Tomasz Babul, Anna Olbrycht, Szymon Pawlik, Janusz Trojanowski

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The influence of glow-discharge nitriding on the properties of thermally sprayed steel coatings

Abstract

Hybrid technologies are one of the directions of materials engineering development. They contribute to the subject of research on improving the performance of thermally sprayed steel coatings by thermo-chemical treatment.

The paper presents the test results of arc spraying stainless steel coatings and then glow-discharge nitrided. The glow-discharge nitriding was performed with the following parameters: at 450 °C for 6 hours and at 530 °C for 4 hours. The results of the following tests are described and presented: metallographic (SEM), qualitative and quantitative analysis point EDS, measurement of hardness HV, hardness distribution, measurement of roughness parameters (Ra, Rz), wear resistance by the Amsler method.

The results showed that the glow-discharge nitriding increases the hardness and the frictional wear resistance of thermal sprayed stainless steel X46Cr13 and X2CrNi18-9 coatings. The hybrid technology, combining thermal spraying of martensitic stainless steel X46Cr13 and glow-discharge nitriding at 530 °C for 4 hours, provides formation of a coating with the highest hardness and wear resistance of all the tested coatings. This coating can be applied to the regeneration of machine parts, which are required to have particularly high useful properties.

Keywords:
thermal spraying;
arc spraying;
glow-discharge nitriding;
coating X46Cr13;
coating X2CrNi18-9;
Vickers hardness;
wear resistance;
Amsler method

Introduction

Thermal spraying technology is used to apply coatings on new machine parts in order to improve the usable properties of their surfaces or to regenerate worn parts [1÷8]. As a result of regeneration, the parts are repaired and their dimensions are restored, their durability is significantly increased, and thus the life of the device, part of which is covered by the coating [9], becomes longer. A thermally sprayed stainless steel, especially austenitic steel used for regeneration often have too low hardness and abrasion resistance. In order to increase the properties of thermal sprayed coatings, one of the surface engineering technologies can be used. Such technology, improving both mechanical properties, e.g. hardness, resistance to wear, as well as anti-corrosion properties of the surface layers by modification of its chemical composition and microstructure is called glow-discharge nitriding. The glow-discharge nitriding technology is more and more widely used in industry as an effective and economical method of increasing the usable properties of machine parts and tools. The advantage of this method is the ability to precisely regulate the structure of the nitrided layer, conduct the process at a temperature of as little as 400 °C, and the ability to regulate the phase composition of the produced layers by changing the chemical composition of the reactive atmosphere, which allows the production of composite layers in one technological process. The economic competitiveness in relation to classic gas technologies results from the low consumption of electricity and gas atmosphere components, and in particular from the reduction of costs of labor-intensive finishing operations due to minimum dimensional changes [10÷12].

There are very few papers in national and world literature on the use of hybrid technology that combines two technologies of surface engineering: thermal spraying and glow-discharge nitriding. L. Berkowski studied selected regenerative

dr hab. inż. **Tomasz Babul,** prof. IMP; mgr inż. **Anna Olbrycht;** inż. **Szymon Pawlik;** inż. **Janusz Trojanowski**
– Institute of Precision Mechanics, Warsaw, Poland;

Corresponding author: anna.olbrycht@imp.edu.pl

coatings applied by various methods nitrided with gas as well as glow-discharge [13]. He stated, that after glow-discharge nitriding at 520 °C for 8 hours, the coating of 4H13 steel sprayed with an arc method increases the hardness by about 600 HV0.1, while the coating resistance to friction wear does not change. Paper [14] presents the results of tests of coatings sprayed thermally with 40H13 and H18N10T wires, which are then subjected to glow-discharge nitriding in various process parameters. A significant increase in hardness and abrasion resistance of coatings after glow-discharge nitriding was found. In the paper [15], plasma-sprayed austenitic 316L corrosion-resistant steel was tested after low-temperature nitriding. A layer made of nitride phase „S" (S-phase), also known as expanded austenite, which increases the hardness of the surface while maintaining corrosion resistance, was found.

The paper investigates the effect of the glow-discharge nitriding process, with different process parameters, on the microstructure and properties of the thermally sprayed stainless steel coatings.

Research methodology

Coatings were sprayed using ø2.5 mm steel wires: austenitic X2CrNi18-9 (1.4307/304L)(C <0.03%, Si <1.0%, Mn <2.0%, Cr 17.5÷19 , 5%, Ni 8.00÷10.5%) and martensitic X46Cr13 (1.4034/4H13) (C 0.45%, Mn 0.5%, Si 0.6%, Cr 13.5%, Mo 0.5%, V 0.2%). An LD-U2 type arc spray gun manufactured by OSU-Maschinenbau was used to spray the coatings. The coatings were sprayed on two types of samples: for steel samples 42CrMo4 (1.7225/40HM) ø25 mm (for metallographic and hardness tests) and for samples made of X2CrNi18-9 steel with dimensions of 25 x 10 x 4 mm (for tribological tests). Prior to spraying, the samples were blasted using an electrocorundum with a granularity of 14 to obtain the surface cleanliness of Sa3 and the roughness of R_{y5} – 45 µm. The thermally sprayed coatings were then subjected to glow-discharge nitriding under N_2:H_2 athmosphere at a ratio of 30%:70% at the cathode potential with the following parameters: at 450 °C for 6 hours and at 530 °C for 4 hours. Before nitriding, thermally coated surfaces were grinded.

The observation of the structure of thermal sprayed coatings as well as the qualitative and quantitative analysis was performed using a HITACHI S-3500N scanning microscope equipped with an EDS X-ray spectrometer. The measurement of hardness on the surface of the coatings was made using the STRUERS DURA SCAN 70 hardness testing machine. Wear resistance due to friction was determined on the friction-wear machine A-135 of the type Amsler in accordance with the PN-82/H-04332 standard [16] in system of a plate (sample) with a thermally sprayed coating with dimensions of 25 x 10 x 4 mm and a roll (counter-sample) made of 40H tempered steel, hardness of ~30 HRC. The rotational speed of the roll was 200 rpm. The test was performed under sliding friction conditions using Lux10 oil and 20 daN load. The width and depth of traces of wear were measured with an accuracy of 0.01 mm using an optical microscope. The roughness parameters Ra and Rz of thermally sprayed grinded coatings before and after nitriding were determined by means of the TIME TR100 instrument with the measuring range Ra 0.05÷15.0 µm and Rz 0.10÷50.0 µm.

Test results

Metallographic tests

Figure 1 shows photos of microstructures of X46Cr13 and X2CrNi18-9 steel arc sprayed coatings: a, b) without nitriding; c, d) nitrided at 450 °C for 6 hours; e, f) nitrided at 530 °C for 4 hours.

The pictures show the structure typical for thermally sprayed coatings. The coatings have a compact structure and are characterized by a good connection to the substrate.

In the X46Cr13 steel coating, after nitriding at 530 °C for 4 hours, a somewhat darker surface layer with a thickness of approx. 40 µm is observed on the surface (Fig. 1e). This may indicate the presence of a nitrogen-saturated diffusion zone in the coating. The existence of this zone is confirmed by the results of qualitative and quantitative analysis performed using a scanning electron microscope equipped with EDS. The presence of nitrogen was found at a depth of approx. 50 µm (1.74% wt.) and at a depth of 5 µm – 6.78% wt. nitrogen (Fig. 2). An equally deep diffusion of nitrogen was found in the case of nitriding X2CrNi18-9 steel coatings at 530 °C for 4 hours, however, the analysis carried out in three places indicates that it is uneven.

On the other hand, low-temperature nitriding at 450 °C for 6 hours of thermally sprayed coating made of X46Cr13 steel causes nitrogen penetration to a depth of approx. 16 µm (2.92% wt.). The highest nitrogen content was found at a depth of 2.5 µm (5.03% wt.). The depth of diffusion of nitrogen into the thermally sprayed of X2CrNi18-9 steel after nitriding at 450 °C for 6 hours is lower than for X46Cr13 steel and amounts to approx. 5 µm (3.31% wt.). A very thin layer was observed on the surface of the coating, in which the nitrogen content was 5.93% wt. (Fig. 3). It is known from the literature that this is so-called S phase, created on the surface of austenitic steel during low-temperature nitriding, which is a supersaturated solution of nitrogen in the austenite network [12,15].

Hardness measurements

The analysis of results of HV0.1 hardness measurements made on the surface of thermally sprayed steel coatings X46Cr13 before and after nitriding indicates that glow-discharge nitriding greatly increases the hardness of the tested coatings (Fig. 4). The highest hardness 1165 HV0.1 was obtained after nitriding at 450 °C for 6 hours, slightly lower 1108 HV0.1 after nitriding at 530 °C for 4 hours.

Nitriding of thermally sprayed coatings from X2CrNi18-9 steel at 530 °C for 4 hours causes more than twice the increase in hardness on its surface to 1114 HV0.1, while the hardness of HV0.1 on the surface of the coating after nitriding at 450 °C for 6 hours increased only at 11%. To explain this phenomenon, an additional measurement of hardness was performed at a lower load – 10 G, it amounted to 1048 HV0.01. This testifies to the existence of a hard, but very thin layer on the surface of the coating, so-called phase S formed on the surface of austenitic steel during low-temperature nitriding. The existence of this layer is confirmed by the photos taken on the scanning microscope and analysis of the chemical composition, showing the content of nitrogen in this layer within about 6% wt.

Hardness distributions made on metallographic specimens show that only glow-discharge nitriding at 530 °C for 4 hours of heat-treated coating with X46Cr13 causes an increase in hardness not only on its surface, but also at a depth of approx. 50 µm (Fig. 5). These results coincide with the results of qualitative and quantitative EDS analysis. It was found that in this sample nitrogen penetrates to a depth of approx. 50 µm.

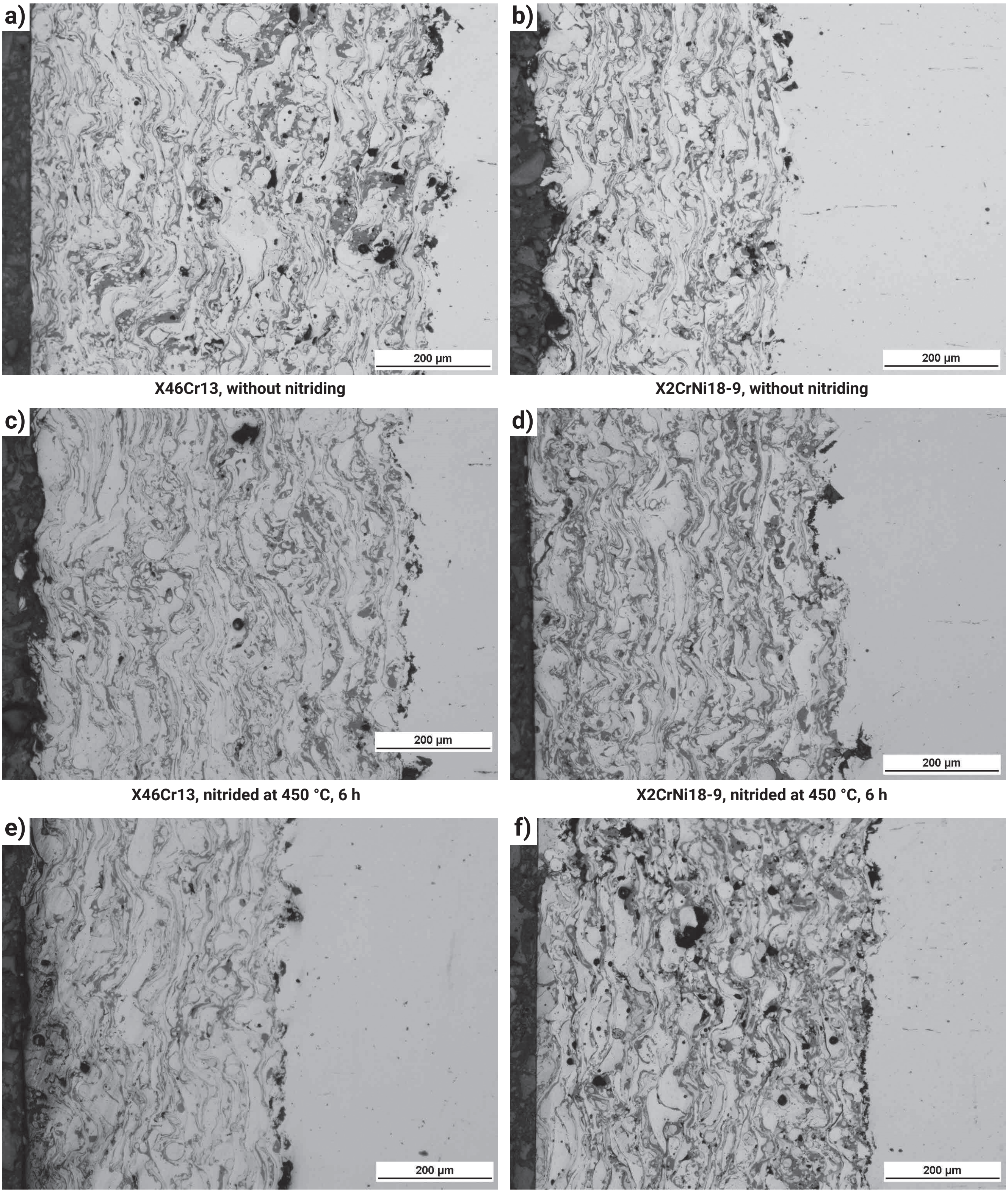
Tribological tests

The tests carried out with the Amsler A-135 wear-resistant machine showed an increase in wear resistance due to the friction of X46Cr13 and X2CrNi18-9 thermally sprayed coatings after glow-discharge nitriding. Figures 6 and 7 show the average wear value *z* (wear depth) depending on the friction time of the thermally sprayed steel coatings X46Cr13 and X2CrNi18-9 without nitriding and with nitriding.

Glow-discharge nitriding at 450 °C for 6 hours of thermally sprayed X46Cr13 steel coatings resulted in a twofold increase in wear resistance. An even better result was obtained after nitriding at 530 °C for 4 hours – a fourfold increase in wear resistance.

The thermal spray coating made of X2CrNi18-9 steel before nitriding has a higher wear resistance than the X46Cr13 steel coating before nitriding (Fig. 7). After glow-discharge nitriding, the wear resistance of the friction increases, reaching a similar value as for the X46Cr13 steel coating after nitriding. The best wear resistance of the X2CrNi18-9 steel coating was found, similar to the X46Cr13 steel sprayed coating, after nitriding at 530 °C for 4 hours.

The measurement of roughness parameters Ra and Rz indicates a slight increase in the roughness of the thermally sprayed coatings from steel X46Cr13 and X2CrNi18-9 after glow-discharge nitriding (Tab. I).



X46Cr13, without nitriding

X2CrNi18-9, without nitriding

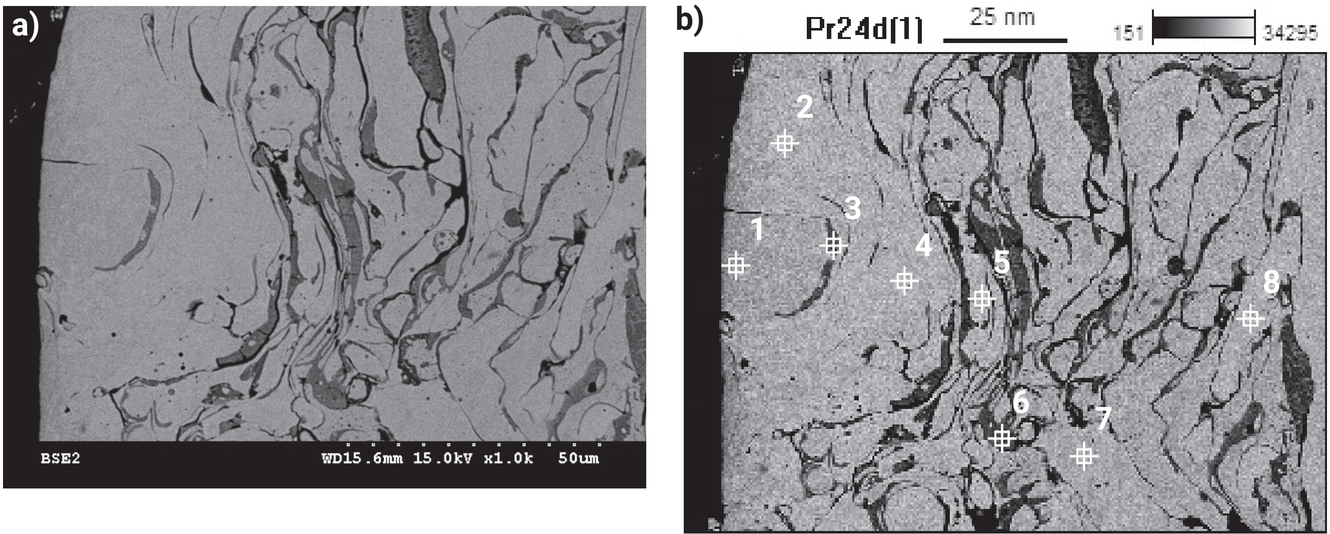
X46Cr13, nitrided at 450 °C, 6 h

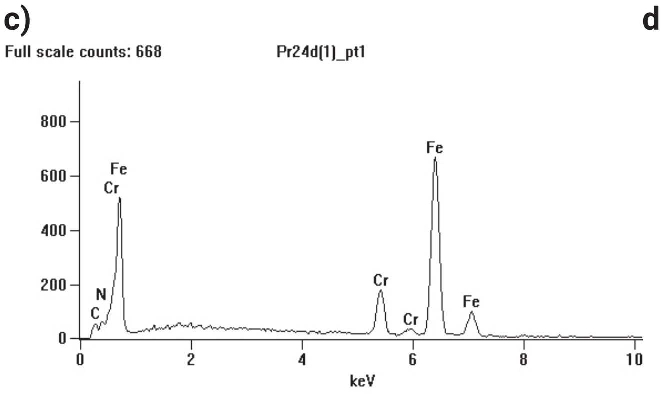
X2CrNi18-9, nitrided at 450 °C, 6 h

X46Cr13, nitrided at 530 °C, 4 h

X2CrNi18-9, nitrided at 530 °C, 4 h

Fig. 1. Microstructure of non-etched thermally sprayed coatings of X46Cr13 and X2CrNi18-9 steel on 42CrMo4 steel: a), b) without nitriding; c), d) nitrided at 450 °C, 6 h; e), f) nitrided at 530 °C, 4 h

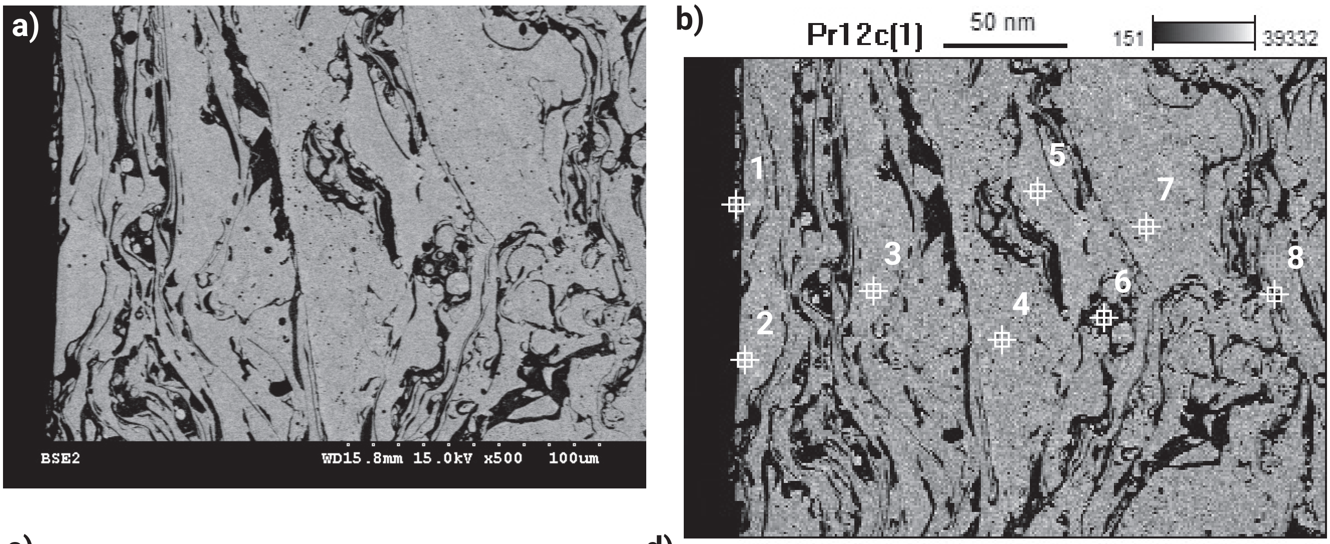


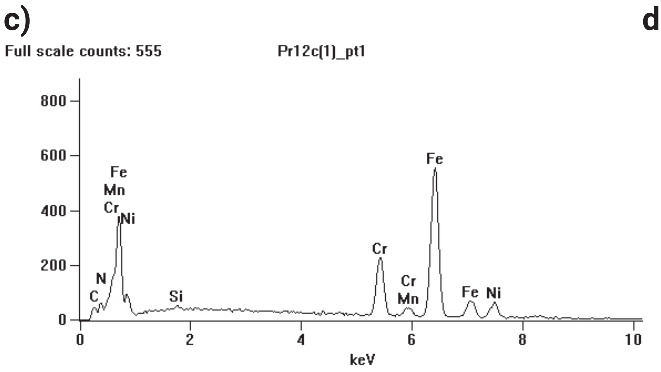


d)

	C	N	O	Si	Cr	Fe
Pr24d(1)_pt1	6,76	5,61			10,03	77,60
Pr24d(1)_pt2	10,22	2,68			11,19	75,92
Pr24d(1)_pt3	8,69		13,32		12,58	65,41
Pr24d(1)_pt4	6,94	2,50			11,88	78,68
Pr24d(1)_pt5	9,13	1,74			9,24	79,90
Pr24d(1)_pt6	8,11		14,43		22,99	54,47
Pr24d(1)_pt7	10,20				11,86	77,93
Pr24d(1)_pt8	9,94			0,27	10,89	78,91

Fig. 2. Coating sprayed of X46Cr13 steel after nitriding at 530 °C, 4 h: a) SEM images of the test sample; b) SEM images of the test sample with marking of the analyzed points; c) EDS spectrum of point 1; d) analysis of chemical composition (results of point analysis)





d)

	C	N	O	Si	Cr	Mn	Fe	Ni
Pr12c(1)_pt1	7,48	5,93		0,20	13,52	0,95	61,02	10,90
Pr12c(1)_pt2	7,12	3,31		0,16	15,93		63,36	10,12
Pr12c(1)_pt3	6,74			0,47	17,95	1,80	63,47	9,58
Pr12c(1)_pt4	10,44			0,52	18,21		62,08	8,74
Pr12c(1)_pt5	8,48			0,48	17,49	1,65	61,40	10,50
Pr12c(1)_pt6	5,20		15,94	0,26	19,00	1,27	53,96	4,38
Pr12c(1)_pt7	8,99			0,65	18,15		61,96	10,25
Pr12c(1)_pt8	6,98			0,39	18,26		64,27	10,11

Fig. 3. Coating sprayed of X2CrNi18-9 steel after nitriding at 450 °C, 6 h: a) SEM images of the test sample; b) SEM images of the test sample with marking of the analyzed points; c) EDS spectrum of point 1; d) analysis of chemical composition (results of point analysis)

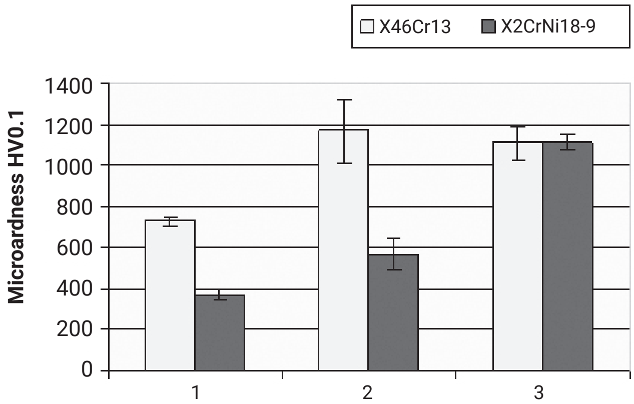


Fig. 4. Microhardness HV0.1 of coatings sprayed of X46Cr13 and X2CrNi18-9: 1 – before nitriding; 2 – after nitriding at 450 °C, 6 h; 3 – after nitriding at 530 °C, 4 h

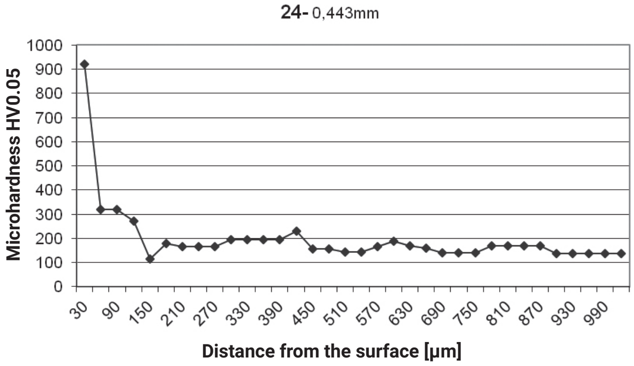


Fig. 5. Distribution of HV0.05 microhardness on a sample with thermally sprayed coating of X46Cr13 nitrided at 530 °C, 4 h

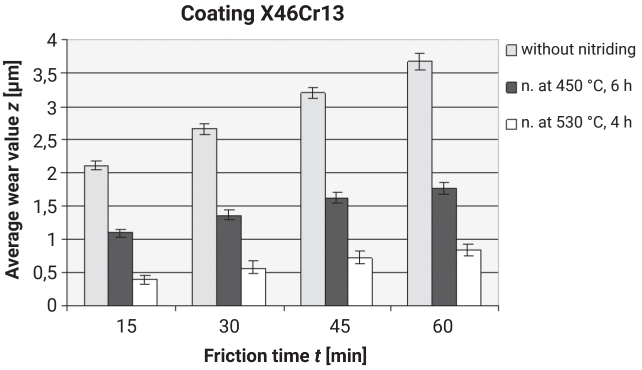


Fig. 6. Average wear value of thermally sprayed coatings made of X46Cr13 steel without nitriding and nitrided at 450 °C, 6 h and at 530 °C, 4 h depending on the time of friction

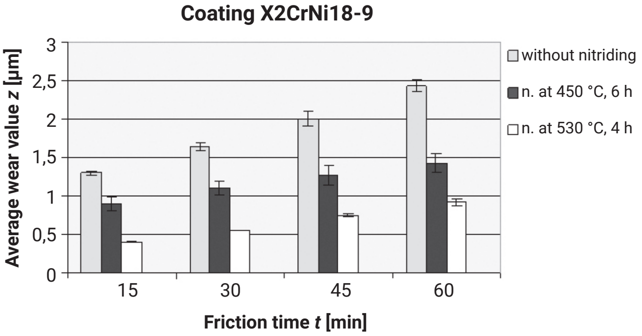


Fig. 7. Average wear value of thermally sprayed coatings made of X2CrNi18-9 steel without nitriding and nitriding at 450 °C, 6 h and at 530 °C, 4 h depending on the time of friction

Table I. Roughness parameters of thermally sprayed coatings before and after glow-discharge nitriding

Coating	Before nitriding		Nitriding at 450 °C, 6h		Nitriding at 530 °C, 4h	
	Ra [µm]	Rz [µm]	Ra [µm]	Rz [µm]	Ra [µm]	Rz [µm]
X46Cr13	0.38	2.97	0.41	3.9	0.51	4.00
X2CrNi18-9	0.43	2.83	0.47	3.80	0.46	3.46

Conclusions

1. The glow-discharge nitriding increases the hardness and wear resistance due to the friction of the X46Cr13 and X2CrNi18-9 stainless steel thermally sprayed coatings.
2. Glow-discharge nitriding at 530 °C for 4 h of thermally sprayed X46Cr13 steel coatings creates a surface diffusion layer with a thickness of approx. 50 µm, characterized by high hardness (1108 HV0.1) and very good resistance to wear due to friction. Similar hardness and wear resistance were obtained for X2CrNi18-9 sprayed coatings after glow-discharge nitriding, but diffusion of nitrogen into the coating was uneven.
3. After low-temperature glow-discharge nitriding at 450 °C for 6 hours of thermally sprayed X46Cr13 steel coatings, the surface hardness increases to 1165 HV0.1. It also increases resistance to friction wear, but it is lower than after nitriding at 530 °C for 4 hours. However, on the surface of the X2CrNi18-9 sprayed coating, a very thin, hard layer (1048 HV0.01) is created with a similar wear resistance as in the X46Cr13 steel coating.

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