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GLOW DISCHARGE ASSISTED NITRIDING OF CHROMIUM STEEL 3H13

Keywords

Glow discharge nitriding, X30Cr13 steel, nitrided layers, structure, corrosion, wear resistance.

Abstract

The paper discusses the effects of the glow-discharge assisted nitriding of 3H13 (X30Cr13 PN-EN 10088-1:1998) steel carried out under various conditions upon the microstructure, chemical composition, phase composition and topography of the steel surface. Moreover, this paper presents also how this process improves the performance properties of the steel, such as its corrosion and frictional wear resistance. The present experiments were intended to be the initial stage of the study aimed at developing the fundamentals of new hybrid technologies of composite surface layers, based on a combination of glow discharge nitriding with ion implantation, Ion Beam Assisted Deposition (IBAD) and Pulsed Laser Deposition (PLD).

Introduction

The basic group of metallic materials commonly used for fabricating medical instruments comprises corrosion-resistant steels, e.g. martensitic chromium steels [1]. The properties of these steels can be effectively modified by heat treatments and also by glow discharge assisted nitriding and what is known as hybrid techniques, i.e. processes that combine glow discharge nitriding with various surface engineering techniques [2-5]. These techniques permit increasing the hardness of the steel and improving its resistance to corrosion and frictional wear, thereby increasing the reliability and stability of the medical instruments made of this steel. The paper describes how the structure and performance properties, such as the resistance to corrosion and frictional wear, of 3H13 steel are affected by glow discharge nitriding, with special attention paid to the possibility of modifying the phase composition and topography of the surface of the thus produced nitrided layers by controlling the nitriding process parameters.

1. Experimental methods

Samples made of 3H13 steel (0.3%C, 0.49%Si, 0.66%Mn, 12.26%Cr, 0.018%P, 0.025%S) were subjected to nitriding under glow discharge conditions at temperatures of 480 and 530^{o}C.

The microstructure of the samples was examined in an Olimpus 1X70 optical microscope and a Hitachi S-35000N scanning electron microscope. The metallographic cross-sections were etched with a Mi-19Fe etchant (3g $FeCl_2$, 10cm^3 HCl, 90cm^3 C_2H_5OH). The chemical composition was examined on sample cross-sections using the EDS method, whereas the phase composition was examined in a Brucker D8 Discover X-ray diffractometer using CuK_α and CoK_α radiations. The corrosion resistance was measured by the potentiodynamic method (Atlas-Sollich measuring set) in an aqueous 0.5M NaCl solution, by polarizing the samples over the potential range from -1000mV to +2000mV (at a potential variation rate of 10mV/s, within the corrosion potential region). The potential was measured with respect to the potential of a saturated calomel electrode (SCE). Prior to the measurement, the samples were immersed in an aqueous 0.5M NaCl solution for 24 hours to let the corrosion potential stabilize. The microhardness was measured with a Zwick Materialprüfung 3212002 hardness-meter. The frictional wear resistance was examined by the ‘three rollers + taper’ method using a T-04 device at a unit load of 200MPa, according to the PN-83/H-04302 Standard. The surface roughness was measured with a Form Talysurf Series 2 Taylor-Hobson scanning profilometer.

2. Results

Fig. 1 shows the microstructure and appearance of the surface of the nitrided layers produced on 3H13 steel by glow discharge nitriding at temperatures of 480 and 530^{o}C.

The layers nitrided at a temperature of 480°C are about 11 μm thick and their surface hardness is 1120 HV0.05. The layers produced at 530°C are thicker, with a thickness of about 20μm, and have a higher microhardness of 1220 HV0.05. The microhardness of the starting material was 350 HV0.05.

Table 1 compares the surface roughness parameters of the samples in the starting state and after glow discharge assisted nitriding at 480°C and 530°C, measured in the center and at the edge of the samples.

Fig. 2 shows the linear distribution of elements in the nitrided layer. In the sample subjected to nitriding at the temperature of 480°C, the nitrogen concentration persists at a constant level (about 4.8 wt.%) down to 13 μm from the sample surface. In the samples nitrided at 530°C, nitrogen diffuses much deeper, namely to a depth of about 86μm. The maximum nitrogen concentration (about 4.23 wt.%) occurs at a depth of about 11μm. Then it slightly decreases with depth to become very small at about 81μm, and further down at 86μm, it reaches a value close to that in the starting condition.

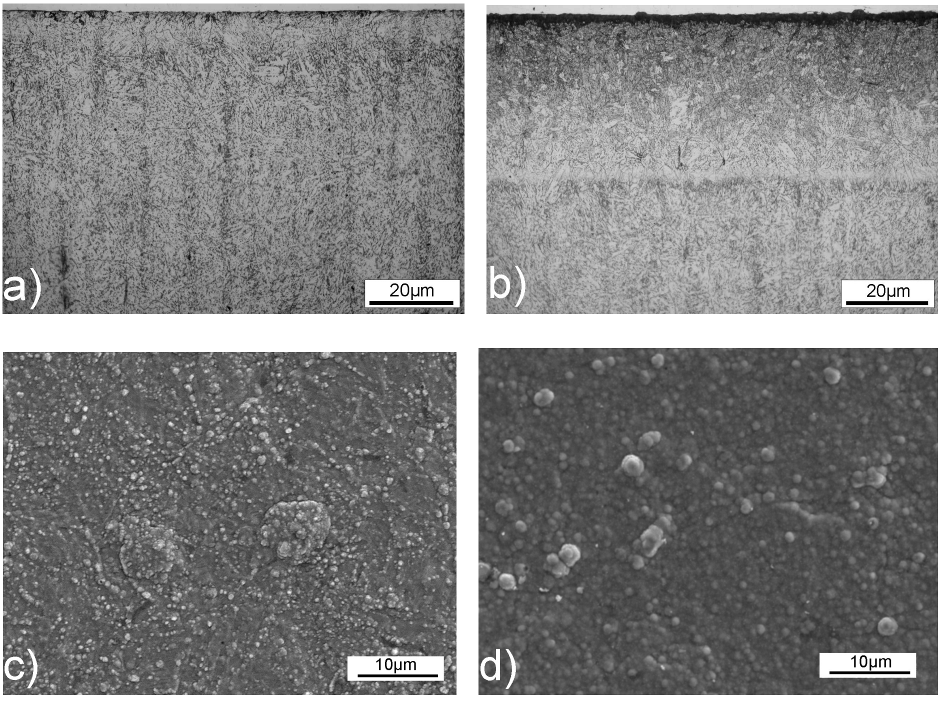

Fig. 1. Microstructure of the layers produced on 3H13 steel by glow discharge nitriding: (a) at 480°C and (b) at 530°C, and the surface appearance of these layers: (c) produced at 480°C and (d) produced at 530°C

Table 1. Stereometric parameters characterizing the surface topography of 3H13 steel in the starting condition and after glow discharge assisted nitriding carried out at temperatures of 480°C and 550°C

Parameter	Starting state [µm]	Nitriding at 480°C		Nitriding at 530°C	
		Sample center [µm]	Sample edge [µm]	Sample center [µm]	Sample edge [µm]
R_a	0,109	0,209	0,183	0,294	0,364
R_q	0,144	0,294	0,286	0,395	0,585
R_p	1,07	2,84	4,04	2,55	4,46
R_v	0,914	2,17	2,37	1,32	2,65
R_t	1,99	5,01	6,41	3,87	7,1
R_z	1,66	3,9	4,61	3,76	6,25

R_a - arithmetic mean deviation of the roughness profile, R_q- square mean deviation of the roughness profile, R_p - maximum height of the roughness profile, R_v - maximum depth of the roughness profile, R_t - maximum distance between the lowest and the highest points of the roughness profile ($R_t = R_p + R_v$), R_z -means the difference between the five highest points and 5 deepest points of the roughness profile (in accord with ISO 4287/11984)

The phase composition of the nitrided layer produced at 480°C was examined by performing the standard phase analysis in the Bragg-Brentano geometry [7], which however only gives an approximate image of the surface layer. The two images obtained by using CuK_α radiation (to a depth of 4µm) and CoK_α radiation (to 23 µm) differ only slightly from one another, and in both the broad (diffused) maxima can be attributed to CrN and -εFe_3N phases (Fig. 3).

A detailed phase analysis of the surface layer (to a depth of about 2µm) was made using the parallel beam geometry, with the beam striking the surface at various angles (3 to 21°). This method gave diffraction images that informed us about the phase composition down to a depth of 0.5 to 2 µm (Fig. 4). The strongest reflexes due to the CrN, ε-Fe_3N, ζ-Fe_2N phases and to the over-saturated Fe(N) solution partially overlap and are partially shifted with respect to one another depending on the phase composition. Therefore, at depths from 2 to 12 µm the layer seems to be a mixture of these phases with various nitrogen concentrations.

In order to reveal the structure of the layer, its phase composition was examined at every 7 µm of the depth by grinding gradually away at the sample surface. After each grinding, the Bragg-Brentano image obtained with CoK_α (Fig. 6) radiation was recorded (Fig. 5). The analysis was performed at various angles and indicated that the nitrogen had diffused to a depth of 33 µm and that the basic phase present in the layer was nitrogen-oversaturated martensite with a strong tetragonal deformation and ε-Fe_3N type nitride precipitates visibly within it (Fig. 7). To verify this hypothesis further studies are required.

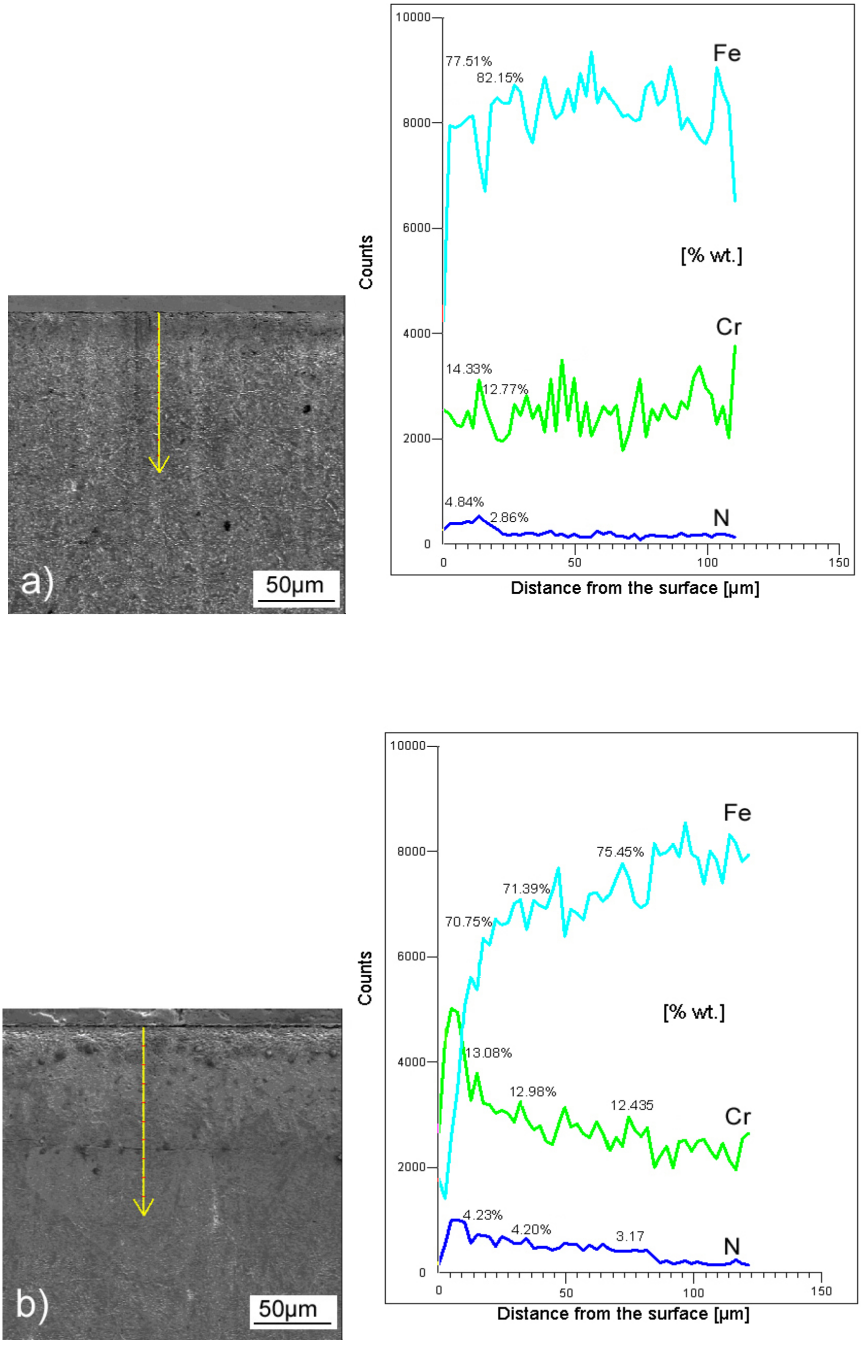

Fig. 2. Distribution of elements (iron, chromium and nitrogen) in the nitrided layers produced on 3H13 steel by glow discharge assisted nitriding at temperatures of 480°C (a) and 530°C (b)

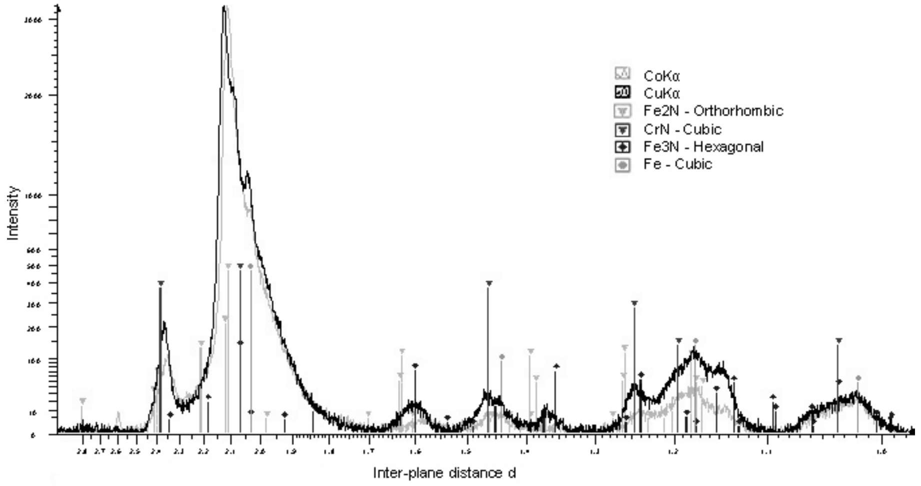

Fig. 3. Diffraction of 3 patterns (CuK_{α} and CoK_{α} radiation) of the sample surface nitrided at 480°C

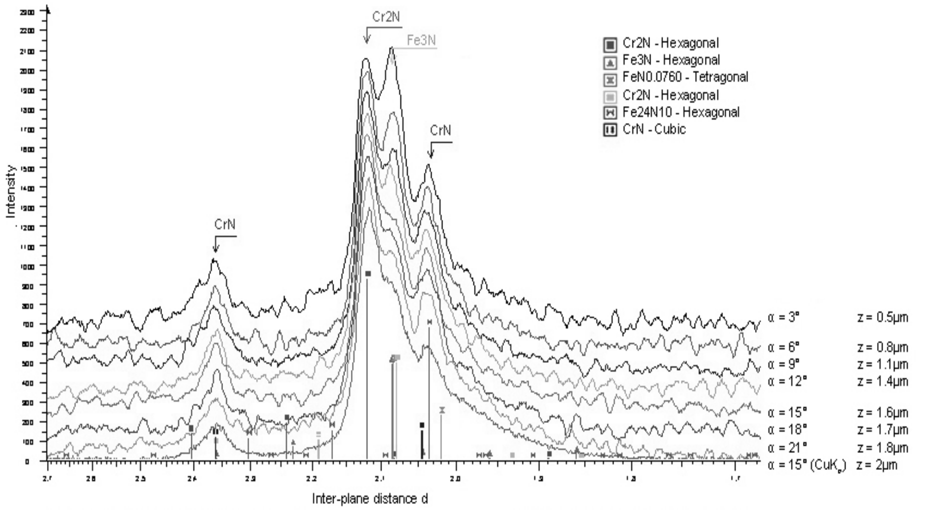

Fig. 4. Phase composition of the surface layer of a sample nitrided at 480°C as a function of the distance from the layer surface (CuK_{α} radiation incident at α angle)

The layer produced by glow discharge-assisted nitriding at a temperature of 530^{0}C is composed of ε-Fe_3N, γ-Fe_4N and CrN type nitrides. The ε-Fe_3N phase is found on the surface, whereas the CrN phase is placed slightly deeper. The γ-Fe_4N phase is distributed uniformly within the entire volume of the layer. At a depth of 2 μm we can see martensite (Fig. 8).

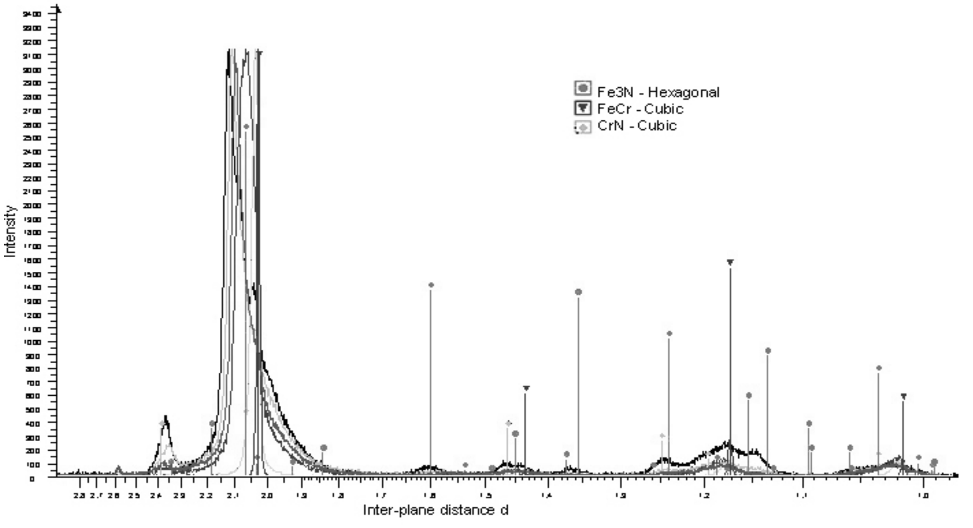

Fig. 5. Diffraction patterns obtained for a nitrided layer produced at 480°C after successive grinding operations

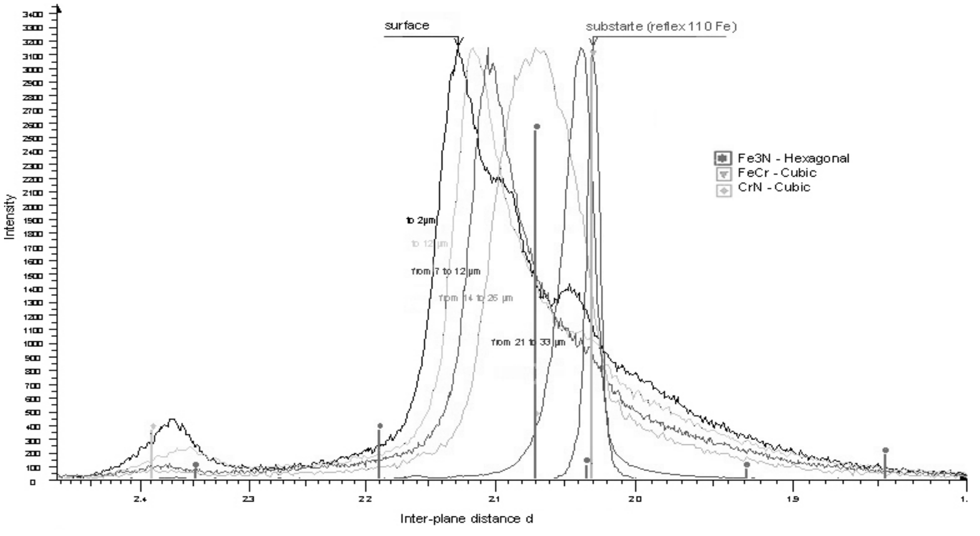

Fig. 6. Structural changes in the layer nitrided at a temperature of 480°C as a function of the distance from the layer surface

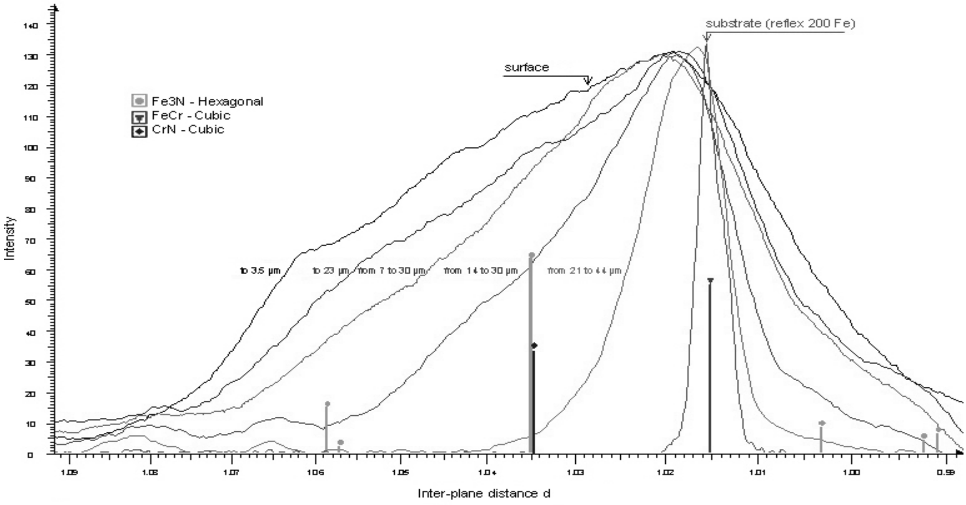

Fig. 7. Changes in the structure of the nitrided layer produced at 480^{o}C, visible over its cross-section from the surface down into the layer interior within the region of the reflex from the (220) plane

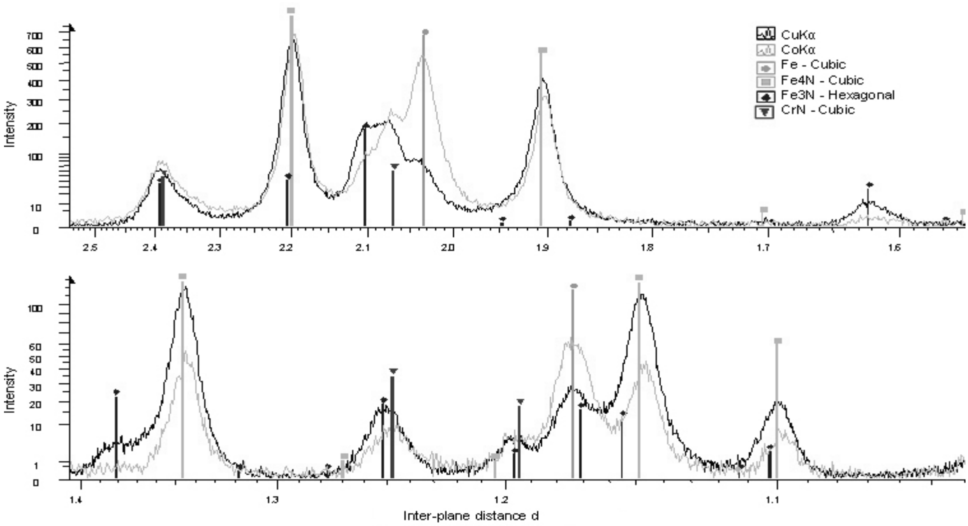

Fig. 8. Diffraction patterns (CuK_{α} and CoK_{α} radiations) of the surface layer nitrided at 530^{o}C

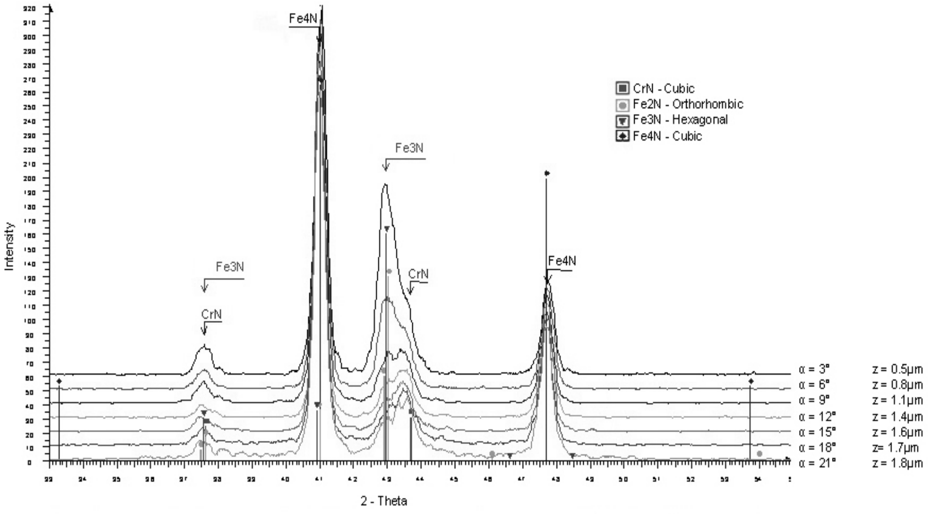

Fig. 9. Phase composition of the surface layer of a sample nitrided at 530°C as a function of the distance down from the layer surface; images obtained with CuK_{α} and CoK_{α} radiation

Glow discharge assisted nitriding carried out at a temperature of 480°C did not decrease the good corrosion resistance of 3H13 steel; whereas, the process conducted at 530°C slightly decreased the corrosion resistance (Fig. 10, 11).

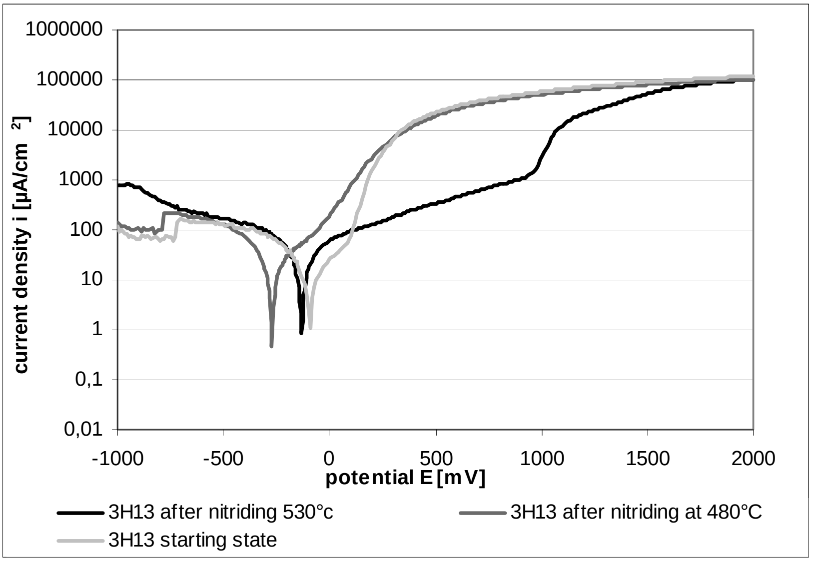

Fig. 10. Polarization curves of 3H13 steel in the starting condition and after nitriding at temperatures of 480°C and 530°C

When comparing the results of the corrosion measurements of the steel samples nitrided at the two different temperatures, we can see that the corrosion current densities differ only slightly, but the type of corrosion is different: the samples nitrided at 480°C undergo uniform corrosion, whereas those nitrided at 530°C undergo pitting corrosion (Fig. 11). The frictional wear resistance, on the other hand, increases significantly (Fig. 12): the sample of the starting material is

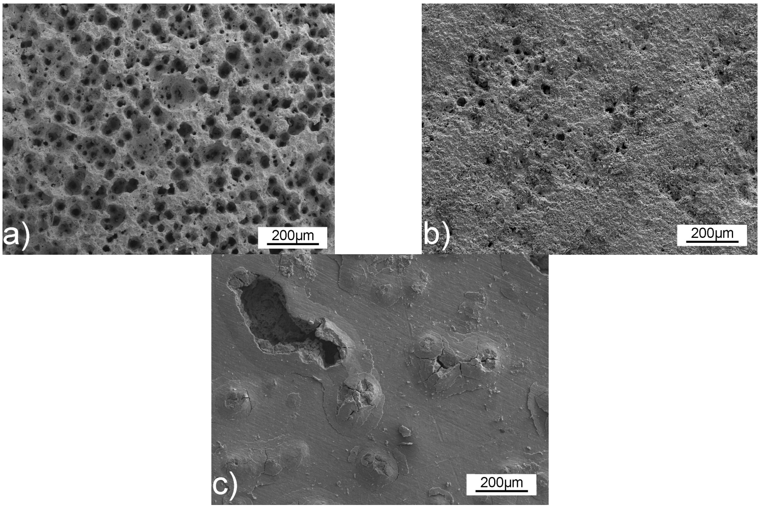

Fig. 11. Appearance of the surface of 3H13 steel after corrosion measurements: a) starting condition, b) after nitriding at 480°C and c) after nitriding at 530°C

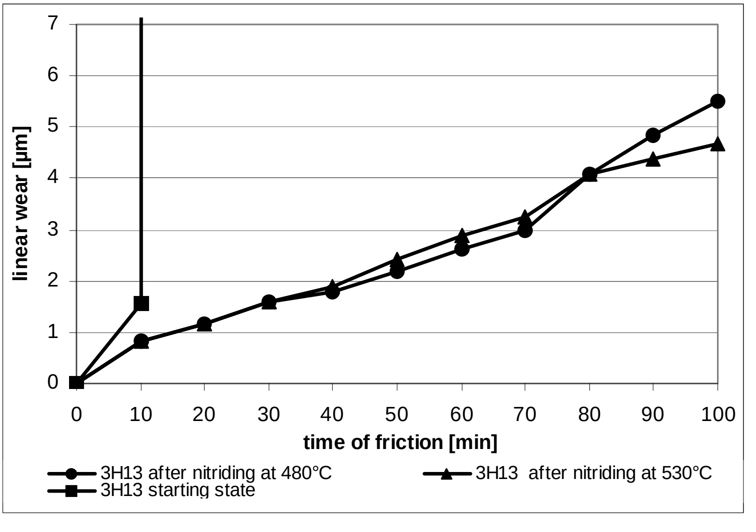

Fig. 12. Linear wear of 3H13 steel in the starting state and after nitriding at 480°C and 530°C as a function of friction time; measured under a unit load of 200 MPa

seized as early as after 10 min of testing, whereas the nitrided samples (irrespectively of whether nitrided at 480°C or at 530°C) show little linear wear even after 100 min of the test. The linear wear measured in the samples nitrided at 480°C was about 5.5 μm, and in those nitrided at 530°C it was about 4.69 μm after 100 minutes of the test.

Conclusions

Glow discharge assisted nitriding of chromium steel permits modifying precisely their surface topography, phase composition, chemical composition and microstructure so as to prepare the steel surface for producing thin (even less than 1 μm thick) coatings of Si_3N_4, CrN, c-BN or DLC type with specific performance properties, tailored to suit expected applications, and with good adherence to the substrate. In this way, it will be possible to take advantage of the synergic effects of the surface treatments applied, such as glow discharge assisted nitriding combined with Ion Beam Assisted Deposition (IBAD), ion implantation and Pulsed Laser Deposition (PLD) [2, 6] to optimize the corrosion resistance, frictional wear resistance and fatigue strength of chromium steels intended for the fabrication of medical instruments and other precision products and tools.

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References

1. Paszenda Z., Tyrlik-Held J.: Surgical Instruments, Publications of Politechnika Śląska (Silesian University of Technology), Gliwice, Poland, 2003 (in Polish).
2. Burakowski T., Wierzchoń T.: Surface Engineering of Metals, CRC Press, Boca Raton, London, New York, 1999.
3. Wierzchoń T.: Structure and properties of multicomponent and composite layers produced by combinated surface engineering methods, Surface and Coatings Technology, 2004, vol. 180-181, p. 458-464.
4. Wierzchoń T.: Lines of development of surface engineering, Problemy Eksploatacji, 2004, vol. 3, p. 251-267.
5. Wierzchoń T., Ulbin-Pokorska I., Precht W., Sikorski K.: Structure and properties of composite layer produced by combinated methods of surface

treatment, Proc. 12th Int. Fed. H.T.S.E., Melbourne, Australia, 2000, vol. 2, p. 31-35.
6. Research project No PW-004/JTE/04/2004, research task No II.1. Development of technology of nitrided layers with precisely specified structure, phase composition and surface topography, produced on selected grades of steel by glow discharge assisted nitriding.
7. Jenkins R., Snyder R.L.: Introduction to X-ray powder diffractometry, Chemical Analysis, vol. 138, A Wiley - Interscience Publication, John Wiley & Sons, INC, 1996.

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Azotowanie jarzeniowe stali chromowych

Słowa kluczowe

Azotowanie jarzeniowe, stal X30Cr13, warstwy azotowane, struktura, korozja, zużycie.

Streszczenie

W artykule przedstawiono wpływ warunków azotowania jarzeniowego stali 3H13 (X30Cr13 PN-EN 10088-1:1998) na mikrostrukturę, skład chemiczny i fazowy, topografię powierzchni, a także właściwości użytkowe, takie jak: odporność na korozję i zużycie przez tarcie. Praca stanowi pierwszy etap badań ukierunkowanych na opracowanie podstaw technologii hybrydowych wytwarzania kompozytowych warstw powierzchniowych łączących proces azotowania jarzeniowego z metodami implantacji jonów, IBAD oraz PLD.