

THE PROPERTIES OF HARD COATING COMPOSED OF s-PHASE OBTAINED BY PVD METHOD

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Summary

S-phase usually is obtained by low temperature (<500°C) nitriding of austenitic stainless steel. It is hard and wear resistant phase with good corrosion properties. The paper presents the results of an investigation into coatings composed of S-phase produced by reactive magnetron sputtering. The microstructure and phase composition of the layers were investigated by scanning electron microscopy, X-ray diffraction and glow discharge optical spectroscopy. Potentiodynamic corrosion tests and friction studies were used to characterize the exploitation properties of the coatings.

Keywords: reactive magnetron sputtering, austenitic stainless steel X10CrNi18-10, expanded austenite, S-phase, corrosion resistance,

Właściwości twardych powłok z fazy S wytworzonych metodą PVD

Streszczenie

Faza S tworząca się podczas niskotemperaturowego (<500°C) azotowania stali austenitycznej charakteryzuje się dużą twardością oraz dobrymi właściwościami tribologicznymi i odpornością na korozję. Przedstawiono wyniki badań właściwości powłok zbudowanych z fazy S i wytworzonych w procesie reaktywnego rozpylania magnetronowego. Badania mikrostruktury prowadzono metodami mikroskopii skaningowej. Skład fazowy ustalono metodą dyfrakcji rentgenowskiej w geometrii Bragg-Brentana oraz geometrii stałej wartości kąta padania. Określono zawartość azotu w powłokach metodą mikroanalizy rentgenowskiej (WDS) i (GD-OES) oraz właściwości korozyjne powłok metodą potencjometryczną, natomiast odporność na ścieranie metodą kulka-tarcza.

Słowa kluczowe: reaktywne rozpylanie magnetronowe, stal austenityczna X10CrNi18-10, „austenit przesycony azotem”, faza S, odporność na korozję i ścieranie

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1. Introduction

Austenitic stainless steel is a common constructional material, which thanks to its good corrosion resistance is widely applied in food and chemical industry. Its application is however limited due to relatively low mechanical properties and wear resistance. Therefore surface treatment which can offer an opportunity to improve these properties is of a big importance. Particularly promising is the so called “low temperature nitriding” which enables hard and corrosion resistant layers to be formed on the surface of austenitic stainless steel. These properties are obtained thanks to formation of nitrided layers composed of S-phase, which can be produced by both plasma [1-4] and gas [5-8] treatment. This process, however, even though it has been investigated for many years now still has very limited practical applications. The main problem which the treatment faces is high susceptibility of S-phase to decompose into chromium and iron nitrides which reduces the corrosion resistance of the layers [1, 5]. It was demonstrated that coatings composed of S-phase can be also obtained by reactive magnetron sputtering [9-11] and their composition can be easily adjusted by regulation of nitrogen content in the reactive atmosphere. Previous results [10] have shown that coatings exhibit good adhesion and mechanical properties. In the present study exploitation properties of the coatings composed of S-phase with various nitrogen contents were investigated.

2. Experimental

The investigations were conducted on coatings produced by reactive magnetron sputtering on austenitic stainless X10CrNi 18-10 steel. The samples with the diameter of 28 mm and 3 mm in thickness were ground and polished mechanically before the treatment. Before the deposition process ion sputtering was used to clean surface of the samples in the reactor chamber. The substrate temperature of 300°C was maintained during the deposition and negative bias was applied. As a reactive atmosphere a mixture of argon and nitrogen was used with various quantity of nitrogen. The set-up used in experiments was presented elsewhere [10] and the details of the process are presented in Table 1.

Table 1. Deposition parameters used in the experiments.

Coating No	Time min	Argon pressure mbar	Nitrogen pressure mbar	Power W	Temperature °C	Bias V	Target
1	15	$2,5 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	750	300	-80	Austenitic stainless steel X10CrNi18-10
2		$2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$				
3		$1 \cdot 10^{-3}$	$2 \cdot 10^{-3}$				

The nitrided layers were investigated using the following techniques:

- scanning electron microscopy (Jeol 6100) to evaluate microstructure and thickness of the coatings,
- X-ray diffraction Bragg-Brentano geometry (XRD) to investigate phase composition: Co K α , for the diffraction angles $2\theta = 20 - 120^\circ$ (X'Pert Panalytical),
- electron probe microanalysis (EPMS-WDS) and glow discharge optical emission spectroscopy (GD OES – Horiba Yvon Jobin) to measure the elements composition,
- potentiodynamic corrosion tests: measurements in 3% NaCl water solution. The exposition surface during the tests was 0,5 cm². The polarisation range was from -1200 to +2000 mV. Platinum was used as the working electrode and Hg/HgCl electrode as a reference one (NEK). For comparison the same tests were also conducted for uncovered X10CrNi18-10 steel and TiN coatings,
- pin-on-disc tests: the friction coefficient was measured in various tribological systems. The normal force was selected according to the Hertz theory not to exceed the plasticity limits of the components. The temperature during the tests was 22-24°C and humidity – 24-30%. The X10CrNi18-10 steel and TiN coating were used as reference materials. The tests parameters are presented in Table 2.

Table 2. Parameters used during the tribological tests

Counterpart material (static partner)	Counterpart radii mm	Normal force N	Sliding linear speed cm/s	Wear distance m
PE-UHMW	10	2	1	800
Al ₂ O ₃	3	0,33	3	100
X10CrNi18-10	10	1	3	100

3. Results and discussion

3.1. Microstructure and phase composition of the coatings

The detailed information concerning the phase composition of the coatings is presented elsewhere [10]. The typical diffraction patterns for the coatings are presented in Fig. 1. All the samples were composed of S-phase and no other phases were detected in the coatings. The investigation carried out in Bragg Brentano geometry shown the presence of (200) peaks only, which demonstrates strong texture. This observation suggests that the <100> direction perpendicular to the sample surface is privileged for phase growth. The peaks of ferrite which

can be also seen in the diffraction patterns originate from the substrate as a result of mechanical polishing before the treatment.

The element composition was uniform within the whole range of coatings (Fig. 2 and 3). No segregation was observed. A decrease in the content of main alloying elements (Fig. 2), which is observed within the coatings, is a consequence of nitrogen content increase in this area. Nonetheless, it is proportional for all alloying components which suggests that all these elements are transported from the target to the coatings in the proportion they have in the target (the process maintains the proportion they have in a target material). Nitrogen content in the layers depends on the nitrogen pressure in working atmosphere and was uniform within the whole layers (Fig. 3). The differences in nitrogen content are reflected in diffraction peaks position (Fig. 2). The S-phase lattice parameter increases with nitrogen content and the diffraction peaks are more shifted towards lower 2θ angles, which is in accordance with the observation made for nitrided austenitic stainless steel [1, 8].

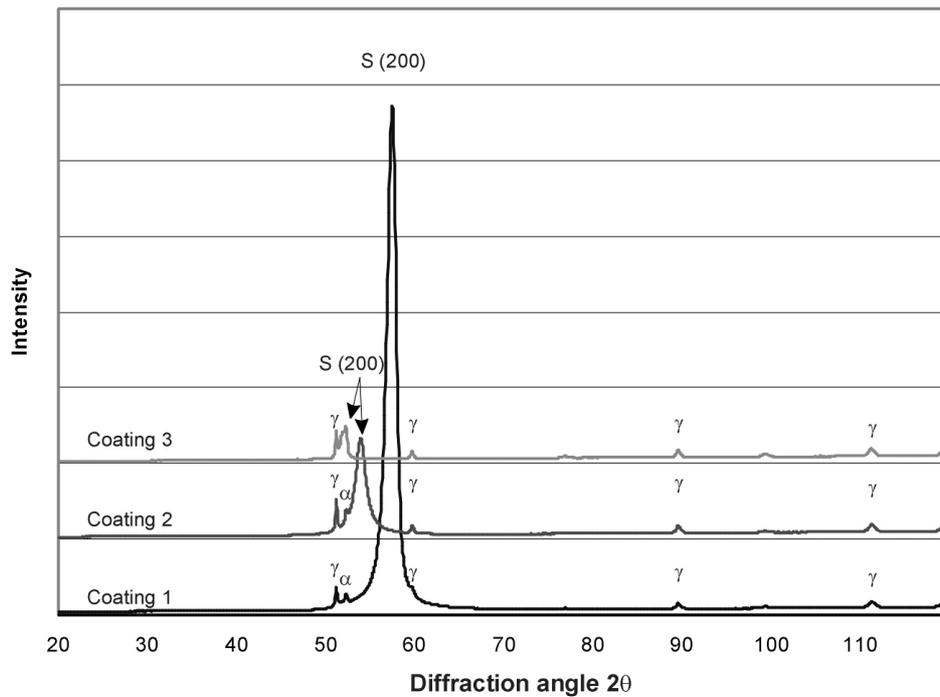


Fig. 1. X-ray diffraction patterns of the coatings: γ – austenite, α – ferrite, S – S phase

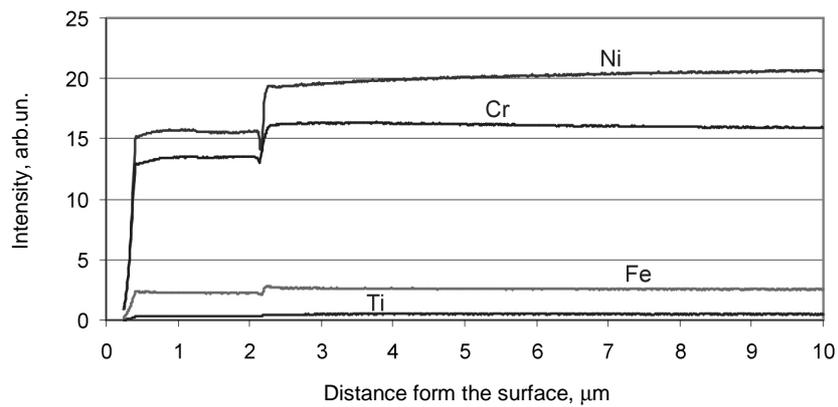


Fig. 2. Profile of alloying elements in coating 2 (GD OES)

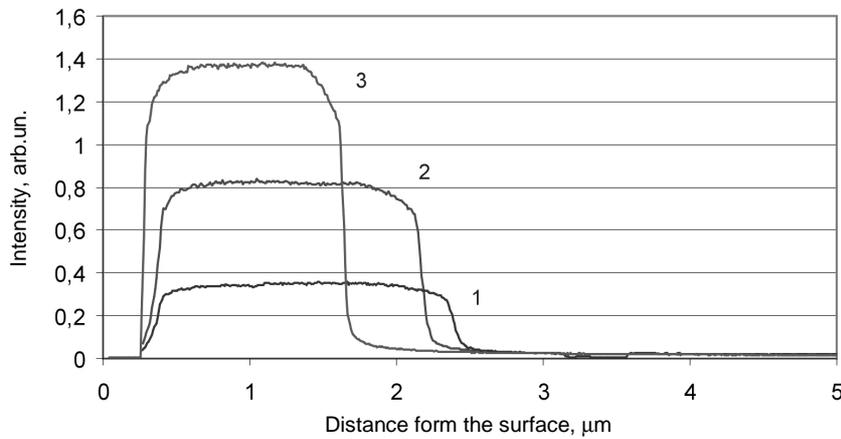


Fig. 3. Nitrogen distribution within the coating thickness; numbers correspond to coatings' numbers as in Table 1

The thickness of the coating was uniform but it varied depending on nitrogen content in the layer (nitrogen partial pressure in the working atmosphere) (Fig. 4). The higher partial pressure of nitrogen the lower rate of layer growth. This is due to the poisoning effect which nitrogen has on the stainless steel, which reduces sputtering rate of the target and in this way the deposition rate as well.

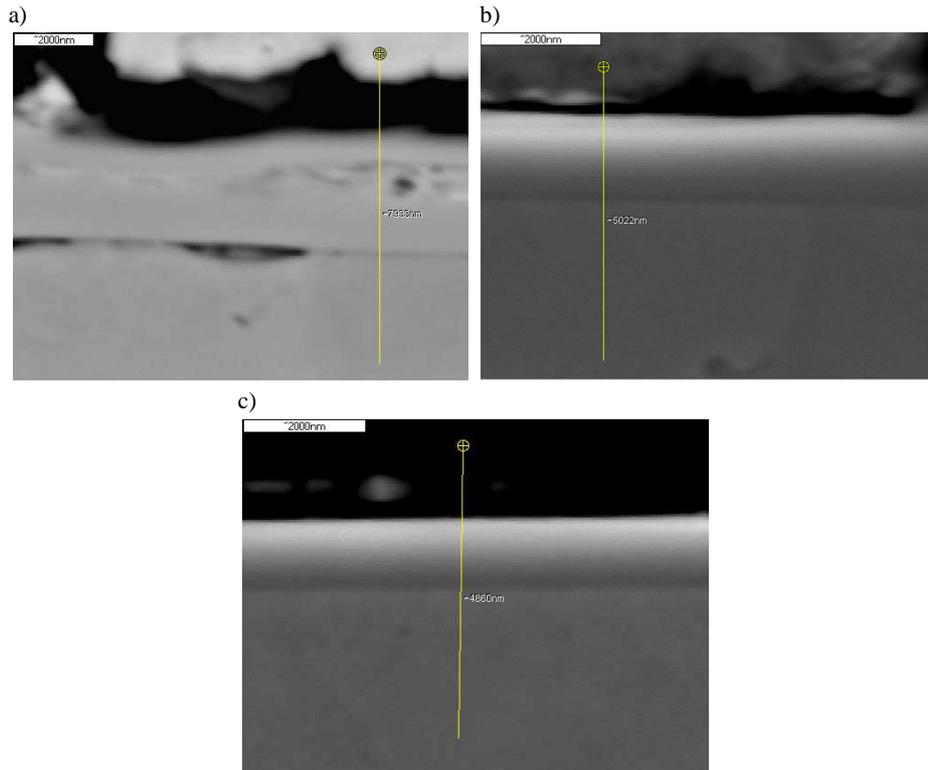


Fig. 4. SEM images of cross-sections of the coating: a) coating 1, b) coating 2, c) coating 3

3.2. Tribological characteristics of the coatings

The friction coefficients measured during tribological tests are presented in Fig. 5 for various tribological systems used in experiments. The coatings made of S-phase present very good tribological behaviour. The friction coefficients are comparable with those measured for titanium nitrides in analogous test conditions. At the same time when a pair X10CrNi18-10 steel substrate X10CrNi18-10 steel pin was investigated the tests were stopped due to the fact that friction coefficient exceeded the allowed limit after 3 m of the test ($\mu = 2$). Nitrogen content had no major effect on the friction coefficient. Only in case when X10CrNi18-10 steel was used as a counterpart a smaller friction coefficient was measured for the sample with higher nitrogen content. It is probably due to the changes in wear mechanism. When comparing the wear tracks of the coatings with the lowest and highest nitrogen content (Fig. 6a and b) the coating with lower nitrogen content demonstrates lower contribution of adhesive wear to the whole wear mechanism. Still, for all the coatings the abrasive wear is dominating. The adhesive mechanism observed for samples

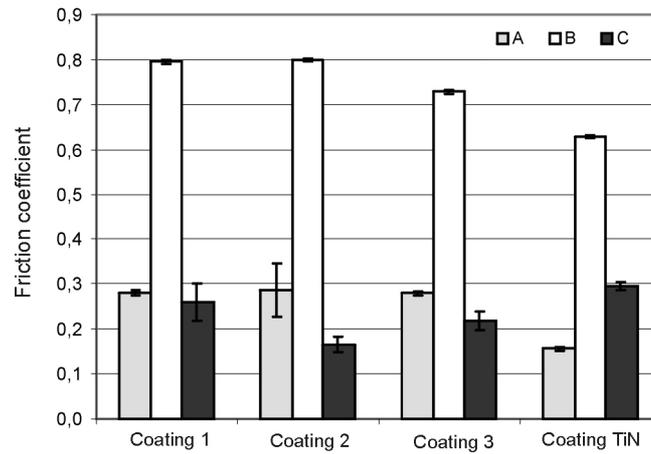


Fig. 5. Friction coefficient for coatings under investigations sliding against various pin materials: A – Al_2O_3 , B – X10CrNi18-10, C – PE-UHMW; tests parameters as in Table 2

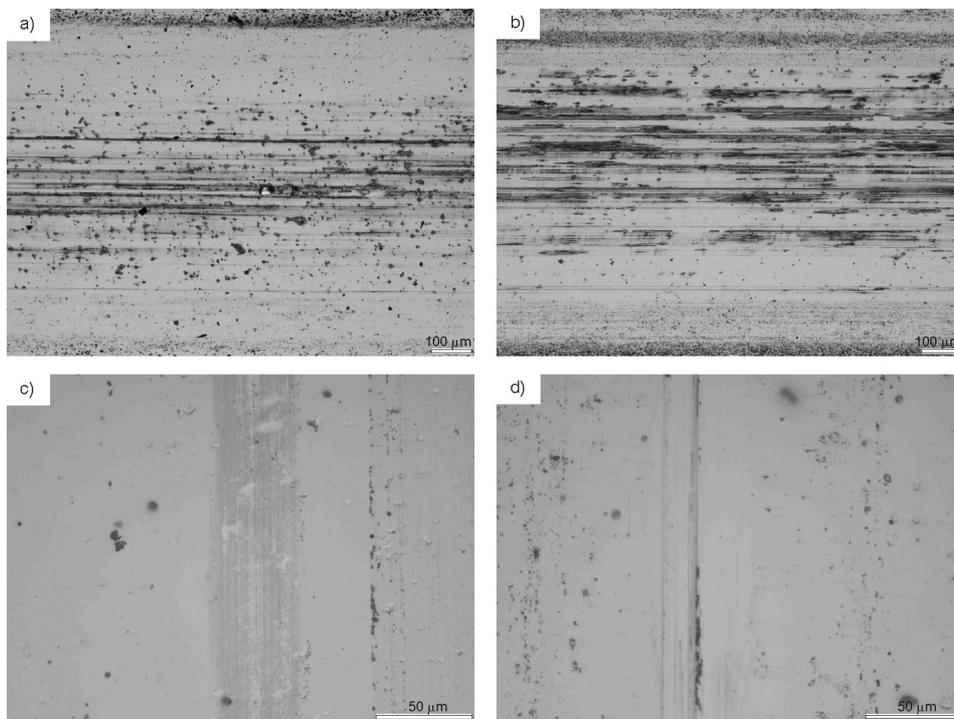


Fig. 6. Wear tracks after tribological tests for various tribological systems used in the experiments: a) coating 3 against pin of X10CrNi18-10 steel, b) coating 1 against pin of X10CrNi18-10, c) coating 3 against pin of Al_2O_3 , d) coating 1 against pin of Al_2O_3

with lower nitrogen content can be a result of higher similarity in lattice parameters between austenite and S-phase with lower nitrogen content.

In sliding tests against ceramic pins only the abrasive mechanism was observed and the wear track was very weak (Fig. 6c and d). The friction coefficient measured for S-phase coatings was slightly higher than for TiN but it did not depend on nitrogen content. S-phase coatings demonstrate significantly lower friction coefficient than TiN coatings in tribological tests conducted against PE-UHMW. In that case no mechanical changes were observed within the wear tracks.

3.3. Corrosion properties of the coatings

The potentiodynamic curves measured for investigated coatings are presented in Fig. 7. To characterize the corrosion properties of the coatings the basics parameters were estimated and compared with non-treated X10CrNi18-10 steel and TiN coatings. They are presented in Table 3.

Table 3. Corrosion parameters for the investigated materials

Corrosion parameters	Austenitic stainless steel X10CrNi18-10	Coating 1	Coating 2	Coating 3	TiN Coating
E_{kor} , mV	-996	-561	-509	-948	-440
E_{pit} , mV	+300	+1240	+955	+1220	+1205
i_{pas} , mA/cm ²	0,027	0,0028	0,0025	0,0097	0,0014

After having analysed the results obtained it can be stated that coatings composed of S-phase have very good corrosion properties in comparison to reference materials. Corrosion potentials of these coatings were more positive in values than those measured for austenitic stainless steel and comparable with the ones measured for titanium nitrides. All these coating have also high pitting potentials comparable with those for titanium nitrides and much higher than for non-treated austenitic stainless steel. The range of passive area of these coatings was very big and characterised by current density much lower than the one measured in analogous area for X10CrNi18-10 steel (10 times less for coating 1 and 2 and 3 times less for coating 3) and only two times higher than that of titanium nitrides coating.

The analysis of the damage on the surfaces after corrosion tests confirmed the observations made on polarisation curves. The surfaces of non-nitrided X10CrNi18-10 steel was covered with numerous pits while on the surface of the S-phase coatings only individual pits can be detected (Fig. 8). Their quantity and size slightly depended on nitrogen content in the layers. They were bigger for lower nitrogen content in the layers but their number increased with nitrogen content.

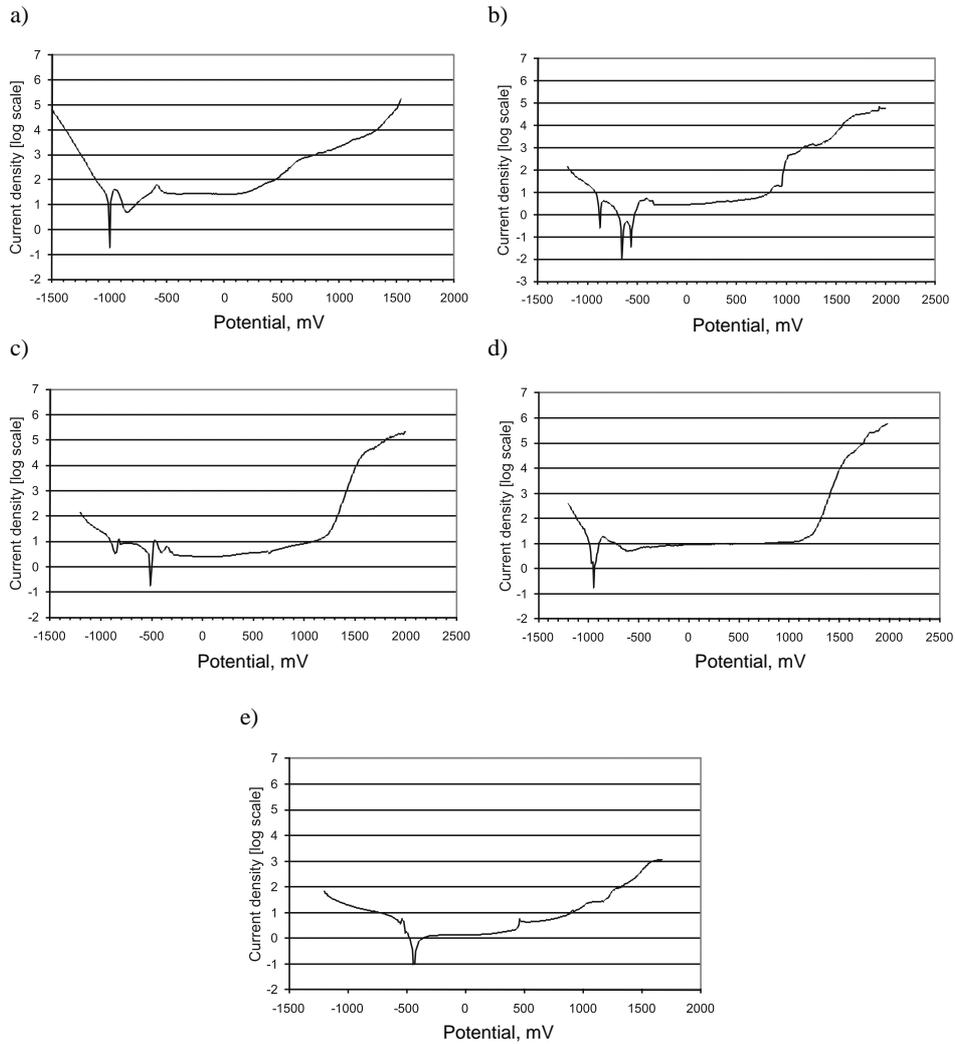


Fig. 7. Potentiodynamic curves: a) X10CrNi18-10 steel, b) coating 1, c) coating 2, d) coating 3, e) TiN coating

Comparing corrosion behaviour of coatings made of S-phase with the layers produced on X10CrNi18-10 steel by gas nitriding it has to be concluded that the latter have worse corrosion resistance. Moreover in this case an increase of nitrogen content usually led to lower corrosion resistance due to chromium or/and iron nitrides precipitation. In the coatings produced by magnetron sputtering which were investigated in present work even if nitrogen content in

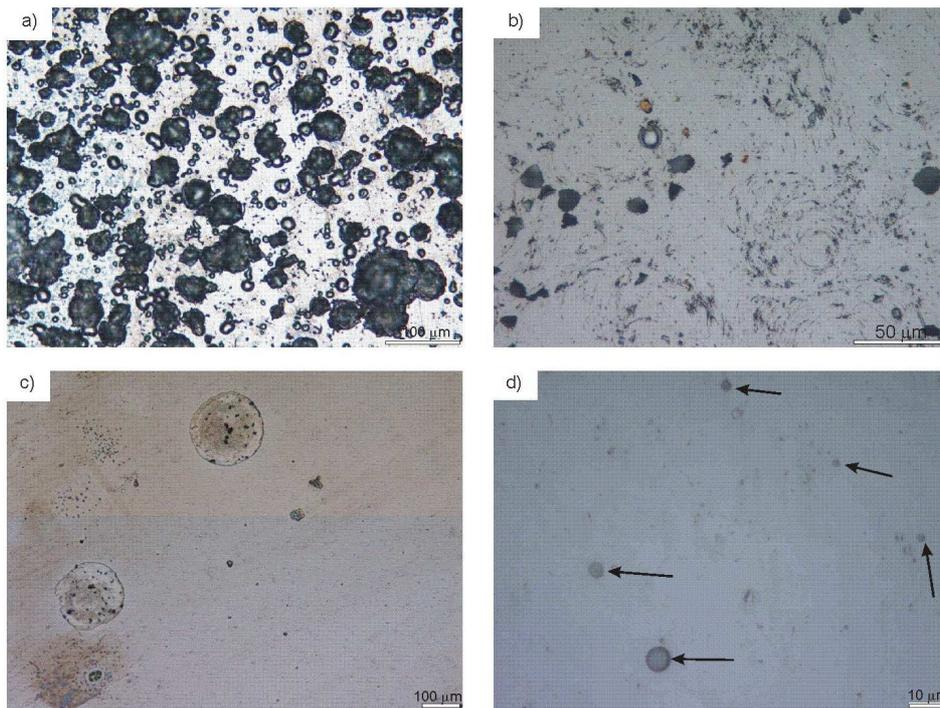


Fig. 8. Surface of the coatings after corrosion tests: a) X10CrNi18-10 steel, b) coating 1, c) coating 2, d) coating 3

the coating was very high nitrides precipitation was not observed. It can be due to a low temperature and short treatment time. In this case it can be observed that an increase of nitrogen content in the layer can improve its corrosion resistance. This phenomenon can be explained by the positive effect nitrogen has on pitting corrosion due to the increase of pH of the solution within the pits [12]. This observation can also explain smaller size of the pits observed for coating with the highest nitrogen content (coating 3).

4. Conclusions

1. Coatings composed of S-phase obtained by reactive magnetron sputtering are characterized by uniform thickness and chemical composition.
2. Deposition of S-phase coatings significantly improves tribological properties of X10CrNi18-10 steel and has beneficial effect on its corrosion behaviour. These coatings exhibit exploitation properties comparable with those demonstrated by titanium nitride coatings.

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