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Structure and properties of surface layers of selected constructional steels after sulfonitriding

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ABSTRACT

Purpose: The main aim of the paper was to investigate the structure and properties of the surface layers of the C45, 42CrS4, 42CrMoS4 steels after sulfonitriding at a temperature of 540 and 570°C. The thickness of zones occurring in the sulphonitric layer was defined just as their chemical and phase composition and microhardness. Moreover, abrasion resistance in the zones of sulfonitrided layers was investigated.

Design/methodology/approach: The following experimental techniques were used: light microscopy (LM), scanning electron microscopy (SEM), X-ray diffraction (XRD) method, Vickers microhardness, abrasion tests.

Findings: Changes of microhardness in the zones of sulfonitrided layers have been presented. It has been stated that the surface layers of steels C45, 41CrS4 and 42CrMoS4 after gas sulfonitriding at 570°C are composed of four zones which are: external zone of sulfides with grain-like structure, zone of nitride phases with compound structure and with round sulfides precipitates, zone of nitride phases with diversified structure depending on chemical composition of the steel base of hardness 262 HV for steel 41CrS4 and 330 HV for steel 42CrMoS4, zone of nitride phases in the form of elongated precipitates in matrix of C45 steel or diffusion zone of micro-hardness 500-700 HV at the distance of 100-110 μm from the surface of 41CrS4 and 42CrMoS4 steels.

Research limitations/implications: Impossibility of microhardness measurement in the external zone of the sulfonitrided layer.

Practical implications: Sulfonitriding is a process of termochemical treatment used for vehicle and device parts on a large scale.

Originality/value: Varied morphology of zones of the upper layers revealed by the method of scanning electron microscopy.

Keywords: Metallic alloys; Sulfonitrided layer; Microhardness; Abrasion resistance

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MATERIALS

1. Introduction

The necessity of reducing the adhesive forces of mating elements of machinery exploited in dry and mixed friction conditions is a base for elaborating many thermochemical and surface treatment operations [1-14]. The effect of these operations is to obtain upper layers with a low friction factor, elevated seizing resistance and adhesive wear. Among the layers which are characterized by such properties, composed antyadhesin layers, produced by adding ammonia to the atmosphere in process of nitriding oxygen, sulphur, phosphorus or their compounds have the largest practical application in the industry [7-10]. Methods of thermochemical treatment consist of simultaneous enrichement of steel and cast iron surfaces with nitrogen and sulphur in sulfonitriding processes [6,9].

The composed structure of sulfonitrided layers (Fig. 1) diminishes the adhesion affinity of the mating elements and resistance to shearing of irregularity of the surface. It also assures elevated hardness of the surface layer, which enables the transfer of pressure in the contact zone. The hardness of surface layers is limited to nitride compounds zone ε, $\varepsilon + \gamma'$, γ' (Fig. 1a) and does not exceed 700 HV for carbon steel and grey, plain cast iron. Therefore sulfonitrided layers on kinds of carbon steel and grey cast iron are used for elements that are loaded with small or medium surface pressure, so for cylinder liners of combustion engines, slide guides, permanent moulds and injection moulds, etc. Sulfonitrided layers on kinds of alloy steel (Fig. 1b) are characterized by hardness that comes to 1300 HV in the nitride compounds zone and from 1200 HV to 1500 HV in internal nitriding zone [14]. Thus those layers find use in parts working in conditions of big axial and punctual thrust in cam mechanisms and gears.

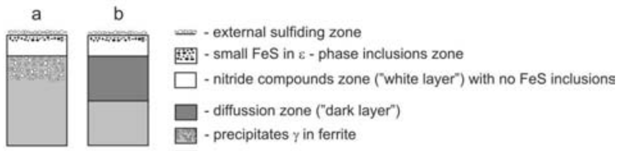

Fig. 1. Structure flowchart of surface layer on the parts after gas sulfonitriding: a - carbon steel and grey plain cast iron, b - alloy steel and alloy cast iron including nitrogen-forming elements [10]

2. Experiments

The research was carried out with unalloyed steel C45 and constructional steels 41CrS4 and 42CrMoS4, which are used to produce device elements whose AA' and BB' surfaces are exposed to seizing in exploitation conditions - Figs. 2, 3. The technology of mating parts of the flange and the shaft contains processes of heat treatment and thermochemical treatment after machining operations.

During the manufacturing process of heat and thermochemical treatment of the flange and its mating element, quenching and tempering is conducted as well as diffusion saturation of their surfaces (A, B) with nitrogen and sulphur in sulfonitriding process to elevate their seizing resistance and abrasion.

The chemical composition of steel taking part in the research was defined spectrometrically and the results are presented in Table 1.

Test pieces of dimensions: 25x35x75 mm were the material for the research. They were treated in the process of quenching and tempering and the process of gas sulfonitriding. Test pieces were hardened in water from temperature of austenitizing 850˚C in the time of 25 minutes and tempered at a temperature of 570˚C in the time of 1.5 h with air cooling.

Heating, hardening and tempering were realized in electric box-type furnaces with forced convection of argon atmosphere.

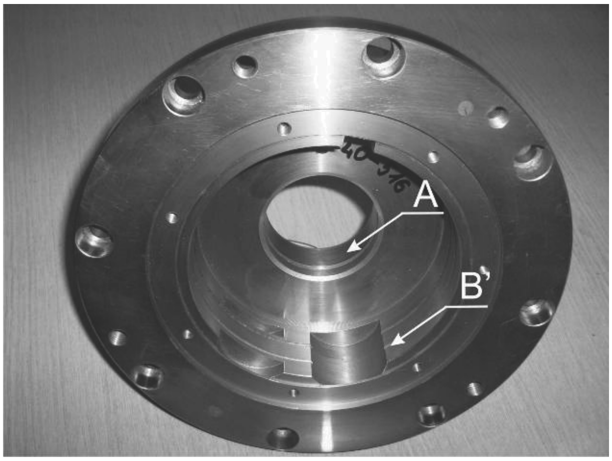

Fig. 2. A view of the flange; A - sulfonitrided surface, B' - the surface mating with the roll part B from Fig. 3

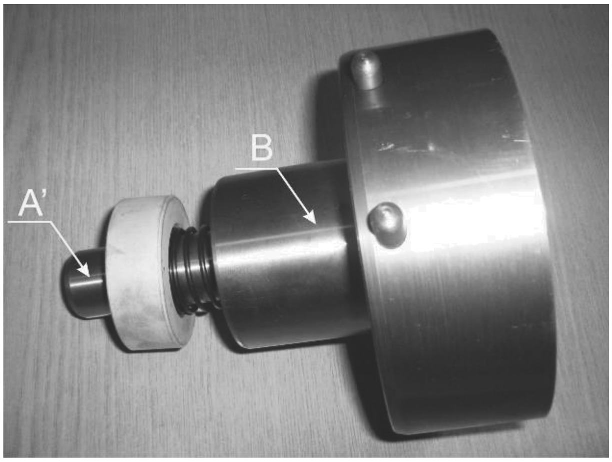

Fig. 3. A view of mating element of the flange; B - sulfonitrided surface, A' - the surface mating with the hole - surface A from Fig. 2

Afterwards, the test pieces were treated by gas sulfonitriding in electric resistance furnace, which was a part of stand equipment for thermochemical treatment - its diagram is presented in Fig. 4. The operation of sulfonitriding steel taking part in the research was realized at a temperature of 540 and 570˚C in the time of 8 h.

Table 1.
Chemical composition according to the analysis of examined kinds of steel

Steel	Mass concentration of elements, %								
names	C	Mn	Si	P	S	Cr	Ni	Al	Mn
C45	0.40	0.66	0.22	0.011	0.001	0.16	0.11	0.017	0.036
41CrS4	0.38	0.81	0.24	0.011	0.007	1.05	0.06	0.019	0.012
42CrMoS4	0.40	0.80	0.31	0.014	0.009	1.05	0.03	0.024	0.181

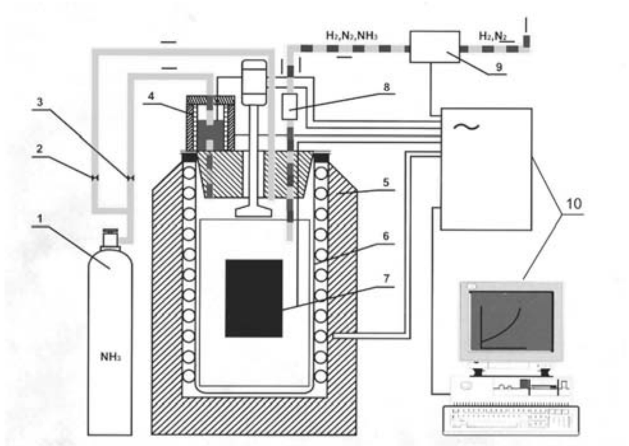

Fig. 4. A diagram of gas sulfonitriding stand: 1 - bottle of ammonia, 2 and 3 - valves regulating intensity of ammonia flow, 4 - tank of liquid sulphur, 5 - furnace, 6 - retort, 7 - sulfonitrided details, 8 - tank, 9 - control meter of ammonia dissociation degree, 10 - registration of parameters of the process [17]

Metallographic researches of the steel structure after quenching and tempering and of sulfonitrided layers diffusively applied in thermochemical treatment were made employing the light microscope LEICA MEF 4A with 1000x magnification.

Observations were carried out on crosswise metalographic specimens. Their surface was prepared for the examination by mechanical grinding and polishing with diamond pastes on the machine of STRUERS.

Observations of the structures of the examined steels after quenching and tempering were carried out on metallographic specimens that were etched by 5% solution of nitric acid in alcohol and the structures of sulfonitrided layers were observed after etching with a reagent on the basis of potassium dichromate. The time of etching was defined experimentally for several kinds of steel and conditions of thermochemical treatment.

The thickness of each zone in sulfonitrided layers was measured on etched metallographic specimens employing the scanning electron microscope SUPRA 25 , produced by ZEISS, with voltage of 20 kV and 5000x magnification.

The chemical composition of micro-areas in zones in sulfonitrided layers was fixed by means of the point - by - point method, using a scattered X - radiation detector (EDS) produced by EDAX, which is a part of scanning electron microscope equipment.

X-ray qualitative phase analysis of sulfonitrided layer on the C45 steel was carried out on diffractometer X- Pert PRO Panalytical, using a lamp with cobalt anode supplied with voltage of 30 kV and filament current of 10 mA in angular range of 2θ, from 30 to 110˚. In the examination a step method was applied, where the length of the measurement step was 0,05˚ of 2θ angle and the time of counting in measurement point was 10 s. On the basis of Bragg's equation the values of interplanar distances d_{hkl} were computed and the intensity of peaks on diffraction patterns was estimated. That allowed to identify phases appearing in the sulfonitrided layer. X-ray research was conducted on a sample cut at an angle of 45˚ to the sulfonitrided surface. The surface of the sample was prepared like the metallographic specimens for the microscopic examination.

Hardness measurements of examined steels after quenching and tempering were conducted by Rockwell's method in the scale C [15].

Micro-hardness research of the sulfonitrided layers of the steel 41CrS4 and 42CrMoS4 was carried out on a microhardness tester FUTURE - TECH FM - 700 with load of 0.098N (10G) [16]. Measurements were made using metallographic specimens.

Abrasion research of the examined steel after sulfonitriding was carried out using specimens of the dimensions: 25x35x75 [mm] and employing an appliance constructed according to the guideline of the standard ASTM G 65-00. Abrasion of the specimens was effectuated in the time of 15 minutes, with a fixed load of 130 N. The rotational speed of the wheel (ø 250 mm, 25 mm thick) mating with the examined material was 200 rotations per minute and the flow rate of the abrasive was 500 g/min. The abrasive was silicon oxid SiO_2 of 220 μm granularity. Abrasion resistance was defined by the mass loss of the examined specimen before and after the wear test. Specimens were weighed on a laboratory balance with ±0.001 g measuring accuracy.

3. Results and discussion

As a result of metallographic observations it has been stated that the examined steels after quenching and tempering is characterized by a structure of small, coagulated carbides in ferritic matrix, defined by high-tempered martensite of hardness between 30 - 34 HRC - Fig. 5.

The upper layer of steel C45, 41CrS4, 42CrMoS4 after sulfonitriding in the thermochemical treatment process has a structure of four zones sedimented in layers, with visibly marked boundaries - Fig. 6 - 10. In those layers we can distinguish successive zones (from the external surface): first zone of external sulfiding, second zone - of sulfides releases in nitride phase ε ($Fe_2(N,C)$), third zone - of nitride phases without sulphur compounds, fourth zone - diffusion zone with nitrides γ' (Fe_4N). Nitrides γ' were observed in this zone in the form of dark, elongated precipitates - Fig. 8 [11, 14].

Phases in C45 steel appearing after sulfonitriding in temperature of 570˚C were defined on the basis of results of X-ray

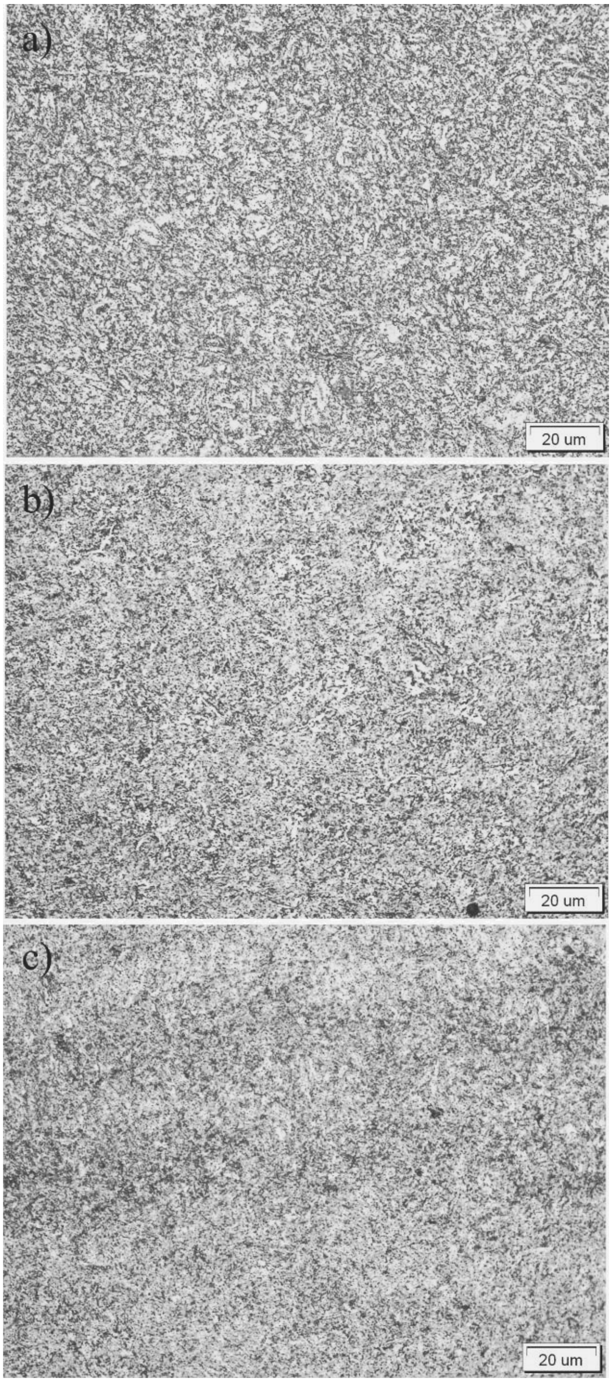

Fig. 5. High - tempered martensite in the structure of steel C45 (a), 41CrS4 (b), 42CrMoS4 (c) after quenching and tempering ($T_{austenitizing}$ = 850˚C, $T_{tempering}$ = 580˚C)

qualitative phase analysis. The identified phases on the peaks come from the planes (110) (200) (211) Feα, planes (112) (114) (116) FeS, (002) (022) (221) Fe_2N, (111) (200) (220) (311) Fe_4N and (112) (022) (230) Fe_3C

The morphology of the zones in the surface layers is diverse and depends on the chemical composition of the examined steel well as on the sulfonitriding temperature. Several zones of the surface layer are characterized by a thickness that is bigger for the alloy steels: 41CrS4, 42CrMoS4 and smaller for steel C45 -Table 2, Figs. 6 - 10.

Table 2.
Thickness of zones in layers of steels C45, 41CrS4, 42CrMoS4 after sulfonitriding in temperature of 570°C.

Number of zone	Type of zone	Thickness of zone [μm]		
		Steel names		
		C45	41CrS4	42CrMoS4
1	external zone of sulfides	1.7-3.2	2.4-3.7	4.0-8.8
2	zone of nitride phases with FeS precipitates	6.7-7.4	4.2-5.6	8.1-9.2
3	zone of nitrides without FeS precipitates	0.5-1.2	8.6-11.2	8.8-9.6
4	diffusion zone	~60	~100	~110

The thickness of the zones grows with the increase of the sulfonitriding temperature. The thickness of several zones in steel C45 after sulfonitriding at a temperature of 570°C is: 1.7-3.2 μm for external sulfiding zone, 6.7-7.4 μm for second zone - of sulfides in nitrides area and 0.5-1.2 μm for the third zone - of nitride phases without sulfides, whereas the thickness of several zones in steel 41CrS4 is: 2.4-3.7 μm for first zone, 4.2-5.6 μm for second zone and 8.6-11.2 μm. Zones in surface layer of steel 42CrMoS4 are characterized by a larger thickness than of steel C45 and 41CrS4. The thickness of several zones in steel 42CrMoS4 is: 4.0-8.8 μm for external sulfides zone, 8.1-9.2 μm for zone of nitride phases with sulfides precipitates and 8.8-9.6 μm for nitrides zone without sulfides. The thickness of the diffusion zone in steel 41CrS4 and 42CrMoS4 is similar and amounts to 100 and 110 μm, while in steel C45 it is about 60 μm. The external sulfiding zone of the surface layers is characterized by a granular structure - Figs. 8-10. Local micro-analysis of chemical composition in this zone indicates the occurrence of sulphur and other elements that are a part of the examined steel - Figs. 8a, 9a, 10a.

Brightly etched nitrogen compounds (ε) with small round sulfide precipitates of dark tinge were observed in the second zone - Figs. 8-10. Results of local micro-analysis in this area show the presence of N, S and other elements being a part of the examined steels - Figs. 8b, 9b, 10b. The third zone of nitrides without sulfide precipitates occurring in alloy steels has a composite structure that undergoes inhomogeneous etching -Figs. 9, 10. On the basis of local micro-analysis results it may be stated that in this zone, nitrogen with Fe, Mn, Cr (Fig. 9c) occurs in steel 41CrS4. Nitrogen and Fe, Mn, Cr, Mo occur in steel 42CrMoS4 (Fig. 10). The presence of Fe, Mn, Cr and Mo in this zone indicates the occurrence of composite nitrides of elements that are

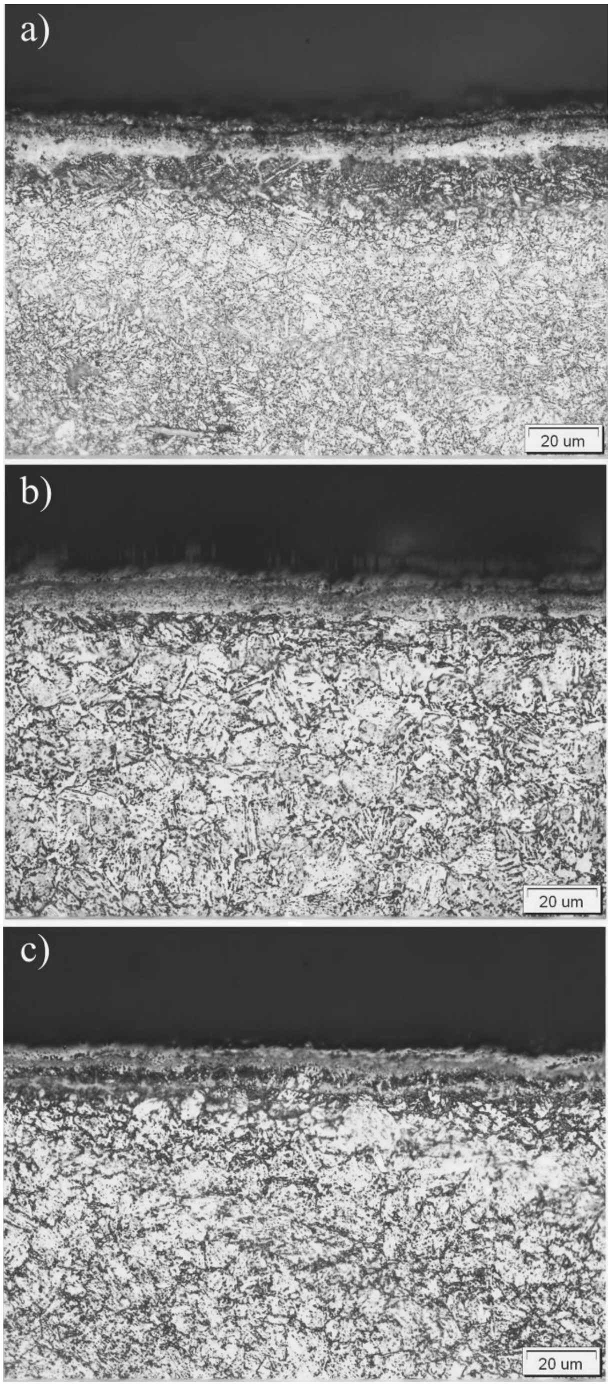

Fig. 6. Surface layer and structure of examined steel after sulfonitriding in temperature of 540°C; a - steel C45, b - steel 41CrS4, c - steel 42CrMoS4

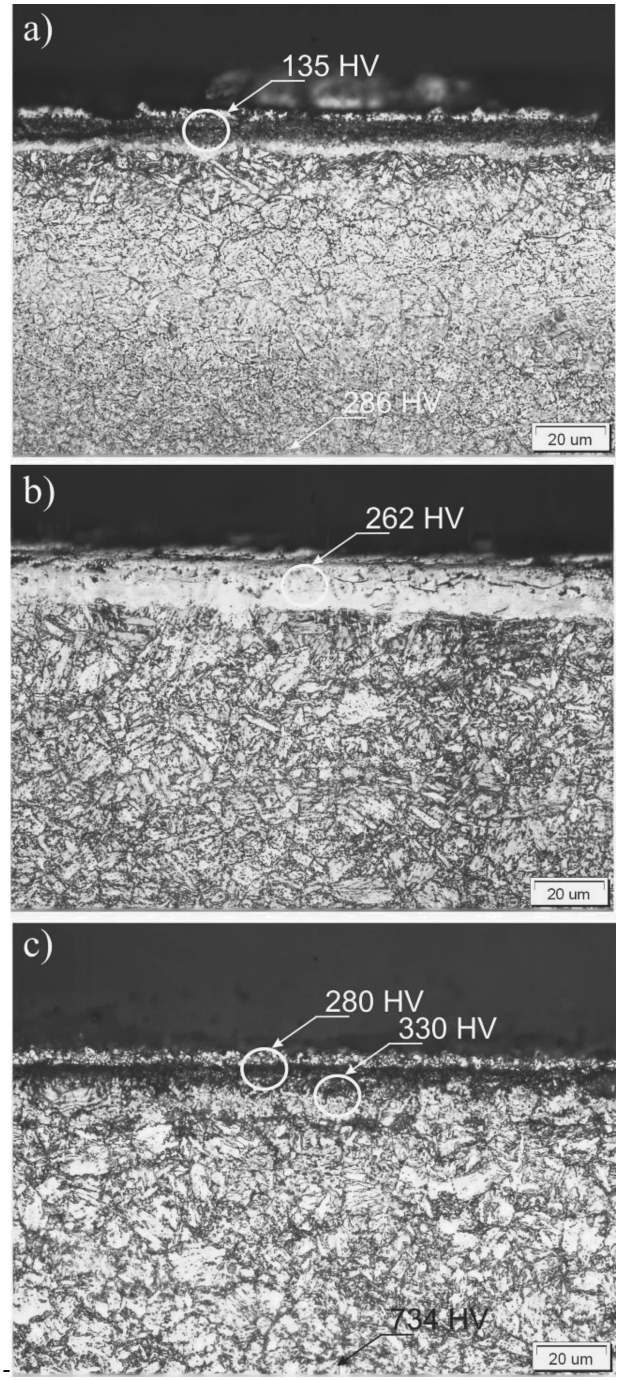

Fig. 7. Surface layer and structure of examined steel after sulfonitriding in temperature of 570°C; a - steel C45, b - steel 41CrS4, c - steel 42CrMoS4

a part of the analysed steel. Because of the small thickness of the first - external sulfiding zone the micro - hardness in this area was not measured. Micro-hardness measurements were taken in the second, third and diffusion zone, using specimens of the examined

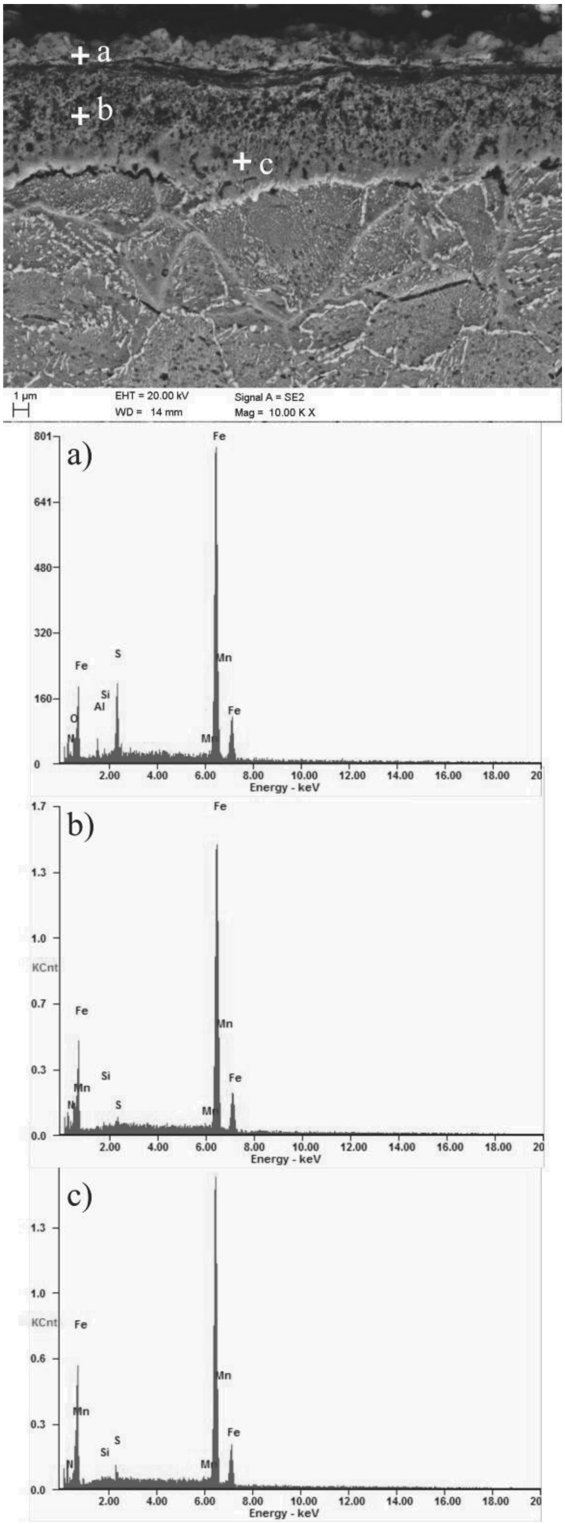

Fig. 8. Microstructure of steel C45 after sulfonitriding in temperature of 570°C and the results of chemical micro-analysis in: first zone (a), second zone (b), third zone (c) (SEM)

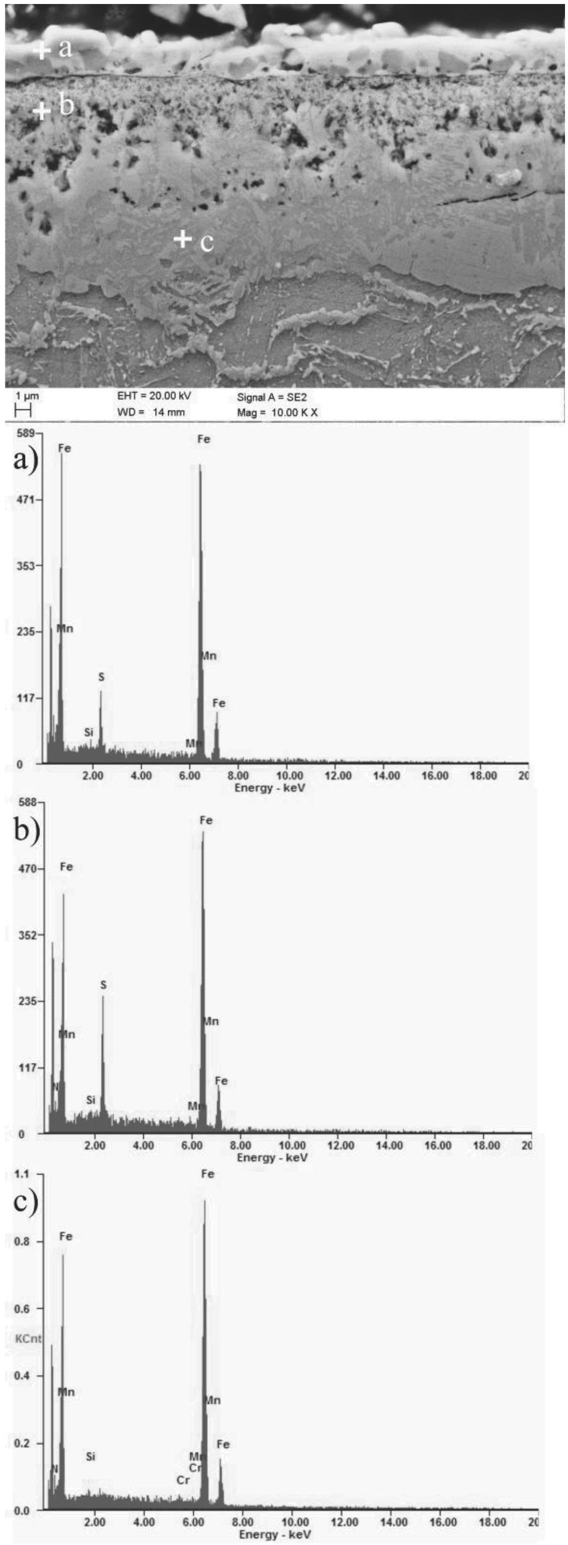

Fig. 9. Microstructure of steel 41CrS4 after sulfonitriding in temperature of 570°C and the results of chemical micro-analysis in: first zone (a), second zone (b), third zone (c) (SEM)

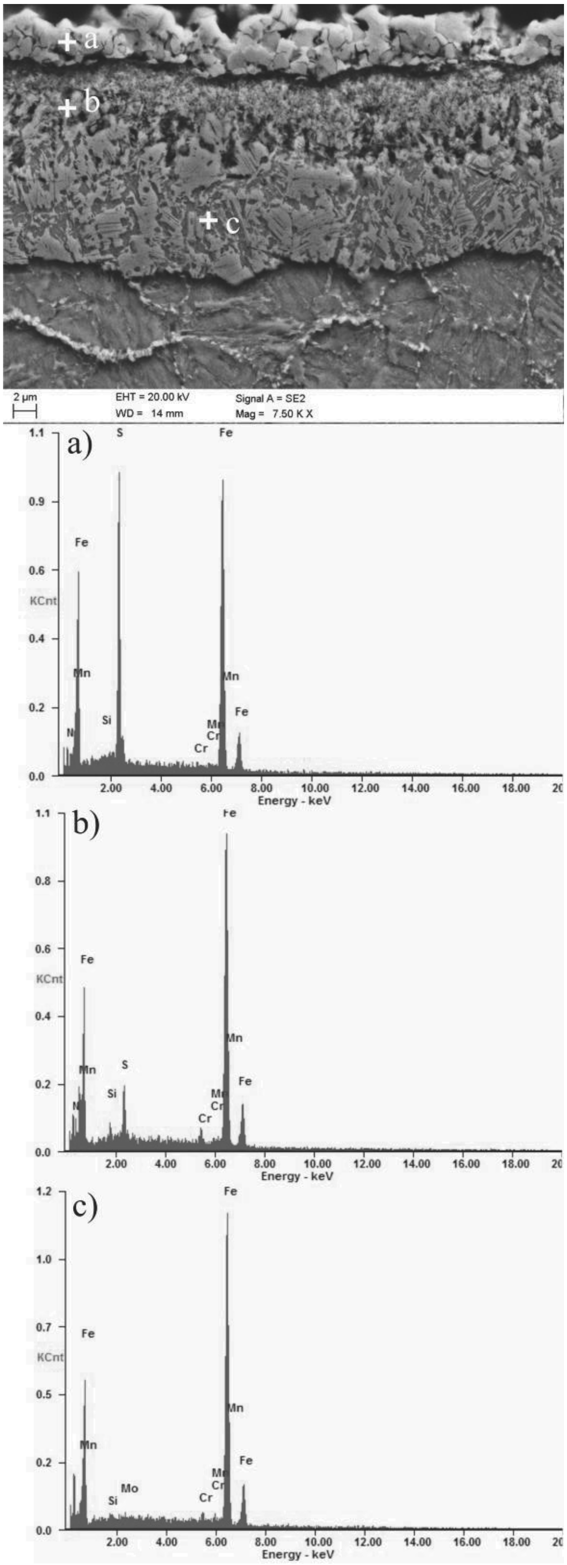

Fig. 10. Microstructure of steel 42CrMoS4 after sulfonitriding in temperature of 570°C and the results of chemical micro-analysis in: first zone (a), second zone (b), third zone (c) (SEM)

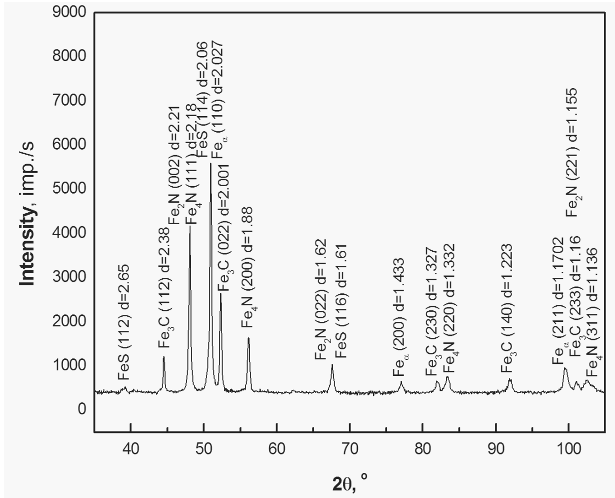

Fig. 11. Diffraction pattern of steel C45 after sulfonitriding in temperature of 570°C

steel after sulfonitriding at a temperature of 570°C. The value of micro-hardness measured at the boundary of the external sulfiding zone and the zone of nitride phases with sulfide precipitates is about 135 HV in steel C45. Micro-hardness amounts to 416 HV at the distance of 50 μm from the surface of the steel and at the distance of 100 μm - 286 HV - Fig. 7a. - The results of micro-hardness measurements of several zones of steels 41CrS4 and 42CrMoS4 have been shown in Fig. 7b, c. The micro-hardness of steel 41CrS4 is 262 HV in the zone of phases free from sulfide precipitates and at the distance of 50 and 100 μm it amounts to 617 and 453 HV - Fig. 7b. Micro-hardness measured in the second zone of the surface layer of steel 42CrMoS4 is 280 HV and in the third zone - 330 HV. At the distance of 110 μm from the specimen surface, micro-hardness amounts to 734 HV - Fig. 7c.

The morphology and the properties of the surface layers influence considerably the abrasion wear resistance of the examined steel. The results of abrasion tests are presented in Table 3. The maximum mass decrement in the abrasion test is noticed in steel after sulfonitriding at a temperature of 540°C. The mass decrement of steel C45 is 0.168 g, for steel 41CrS4 is 0.148 g and of steel 42CrMoS4 is 0.121 g. After sulfonitriding at a temperature of 570°C steel 42CrMoS4 is characterized by a minimum mass decrement of only 0.090 g; on the contrary, steel C45 is characterized by a maximum mass decrement amounting to 0.132 g - Table 3.

Table 3.
Results of abrasion tests of steels C45, 41CrS4, 42CrMoS4 after sulfonitriding in temperatures of 540°C and 570°C

Temperature of sulfonitriding [°C]	Mass decrement [g] Steel names C45	41CrS4	42CrMoS4
540	0.168	0.148	0.121
570	0.132	0.092	0.090

4. Conclusions

On the basis of metallographic research it has been stated that the surface layers of steels C45, 41CrS4 and 42CrMoS4 after gas sulfonitriding at 570°C are composed of four zones which are:

- external zone of sulfides with grain-like structure,
- zone of nitride phases with compound structure and with round sulfides precipitates,
- zone of nitride phases with diversified structure depending on chemical composition of the steel matrix of hardness 262 HV for steel 41CrS4 and 330 HV for steel 42CrMoS4,
- zone of nitride phases in the form of elongated precipitates in matrix of C45 steel or diffusion zone of micro-hardness 500-700 HV at the distance of 100-110 μm from the surface of 41CrS4 and 42CrMoS4 steels.

X-ray research allowed to identify phases occurring in specimens of steel C45. Peaks appearing in the diffraction pattern indicate the presence of Feα , iron sulfide FeS, iron nitride $Fe_2N(\varepsilon)$, $Fe_4N(\gamma')$ and carbide Fe_3C in the analysed material.

As a result of the conducted abrasion resistance tests we can claim that steel 41CrS4 and steel 42CrMoS4 after sulfonitriding in temperature of 570°C are characterized by minimum mass decrement. The thickness of the zones in the surface layer is relatively big in both these kinds of steel.

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