep diffusion layer. In variant II, a temperature of 540°C

TABLE 2

Parameters of the heat and thermo-chemical treatment processes of X153CrMoV12 steel

Mode	Parameters
I	Quenching: Austenitizing 1060°C/15 min), cooling: $\text{N}_2$ Deep cryogenic treatment: -180°C/32 h Tempering: 550°C/2h, cooling: $\text{N}_2$ Nitriding: 530°C, atm: 50% $\text{NH}_3$ – 50% $\text{NH}_3$ diss, 10h, Np. = 1,6
II	Quenching: Austenitizing 1060°C/15 min), cooling: $\text{N}_2$ Tempering: 550°C/2h, cooling: $\text{N}_2$ Nitriding: 540°C, atm: 100% $\text{NH}_3$ , 10h, Np. = 5,8 Deep cryogenic treatment: -180°C/32 h
III	Nitriding: 580°C, atm: 100% $\text{NH}_3$ , 6h Quenching: Austenitizing 1060°C/15 min), cooling: $\text{N}_2$ Deep cryogenic treatment: -180°C/8 h Tempering: 520°C/4h, 100% $\text{NH}_3$ , cooling: $\text{N}_2$

and nitriding atmosphere of 100%  $\text{NH}_3$  were used to create a thick surface layer of iron nitrides. In variant III, nitriding was carried out at high temperature of 580°C and 100%  $\text{NH}_3$  atmosphere in order to nitrogen saturate the surface of the samples as much as possible.

After the treatments were carried out, the samples were subjected to metallographic tests (light and scanning microscopy), wear resistance tests, corrosion resistance tests and hardness measurements at the surfaces and cross-sections of samples. Observations of the metallographic specimens (etched with 3-% Nital) were performed with aid of metallographic microscope Nikon Eclipse LV150 with magnification up to  $\times 500$ . Electron microscopy imaging was carried out with aid of HITACHI HD2700 STEM microscope with magnification up to  $\times 2500$ . Vickers hardness tests were carried out using INNOVATEST hardness meter. The distance between hardness measurements at hardness distribution was 25  $\mu\text{m}$ . The measurements were aimed at avoiding large precipitations of carbides and carbonitrides. Phase composition studies of nitrided layers were made using a Rigaku MiniFlex II diffractometer with monochromated  $\text{CuK}\alpha$  radiation, a step size of 0.01° (2 $\theta$ ) per 3 second.

Test of wear resistance was carried out in a 3 rollers-cone system. 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 50, 100, 200, 300 and 400 MPa.

Corrosion resistance was tested by means of potentiodynamic method. The measurements were carried out at room temperature in an oxygenated solution containing chloride

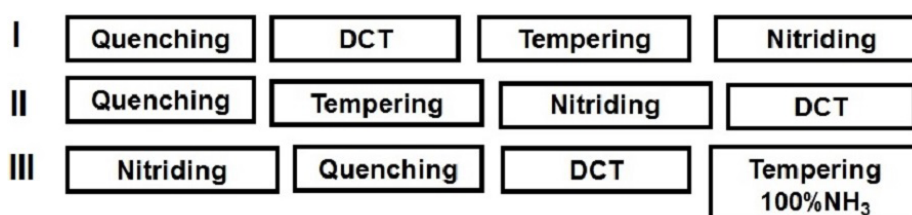


Fig. 1. Block diagram of heat and thermo-chemical treatment modes of X153CrMoV12 steel

ions, ie: 0.5M NaCl solution with pH neutral and acidified to pH = 3 (pH corrected using hydrochloric acid) and in a solution of 0.5M Na<sub>2</sub>SO<sub>4</sub> with neutral pH and pH = 3 (pH adjusted using sulfuric acid).

### 3. Results and discussion

After quenching and tempering of samples made of X153CrMoV12 steel, a typical structure of tempered martensite, retained austenite with numerous precipitates of primary and secondary carbides was obtained. In the case of samples subjected to quenching, DCT and tempering, the obtained structure was characterized by a larger number of fine-grained carbides with longitudinal shapes, arranged parallel to each other. The obtained microstructures are shown in Fig. 2. The process of DCT should be considered as a process that allows proceeding of the isothermal martensitic transformation occurring in high carbon steels at temperatures  $-100 \div -196^{\circ}\text{C}$  [8]. According to current literature reports, in addition to the athermal martensitic transformation, very important role appears to play a martensitic transformation with the isothermal kinetics at temperatures range of  $-100 \div -196^{\circ}\text{C}$ . The processes taking place during the isothermal martensitic transformation and subsequent processes of nucleation and growth of carbides, occurring during the heating to the tempering temperature and soaking at this temperature, seem to play a key role in explaining the effect of DCT on the properties of the steel [10]. Longer cryogenic treatment time gives similar but even finer microstructure, and increased hardness [11]. The process of DCT led to a significant increase in the amount of carbide precipitations present in the steel microstructure. This result is consistent with the observations of the authors in the paper [7], in which there was observed an increase in the content of carbide phase

from 18% to 26%. A major difference between the steel microstructures was also a more homogenous distribution of carbides in the case of steel subjected to DCT, which is consistent with the results of the described in several publications [7,18]. Larger carbides may be primary carbides of M<sub>23</sub>C<sub>6</sub> and M<sub>7</sub>C<sub>3</sub> type, while the smaller ones are probably MC and M<sub>2</sub>C secondary carbides.

In the mode I, the application of deep cryogenic treatment before tempering and subsequent nitriding caused an increase in the hardness in the nitrided layer. This indicates a higher saturation of the sub-surface zone with nitrogen, as compared to nitrided layers obtained on X153CrMoV12 steel subjected to simple hardening and tempering.

With the use of DCT, a greater thickness of the surface layer of iron nitrides was obtained. After the treatment mode without DCT, the nitrided layer consisted of a surface layer of iron nitrides with a thickness of 0-1  $\mu\text{m}$  and an internal nitriding layer of about 100  $\mu\text{m}$  (determined by the criterion: core hardness + 50HV0,5). However, when the DCT process was applied, the nitrided layer consisted of a surface layer of iron nitrides with a thickness of 4 mm and an internal nitriding layer with a thickness of about 140 mm. The surface hardness was higher for the variant with DCT and reached the following values: 1111 HV1  $\pm 12.7$  (without DCT) and 1235 HV  $\pm 15.6$  (with DCT). At the same time, it should be noted that DCT increased also the hardness of the core from 620 HV0,5 to 700 HV0.5. The obtained microstructures are shown in Fig. 3. Distributions of hardness at the sample cross-sections are shown in Fig. 5. The XRD analysis showed that the nitrided layer produced in mode I on the surface consisted of nitrides Fe<sub>3</sub>N and Fe<sub>4</sub>N (Fig. 4).

After the nitriding, the samples were characterized by very good tribological properties. In case of samples subjected to DCT between hardening and tempering, the tests of resistance to wear have shown an increase of resistance to wear. Deep cryogeni-

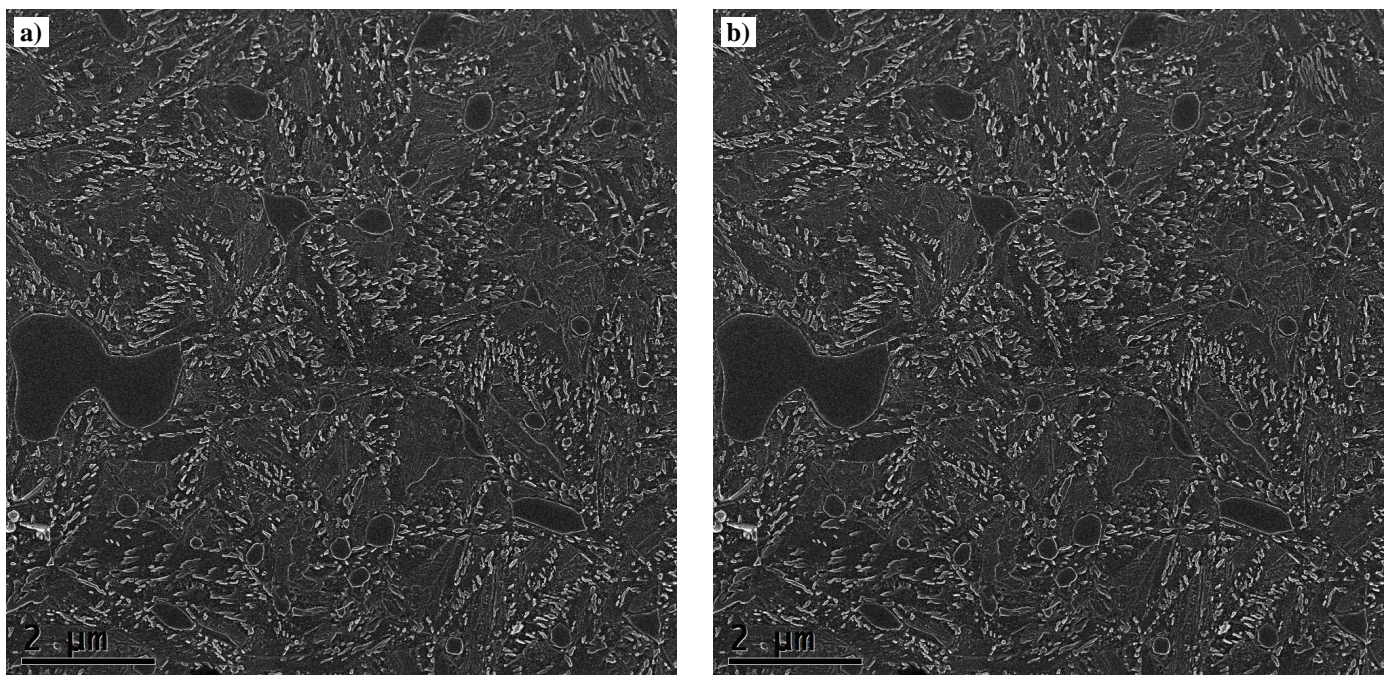


Fig. 2. Microstructures of X153CrMoV12 steel after quenching and tempering (a) or quenching, DCT and tempering (b)

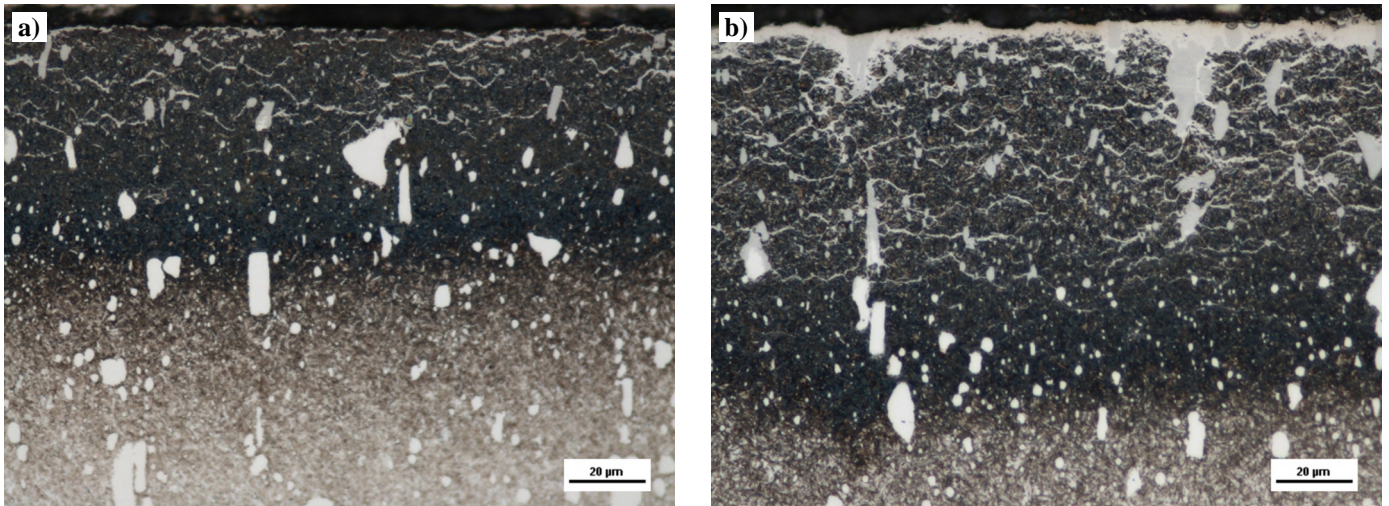


Fig. 3. Microstructures of surface layers obtained after treatments according to mode I: without DCT (a), with DCT (b)

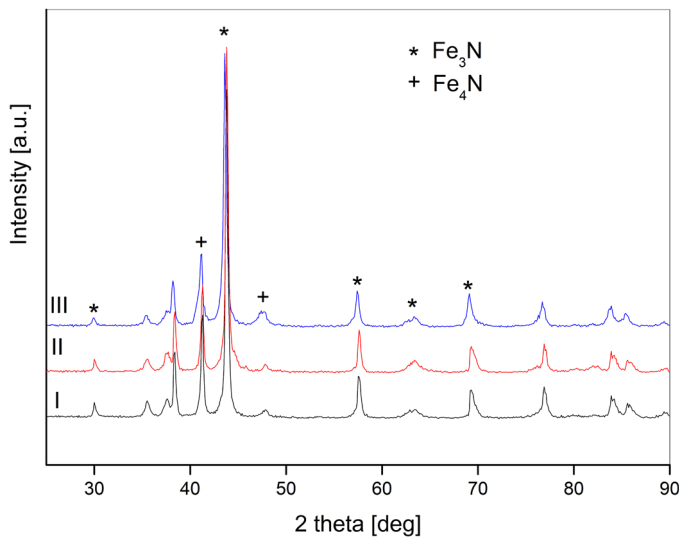


Fig. 4. XRD patterns of X153CrMoV12 after 3 modes of heat and thermo-chemical treatment with DCT (I, II, III)

cally treated samples were characterized by lower linear wear regardless of the load applied to the friction node: 50; 100; 300 or 400 MPa. The results of wear resistance measurements are shown in Figure 6.

The increase in wear resistance of nitrided steels is caused by the combination of both nitriding and DCT treatments. While nitriding is responsible for improved wear resistance, finer microstructure obtained through DCT could improve fatigue properties of the tool steels. This is confirmed by the research of other researchers [11,12]. The authors in their article [11] showed that combination of higher austenizing temperature, DCT and/or nitriding results in increased surface hardness and hardness in nitrided layer. Authors of work [12] concluded that better diffusion of nitrogen along the steel surface layer is promoted by high residual stresses formed by DCT.

In the case of treatments according to mode II, the use of deep cryogenic treatment after nitriding did not cause any significant differences in the hardness and thickness of nitrided

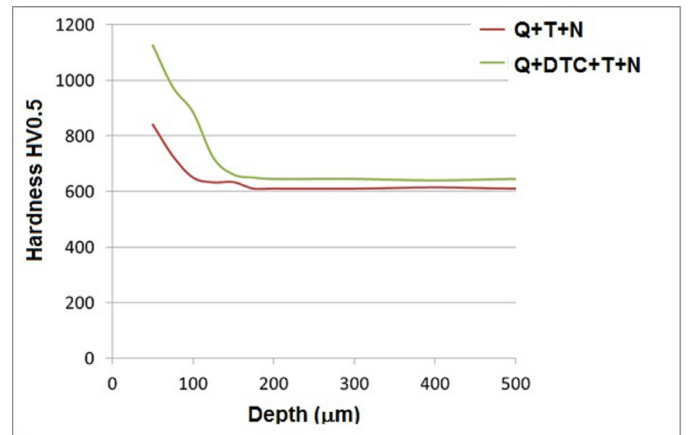


Fig. 5. Hardness distributions at the cross sections of surface layers obtained after treatments according to mode I: without DCT (Q+T+N), with DCT (Q+DCT+T+N)

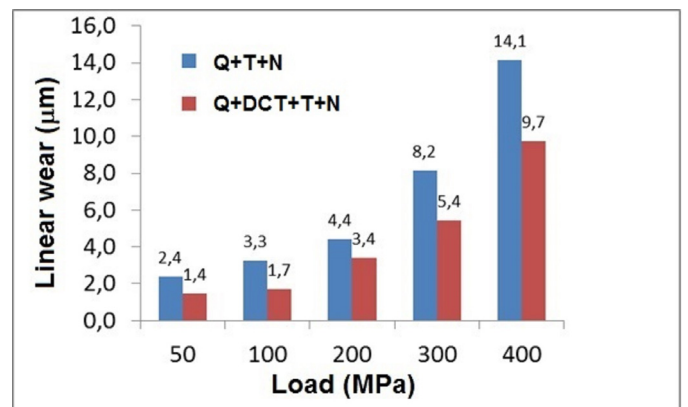


Fig. 6. Linear wear of layers obtained after treatments according to mode I: without DCT (Q+T+N), with DCT (Q+T+DCT+N)

layers. The surface hardness of the obtained nitrided layers was as follows: 1086 HV1 ±2.5 (without DCT) and 1138 HV1 ±2.5 (with DCT). Similar microstructures of nitrided layers were obtained, i.e. the thickness of surface iron nitrides was about 16 mm while internal nitriding zone was 120 mm thick (Fig. 7). The

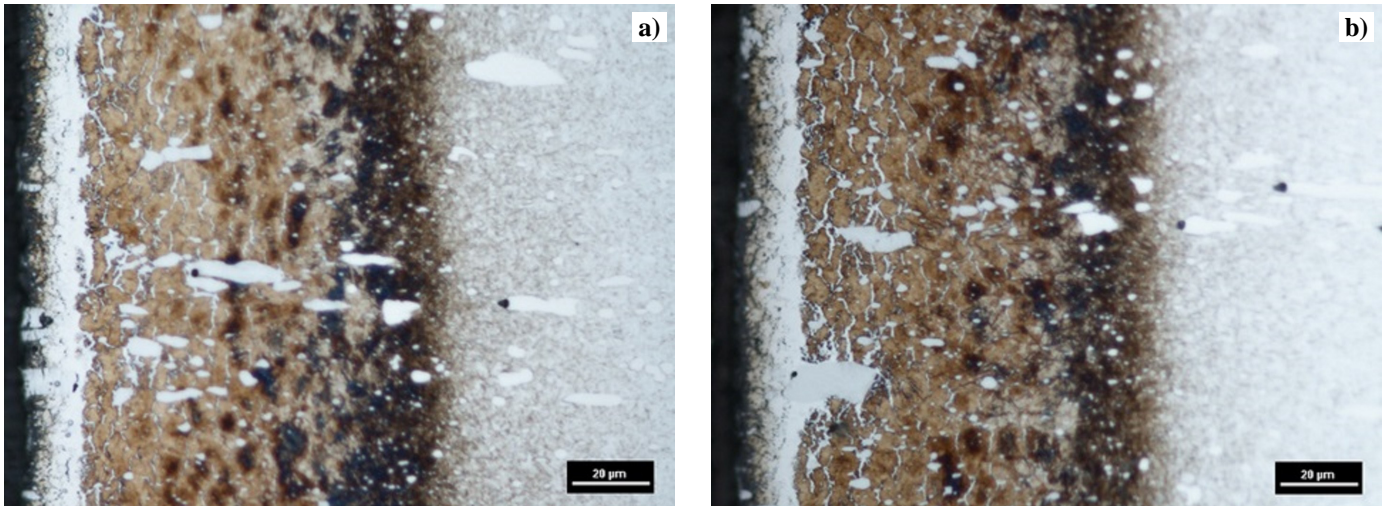


Fig. 7. Microstructures of surface layers obtained after treatments according to mode II: without DCT (a), with DCT (b)

XRD analysis showed that the nitrided layer produced in mode II on the surface consisted of nitrides  $Fe_3N$  and  $Fe_4N$  (Fig. 4). The wear resistance tests showed no significant differences in the linear wear for samples with or without DCT (Fig. 8).

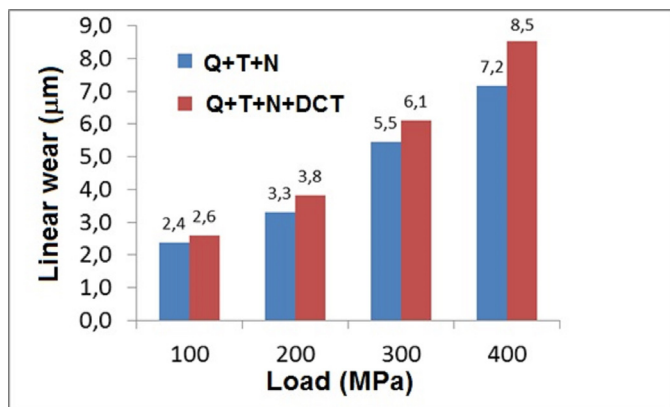


Fig. 8. Linear wear of layers obtained after treatments according to mode II: without DCT (Q+T+N), with DCT (Q+T+N+DCT)

An important difference was noted in the case of corrosion resistance. In the neutral pH environment, the formed nitrided layers ensure corrosion resistance of the steel. In comparison with steel subjected to conventional heat treatment, a more positive corrosion potential (about  $0.3 V_{NEK}$ ) and the ability to permanently passivate were recorded. The DCT process additionally reduces the intensity of processes in the area of active dissolution. Acidification of the environment to  $pH = 3$ , as in the case of measurements carried out in chloride solution, caused occurrence of two maxima in the active range. The first maximum point was at the potential of  $-0.65 V_{SE}$ , while the second at the potential of  $-0.28 V_{SE}$ . When comparing the courses of the curves for steels subjected to nitriding or DCT and nitriding, it should be noted that although they are comparable, in the case of DCT the curve runs at lower current density values. Acidification of the sulphate environment significantly increases the intensity of corrosion processes in all samples. The rest potential course and polarization curves registered in  $0.5M NaCl$  at  $pH = 3$  are shown in Figure 9. Increase in corrosion resistance is manifested

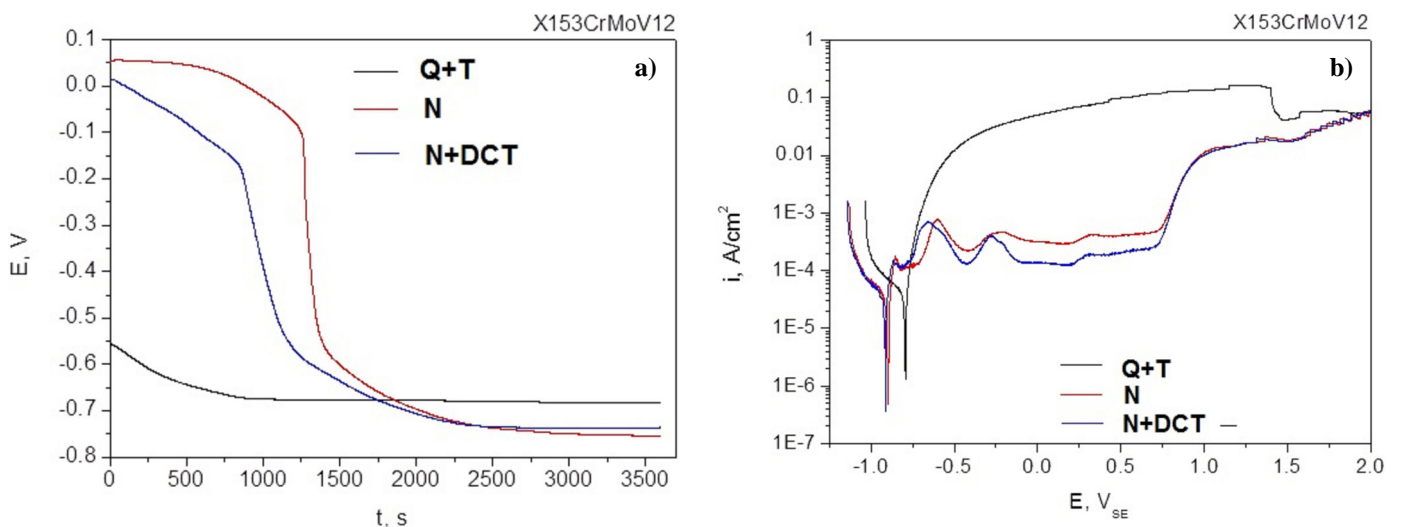


Fig. 9. The rest potential course  $E = f(t)$  (a) and polarization curves  $i = f(E)$  for X153CrMoV12 steel registered in  $0.5M NaCl$  at  $pH = 3$  (b)

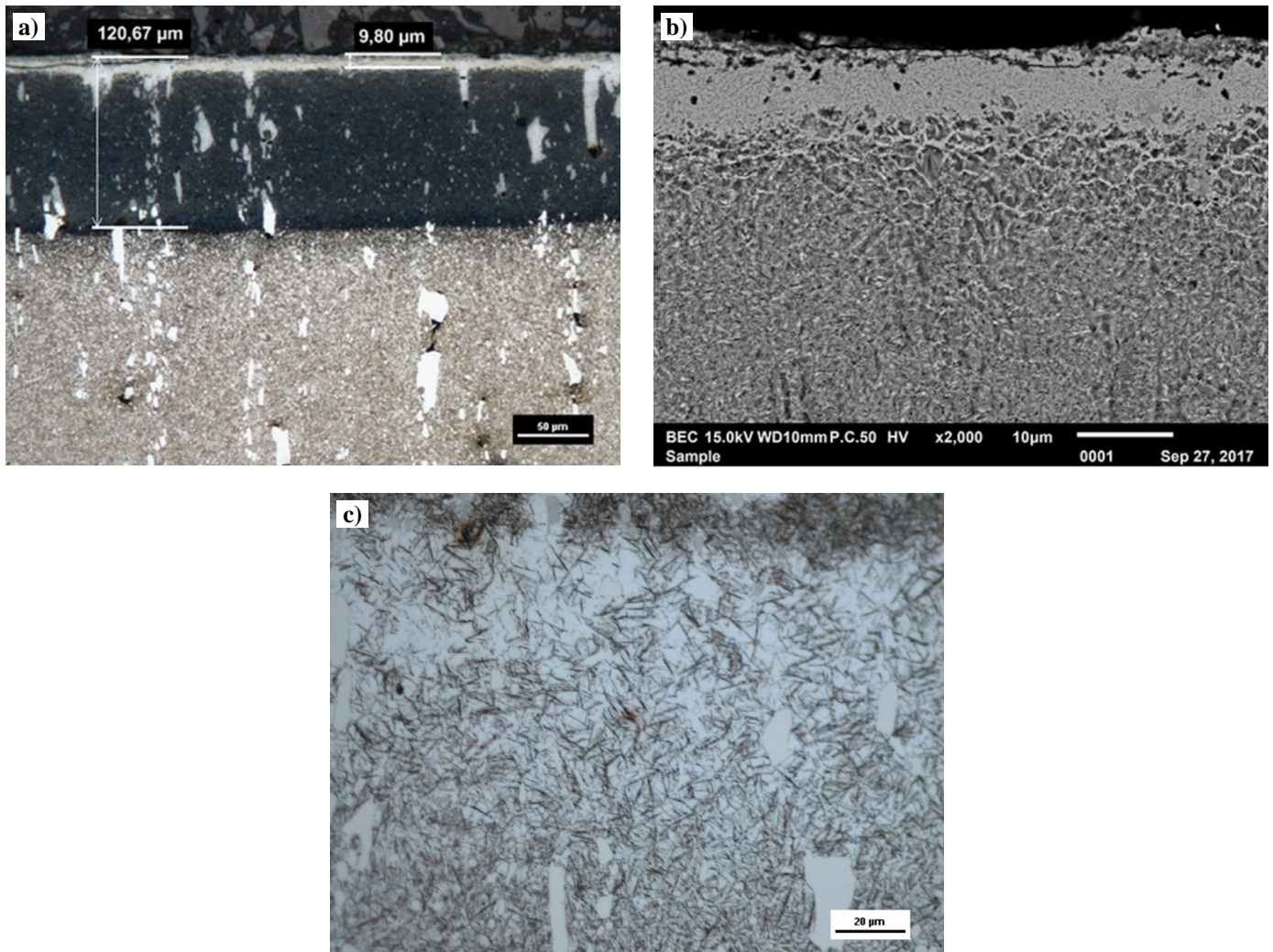


Fig. 10. Microstructures of surface layers obtained after treatments according to mode III with DCT: nitrided layer with visible diffusion layer (a), sub-surface layer of iron nitrides (b) and transition zone (c)

by lower values of current density in the active range and more positive value of corrosion potential, when compared with steel solely nitride. The passivation processes occur at lower values of current density for polarization curves recorded in a solution containing chloride ions.

In the case of samples heat-treated according to mode III, the application of deep cryogenic treatment in the sequence of heat treatment of nitrided steel increased the thickness of the obtained layers (from 240 to 280  $\mu\text{m}$ ). The DCT process caused an increase of the surface hardness. In the subsurface zone, a layer of iron nitrides with a thickness of approx. 9-10  $\mu\text{m}$  was obtained. Fig. 10 shows obtained microstructures of nitrided layers after heat treatment according to mode III. The XRD analysis showed that the nitrided layer produced in mode III on the surface consisted of nitrides  $\text{Fe}_3\text{N}$  and  $\text{Fe}_4\text{N}$  (Fig. 4). Fig. 11 shows the distribution of hardness at the cross section of nitrided layer. The use of ammonia during the tempering allowed to avoid the de-nitriding of the layer.

Regardless of the application of the deep cryogenic treatment process, the surface hardness was at a similar level:  $1230 \text{ HV}_1 \pm 14.7$  (without DCT) and  $1250 \pm 14.7$  (with DCT). It

should be noted that the heat treatment of nitrided layer (according to variant III with a tempering in a suitable atmosphere) caused the formation of thicker nitrided layers than in case of conventional nitriding. The nitrided layer was thicker by approx. 100%, increasing its thickness from 120 to about 240-280  $\mu\text{m}$ , with nitriding in 4 hours shorter time (comparison of nitriding mode I with mode III). These layers are characterized by a deep transition zone, appearing metallographically with a white structure with numerous precipitates of carbonitrides in the form of needles (Fig. 10c). The nature of these precipitates requires in-depth X-ray and microscopic analysis. The use of DCT influenced both the increase in the hardness of the nitrided layer and the hardness of the material core. The hardness for samples without DCT was 629  $\text{HV}_0.5$ , while for deep cryogenically treated samples was 716  $\text{HV}_0.5$ .

For nitrided layers subjected to heat treatment with DCT, higher resistance to friction wear was observed, characterized by low linear wear at high loads, in comparison with nitrided layers formed on hardened and tempered samples (mode I). It was also found that DCT reduces the linear wear of samples by 20 to 30% (Fig. 12).

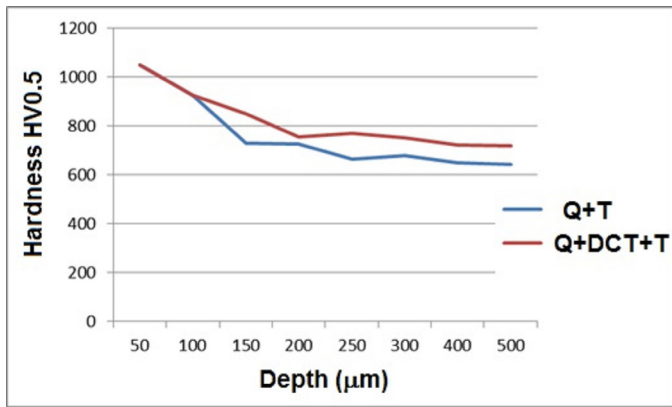


Fig. 11. Hardness distributions at the cross sections of surface layers obtained after treatments according to mode III: without DCT (Q+T), with DCT (Q+DCT+T)

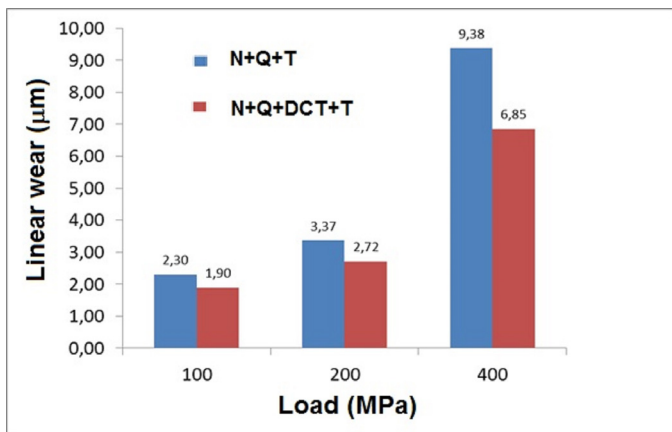


Fig. 12. Linear wear of layers obtained after treatments according to mode III: without DCT (N+Q+T), with DCT (N+Q+DCT+T)

#### 4. Conclusions

After testing the X153CrMoV12 steel samples subjected to heat and thermo-chemical treatments according to variants I-III, it was found that deep cryogenic treatment improves the properties of nitrided layers, in particular:

- DCT performed during heat treatment of X153CrMoV12 steel increases the precipitation of fine carbides, which cause higher strengthening.
- The use of DCT during heat treatment of X153CrMoV12 steel prior to the nitriding process increases the hardness of the nitrided layer and increases the resistance to wear.
- The use of DCT after the X153CrMoV12 steel nitriding process increases the corrosion resistance of the layer.

- The use of DCT during heat treatment of nitrided layers increases the thickness of the nitrided layer, resistance to wear and at the same time increases the hardness of the core.

#### Acknowledgement

This research was supported by Eureka Programme (Eureka E!9170 "CRY-ONITRIDE" Project).

#### REFERENCES

- [1] V. G. Vorobjev, Gosudarstvennoye Izdatelstvo Oboronnoy Promyshlennosti, Moskva, 106 (1954).
- [2] R.F. Barron, 21st Inter-Plant Tool and Gage Conference. Shreveport, LA, USA, ASM Handbook **4**, 205 (1982)
- [3] I. Wierszyłowski, L. Szcześniak, *Obróbka Plastyczna Metali* **1**, 31-36 (2005).
- [4] A.I. Tyshchenko, et al., *Materials Science and Engineering A* **527**, 7027-7039 (2010).
- [5] V. Leskovšek, B. Ule, *Heat Treatment of Metals* **3**, 72-76 (2002).
- [6] J. Jeleńkowski, P. Wach, A. Ciski, T. Babul, *Materials Science (Inżynieria Materiałowa)* **6** (190), 673-676 (2012).
- [7] K. Amini, A. Akhbarizadeh and S. Javadpour, *International Journal of Minerals. Metallurgy and Materials* **19** (9), 795-798 (2012).
- [8] V.G. Gavriljuk et al., *Acta Materialia* **61**, 1705-1715 (2013).
- [9] A. Molinari, M. Pellizzari et al., *Journal of Materials Processing Technology* **118**, 350-355 (2001).
- [10] J.Y. Huang, Y.T. Zhu, X.Z. Liao, I.J. Beyerlein, M.A. Bourke, T.E. Mitchell, *Materials Science and Engineering, A* **339**, 241-244 (2003).
- [11] B. Podgornik, F. Majdic, V. Leskovšek, J. Vizitnin, *Wear* **288**, 88-93 (2012).
- [12] V. Leskovšek, B. Podgornik, *Materials Science and Engineering A* **531**, 119-129 (2012).
- [13] N.I. Kardonina, A.S. Yurovskikh, A.S. Kolpakov, *Metal Science and Heat Treatment* **52**, 457-467 (2011).
- [14] E.H. Du, Marchie van Voorthuysen, D.O. Borema, N.C. Chechenin, *Metallurgical and Materials Transactions A* **33A** (2002).
- [15] A. Suyazov, M.P. Usikov, B.M. Mogutnov, *Fizika Metallov Metallovedeniye* **42**, 755-763 (1976).
- [16] N. DeCristofaro, R. Kaplow, *Metall. Trans. A* **8** (1), 35-44 (1977).
- [17] K.H. Jack, *Acta Crystallogr.* **3**, 392-393 (1951).
- [18] F. Meng, K. Tagashira, R. Azuma, H. Sohma, *ISIJ International*, **34** (2), 205-210 (1994).