

9

Evaluation of selected steel thermochemical treatment technologies using foresight methods

A.D. Dobrzańska-Danikiewicz^{a,*}, E. Hajduczek^a,

M. Polok-Rubinić^a, M. Przybył^a, K. Adamaszek^b

^a Faculty of Mechanical Engineering, Silesian University of Technology,
ul. Konarskiego 18a, 44-100 Gliwice, Poland

^b BOSMAL Automotive Research & Development Institute Ltd,
ul. Sarni Stok 93, 43-300 Bielsko-Biała, Poland

* Corresponding author: E-mail address: anna.dobrzanska-danikiewicz@polsl.pl

Abstract

Purpose: *The purpose of this chapter is to evaluate the development efficiency of classical steel thermochemical treatment. The criterion assumed for dividing the technologies into groups was the thermochemical treatment kind. Three technology groups were selected to realised research, as follows: nitriding, carburising and diffusion boriding.*

Design/methodology/approach: *In the framework of foresight-materials science research: a group of matrices characterising technology strategic position was created, materials science experiments using: light microscope, transmission and scanning electron microscopes, X-ray diffractometer, microhardness tester, work-stands for testing of thermal fatigue resistance and mechanical fatigue strength, abrasion and corrosion resistance were conducted and technology roadmaps were prepared.*

Findings: *The outcarried research pointed out the great industrial importance of nitriding and carburising and good perspectives for these technology groups. However, diffusion boriding is obsolete and will slowly leave the market.*

Research limitations/implications: *Research concerning steel thermochemical treatment constitute a part of a larger research project aimed at identifying, researching, and characterizing the priority innovative technologies in the field of materials surface engineering.*

Practical implications: *Nitriding and carburising with their popularity and good quality-price relation can be recommended for use in small and medium enterprises. Obsolete diffusion boriding is not recommended for that.*

Originality/value: *The value of this chapter is to evaluate the value of thermochemical treatment technologies in the background environment with their future development perspectives determination including the influence of thermochemical treatment on the quality, microstructure and properties of surface layers obtained by thermochemical treatment.*

Keywords: *Manufacturing and processing; Thermochemical treatment; Carburising; Nitriding; Boriding; Foresight; Technology Roadmapping*

This chapter has been also published as:

A.D. Dobrzańska-Danikiewicz, E. Hajduczek, M. Polok-Rubinić, M. Przybył, K. Adamaszek, Evaluation of selected steel thermochemical treatment technology using foresight methods, Journal of Achievements in Materials and Manufacturing Engineering 46/2 (2011) 115-146.

1. Introduction

The European Union's priority strategy set out in the recent years called Europe 2020 assumes that the development of the continent should be intelligent, supportive to social inclusion and sustainable. The sustainable development idea is presented in Fig. 1. In line with the concept, it is necessary to take extensive actions at the European, national and regional level, to support a more effective, competitive and low-emission economy based on knowledge ensuring high employment and social and territorial cohesion. Five quantitative social objectives have been formulated to implement the adopted development strategy that should be brought into life until 2020. The objectives apply, accordingly, to: high employment, higher R&D and innovation investments, mitigation of the adverse climate change effects and the improved utilisation of energy sources, including RES, more widespread education and shrinking poverty and social exclusion. The Cohesion Policy concentrating on a financial aid for the EU's individual regions is promoting enterprises, including SMEs, being innovative, education and information-communicational systems, managing consciously their knowledge as a strategic resource while taking into account the environment influence. It is crucial in this

context to focus scientific research in a prioritised manner on the most promising fields and disciplines of science likely to have a large impact on Poland's fast civilisational and economic development based on an information society. It is feasible to put the so-defined objectives and plans into life using the concept of e-foresight [1] and a custom methodology of the Computer-aided Integrated Foresight Research [2, 3] that organises, streamlines and modernises the actual foresight research process. The approach proposed can be implemented practically by developing an information technology including: a virtual organisation, web platform and neural networks.

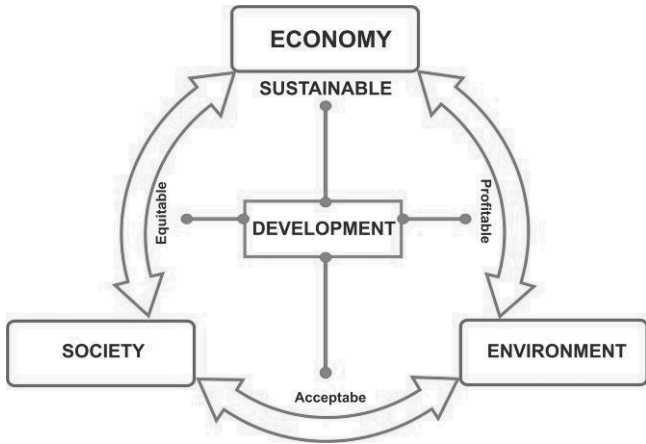


Figure 1. Sustainable development

Thermochemical treatment methods have been long used for producing surface layers on different substrates, including especially metal substrates. They represent one of the most classical methods of formulating the structure and properties of surface in products manufactured using engineering materials [4-7]. The chemical composition and structure of the alloy surface layer is changing, hence the properties of the treated pieces change in such case due to temperature variations and the chemical effect of the medium. This causes the intended diffusion change of the surface layer chemical composition and improves the relevant useful properties of whole parts. Despite the fact that most of the technical issues relating to the technologies have been investigated long ago, some of them continue to be used commonly in the industrial practice [8-33]. This obviously inclines to analyse this group of technologies both in technical and economic terms, thus requiring to assess their development efficiency.

The purpose of this work is to compare the efficiency of the various selected structure and properties formulation technologies accomplished through thermochemical treatment for the

selected engineering materials, using the harmonised chosen knowledge and technology management methods [1, 2], in order to develop technology foresight in this area while taking into account the results of thorough material science studies justifying the development preferences of the analysed technologies. The surface layers tests of the selected machine steels, hot-work tool steels and high-speed steels were carried out in this work to achieve the set goal. The steels were subjected to, respectively, nitriding, carburising, diffusion boriding and the impact of such operations was identified in particular on some useful properties of the products treated in this manner. Considering the myriad of research alternatives available, the materials and technologies mentioned above were selected, first and foremost due to a broad range of heat treatment temperatures preceding thermal and chemical treatment, starting with almost the lowest possible austenisation temperatures for machine steels to the highest ones used for high-speed steels, and secondly due to the fact that thermochemical treatment is used after quenching and tempering as for nitriding and directly after or during quenching as for carburising or boriding. The results of some earlier internal tests [34-45] being performed for many years at the Institute of Engineering Materials and Biomaterials of the Silesian University of Technology were employed in order to demonstrate the possibility of shapening the structure and properties of the selected steel grades using thermochemical treatment methods.

2. Research scope and subject matter

The research conducted is of an interdisciplinary character, and the research methodology employed is primarily concerned with technology foresight [46, 47] being part of the field of science known as organisation and management and surface engineering forming part of the widely-understood materials science. Methods originating from artificial intelligence, statistics, information technology, machine construction and operation, strategic and operational management have also been applied at some stages of the research. The key methodological assumptions of the research are illustrated graphically in Fig. 2.

2.1. Foresight methodology

According to the handling procedure accepted [2, 48, 49], homogenous groups should be distinguished between in the first place for the technologies assessed in order to subject

them to the planned research of an experimental and comparative character. The dendrological matrix of technology value is used to determine the objectivised values of the relevant separated technologies or groups thereof, and the meteorological matrix of environment influence for determining the degree of the positive and negative environment influence on the specific technologies. The methodological structure of the both matrices refers to portfolio methods commonly known in management sciences, and most of all the BCG matrix [50]. Their unparalleled popularity derives from reference to simple associations and intuitive reasoning becoming an inspiration when elaborating methodological assumptions for the dendrological and meteorological matrix [2]. A ten-degree universal scale of relative states presented in Table 1 was used to assess the individual groups of technologies for their value and environment influence degree.

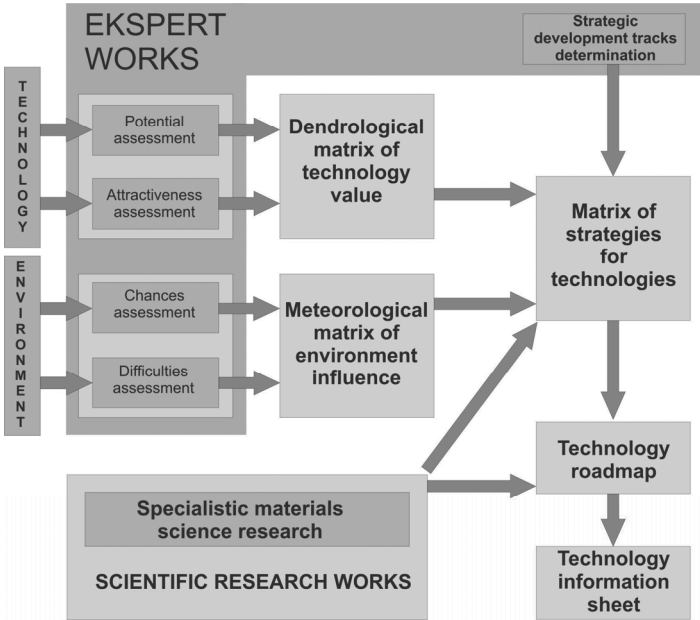


Figure 2. Methodology of interdisciplinary foresight-materials science research

The dendrological matrix of technology value presents assessment results for the relevant technology groups according to the potential being the actual objective value of the specific technology and attractiveness reflecting the subjective perception of the relevant technology by potential users. Depending on the potential value and attractiveness level determined in an expert assessment, each of the analysed technologies is placed into one of the following matrix quarters:

- Quaking Aspen – a weak technology with limited potential and attractiveness with the future success uncertain or impossible,
- Soaring Cypress – a technology with limited potential but high attractiveness with the future success possible,
- Rooted Dwarf Mountain Pine – a technology with limited attractiveness but high potential with the future success possible,
- Wide-stretching Oak – a technology characterised by high potential and attractiveness guaranteeing future success.

Table 1. Universal scale of relative state [2]

NUMBER	Class discriminant	LEVEL	
10	0.95 ←	EXCELLENT	← perfection
9	0.85 ←	VERY HIGH	
8	0.75 ←	HIGH	← normality
7	0.65 ←	QUITE HIGH	
6	0.55 ←	MODERATE	
5	0.45 ←	MEDIUM	
4	0.35 ←	QUITE LOW	← mediocrity
3	0.25 ←	LOW	
2	0.15 ←	VERY LOW	
1	0.05 ←	MINIMAL	

The meteorological matrix of environment influence illustrates graphically the results of influence of external circumstances on the relevant group of technology grouped by the difficulties with negative influence and the opportunities with positive influence on the analysed technologies. Depending on the influence degree of positive and negative environment factors determined in an expert assessment, each of the analysed technologies is placed into one of the following matrix quarters:

- Frosty Winter – the environment produces many difficulties and few chances, thus the success is difficult or impossible,
- Hot Summer – the environment produces many chances and many difficulties, thus the success of the technology in given circumstances is highly risky, but possible,

- Rainy Autumn – the environment is neutral with few difficulties and chances for steady progress,
- Sunny Spring – the environment is friendly with many chances and few difficulties guaranteeing the future success.

The results of expert studies visualised with a dendrological and meteorological matrix were applied in the next stage of research works applied onto the **technology strategies matrix** consisting of sixteen fields corresponding to the individual variants from the set of combinations of technology types with environment types. Mathematic relationships were formulated after entering the concepts of the relative technology value V_n and the relative value of environment influence E_n and a computer programme based on them was created enabling to transfer the specific numerical values from the dendrological and meteorological matrix dimensioned [2x2] to the strategy matrix for technologies dimensioned [4x4] [2]. The matrix of strategies for technologies presents graphically the place of technology including its value and environment influence degree and indicates an action strategy to be adopted with reference to the specific technology considering the factors analysed earlier. The **strategic development tracks** were applied onto the technology strategy matrix consisting of sixteen fields reflecting the predicted situation of the given technology if positive, neutral or negative external circumstances occur. The forecast established concerns the time intervals of 2015, 2020, 2025 and 2030 and presents a vision of future events consisting of few variants.

2.2. Tests material

The materials science investigations were carried out with the selected steel grades with their chemical composition as provided in Table 2. 18CrMnTi4-4 steel is intended for carburising, 38CrAlMo6-10 is machine steel for nitriding, 37CrMoB10-4 is low-alloy hot-work tool steel, X37CrMoV5-1 and X40CrMoV5-1 are Cr-Mo hot-work tool steels of 5-1 type characterised by high resistance to cyclic temperature variations. 40CrWMoVB17-11-16 is multi-component steel and HS6-5-2 and HS12-0-2+C are high-speed steels. The steels were alloyed with a conventional method in electric-arc furnaces and X37CrMoV5-1(vac), X40CrMoV5-1(vac) and 40CrWMoVB17-11-16 steels were remelted in vacuum in an electric-arc furnace at the pressure of approx. 1 Pa, and X40CrMoV5-1(es) steel was subject to electro-

slag remelting. Vacuum remelting and electroslag remelting were applied to produce steel with a higher structural homogeneity and a limited fraction of non-metallic inclusions as compared to the ones remelted conventionally.

Table 2. Chemical composition of the tested steels

Steel type	Concentration of elements, %										
	C	Mn	Si	P	S	Cr	Mo	V	W	Ni	Others
18CrMnTi4-4	0.17	1.10	0.23	0.030	0.040	0.93					Ti 0.09
38CrAlMo6-10	0.40	0.43	0.36	0.015	0.007	1.48	0.26			0.12	Al 0.94
37CrMoB10-4	0.38	1.39	0.23	0.014	0.014	2.43	0.42	0.10		0.17	B 0.003
X37CrMoV5-1	0.44	0.49	0.97	0.016	0.012	5.06	1.28	0.50		0.09	
X37CrMoV5-1(vac)	0.38	0.43	0.81	0.015	0.014	5.41	1.35	0.44		0.23	
X40CrMoV5-1(vac)	0.45	0.42	1.04	0.018	0.020	5.10	1.38	1.02		0.12	
X40CrMoV5-1(es)	0.41	0.34	0.78	0.024	0.005	5.56	1.08	1.27	0.10	0.11	
40CrWMoVB17-11-16	0.40	0.40	0.29	0.017	0.020	4.30	1.67	1.48	2.80	0.28	Co 1.68 B 0.05
HS12-0-2+C	1.06	0.31	0.28	0.030	0.023	4.41	0.64	2.56	11.20	0.22	
HS6-5-2	0.88	0.26	0.37	0.030	0.021	3.90	4.90	1.88	6.20		

The tested steels underwent heat treatment in the conditions given in Table 3 and thermochemical treatment. High-temperature thermochemical treatment operations, i.e. carburising and boriding are conducted prior to heat treatment, and low-temperature operations, i.e. nitriding and its variants are carried out after heat treatment. The gas nitriding of the specimens treated thermally was carried out in a retort in an atmosphere of partially dissociated ammonia, at a temperature of 540°C and 570°C for 0.5 to 8 hrs. Some of the specimens were nitrided in an atmosphere containing 50% NH₃ + 50% N₂, and 25% NH₃ + 75% N₂. Plasma nitriding was performed in VHT equipment in the atmosphere of a gas mixture composed in 90% N₂ + 10% H₂. The specimens were nitrided for 3 h at a temperature of 550°C, pressure of 300 Pa and voltage of 1250 V.

Twist drills with the diameter of 5 mm were made of the same HS6-5-2 steel cast with the hot-rolling method. The drills were heat treated, ground and subjected to selected thermochemical treatment methods, in particular to:

- passivation at a temperature of 540°C for 2 hours in a retort into which distilled water was added drop by drop,
- selective nitriding, i.e. first oxidising in water vapour at a temperature of 540°C for 30 min., and then nitriding in an atmosphere of partially dissociated ammonia at a temperature of 520°C for 30 min.,

- gaseous sulphonitriding in an atmosphere of ammonia with the addition of sulphur vapour, and next vacuum nitriding (with decreased pressure in a retort),
- oxynitriding in a fluidised bed at a temperature of 550°C for 25 min. in an atmosphere of water vapour and partially dissociated ammonia,
- plasma nitriding at a temperature of 505°C for 15 min. in an atmosphere of N₂+H₂ at a pressure of approx. 270 Pa.

Table 3. Heat treatment conditions for the tested steels

Steel type	Temperature, °C	
	Austenitisation	Tempering
18CrMnTi4-4	840	160-300
38CrAlMo6-10	920	500-600
37CrMoB10-4	890	500-600
X37CrMoV5-1	970-1030	500-600
X37CrMoV5-1(vac)	970-1030	500-600
X40CrMoV5-1(vac)	1000-1060	500-600
X40CrMoV5-1(es)	1000-1060	500-600
40CrWMoVB17-11-16	1090-1150	500-650
HS12-0-2+C	1160-1220	510-630
HS6-5-2	1190-1250	510-630

The specimens and the toothed gears made of 18CrMnTi4-4 steel were carburised at a temperature of 880°C in an endothermic atmosphere with the addition of 4% of methane. Carbo-nitriding was carried out in the conditions given, by adding 3 and 6% of ammonia to the carburising atmosphere. After annealing for 2.5 to 17 hrs, as a result of which a 0.2 to 1.65 mm thick layer is produced, the specimens were cooled to the temperature of 840°C and quenched directly in oil, and then tempered for 2 h between 160 to 300°C.

The diffusion boriding of the specimens was performed in powder containing 15% B₄C, 83.6% Al₂O₃, 0.7% NH₄Cl and 0.7% NaF, in heat-resisting steel containers, at a temperature of 950, 1000 and 1030°C for 2 to 12 hours. The containers were cooled in air after boriding at 950°C and 1000°C, and next the X40CrMoV5-1 steel specimens were removed and quenched from 1030°C and tempered at 600°C. After boriding at a temperature of 1030°C, the containers were cooled with a stream of a water suspension in air which enabled to quench the specimens immediately from the boriding temperature, and then the specimens were tempered twice at 600°C.

2.3. Materials science methodology

Structural tests using the methods of light metallography, transmission and scanning electron microscopy and an X-ray structure analysis were carried out to determine the impact of thermochemical treatment conditions and of some functional properties tests on the structure of the tested steels surface layers and core.

Metallographic tests were undertaken with MEF4A light microscopes by Leica with a Leica-Qwin, MeF image analysis system by Reichert and Neophot 2 by Carl Zeiss Jena with the magnification range of 10 to 1000. Some of the structure tests with the magnification of up to 3000 times were made with JXA-50A scanning electron microscopes by JEOL, DSM-940 scanning electron microscopes by Opton and SUPRA 35 by Zeiss, with the accelerating voltage of 20 kV, using back scattered electrons (BSE) and secondary electrons (SE) detection.

The phase composition of the specimens diffusion layers and core was examined with an X-ray qualitative and quantitative phase analysis method using DRON 2,0 and X'Pert diffractometers by Philips. Textures were also examined with a reflection technique with a Siemens-Halske Kristalloflex-4 diffractometer. The penetration depth of X-rays in the conditions applied was estimated at approx. 0.03 to 0.04 mm. For this reason, to determine the phase composition of the thick surface (borided and carburised) layers, diffraction patterns were made after grinding off the subsequent 0.03 mm thick layers from the specimens until the diffusion layer has been removed completely.

The structure of the steel diffusion layers and core was tested by observing thin foils in Tesla BS 540 and JEOL 200CX transmission electron microscopes with the accelerating voltage of 100 to 200 kV. The thin foils made of approx. 0.3 mm thick layers were prepared by cutting off plates from the specimens surface. Next, discs were cut out from such plates with the diameter of approx. 3 mm which were then thinned out mechanically to approx. 0.1 mm. The final electrolytic polishing was performed with a jet method in an electrolyte composed of 20 cm³ H₂SO₄ and 80 cm³ CH₃OH. The thin foils made with the heat treated steels and with the carburised layer were polished electrolytically in a reagent containing 50 g CrO₃ and 490 cm³ H₃PO₄. Some of the thin foils were subjected to ion thinning in a Gatan device. The phase composition and the relative orientation of phases with the matrix was determined with the selected area electron diffraction method.

An X-ray microanalysis with the energy dispersive spectroscopy (EDS) method and wavelength dispersive spectroscopy (WDS) method by means of JXA-50A apparatuses by JEOL,

SEMQ by ARL and SUPRA 35 by Zeiss at the accelerating voltage of 10 to 20 kV was undertaken to identify the distribution of elements in the surface layer of the thermochemical treated specimens. The qualitative analyses of surface and linear elements distribution were made and quantitative analyses in the selected points on the tested sections of surface layers were made.

Variations in the concentration of elements in the nitrided layer and in the substrate were determined also based on tests in the glow discharge optical emission spectroscopy (GDOES) GDS-750 QDP by Leco Instruments. Variations in the concentration of carbon in the carbonised and carbonitrided layers were investigated with LECO equipment, by analysing the chips taken every 0.1 mm from the surface layer to the core.

Dilatometric tests with a differential Adamel dilatometer and with DI-4 and Linceis absolute dilatometers were made to calculate the linear expansion factor for borides and to identify the phase transition temperature in the carbonised layer.

Some mechanical properties of the heat treated steels were determined during the tests. The Rockwell method at the C scale was used to measure the hardness of specimens for the tested tool and high-speed steels after heat treatment and machine steels for carburising and the total load applied was 1471 N. At least 30 measurements for each condition were taken. Impact strength at room temperature and at higher temperature was investigated with a Charpy pendulum machine using 10 specimens for each test variant. Tensile strength and bending strength tests were made with an Instron 1195 tensile testing machine fitted with a high-temperature attachment using 6 specimens for each test variant. The fatigue strength tests of steel with carburised layers were carried out with a PWY tensile testing machine by Schenck according to a neutral and ripple cycle, at a frequency of 16.66 Hz and with the agreed number of cycles $N_G = 10^7$. The results of the strength properties tests were developed statistically by calculating the average value and the average value confidence interval for the confidence level of $\alpha = 0.05$.

Measurements were made with an attachment fitted to an MeF microscope and with a DUH 202 ultra-microhardness tester by Shimadzu on lateral fractures with the Vickers method by applying the load of 0.49 and 0.98 N in order to identify microhardness distribution for the section of diffusion layers. The average hardness value was calculated each time with 5 to 10 measurements carried out within the same distance from the specimen surface.

Thermal fatigue resistance tests were performed with devices enabling direct and indirect specimens heating. A device was used to test heat treated steels enabling the induction heating of the surface layer of the rotating disc being cooled in water. This method ensures a short

thermal cycle. The maximum temperature of the specimens surface was approx. 600°C. The number of thermal cycles during the tests was 3000 or 5000. Indirect heating was used for testing resistance to cyclic temperature steel variations with surface layers, as the induction heating method cannot be used in this case due to the different physiochemical properties of the surface layer and the core. Indirect heating was accomplished by contacting cyclically the specimen with a cooper insert heated to approx. 900°C and cooling was accomplished with a water jet. One cycle within 600-20°C lasted 12 s. As the specimens tested in the device with direct-contact heating were subjected to the corrosive effect of air and water during thermal cycles, therefore, some of the thermal fatigue resistance tests were made with a device where the specimens were heated by means of radiation and convection in an electric furnace and were cooled in water. The specimens, lifted and dropped cyclically, can be placed in air-tight containers securing them against corrosion during thermal cycles. A thermal cycle within the range of 600-80°C set within the distance of approx. 0.1 mm from the solid specimen's heated surface lasts approx. 140 s with the furnace temperature of approx. 860°C. Considering a long thermal cycle of the solid specimens placed in the containers, cylindrical specimens with a smaller thermal capacity were also used. The solid specimens tested without the safety containers were subjected to 100 to 2500 thermal cycles, and the cylindrical specimens placed in the containers underwent between 2500 to 25000 thermal cycles. The thermal fatigue resistance analyses for the specimens were undertaken based on the measurements of depth and density of cracks (the average number of surface cracks formed at the distance of 1 mm). The cracks were measured on the fractures made in the plane perpendicular to the specimens surface. Approx. 50 measurements were taken in 3 specimens for each test variant. The measurements results were established on a statistical basis.

The specimens after the thermal fatigue test, without using the safety containers, were etched in a 40% aqueous water solution of hydrochloric acid in order to remove mineral salts depositing on their surface. The specimens, after etching and drying, underwent gravimetric tests on an analytical WA-31 scale with the measuring accuracy of 0.1 mg to determine mass variations during cyclical temperature variations.

Abrasive wear resistance tests with the pin-on-disc method were carried out with a CSEM THT – High Temperature Tribometer – at a room temperature and in 500°C. A 6 mm Al₂O₃ corundum ball was used as a counter-specimen. The fixed ball was pressed with the force of 7 N against a disc rotating in the horizontal plane at a speed of 50 cm/s during a pin-on-disc test carried out with 1000 and 7500 revolutions with the specimens having their layer nitrided and

after being heat treated. The width of the formed wear tracks was measured with a light microscope after the test and the average volume of the material removed during tribological wear was calculated.

Fatigue strength tests for Z_{gj} tooth root were made at a test stand comprised of two transmission gears with the first gear being a test object and the other being a closing gear. The load applied onto the gears was changed by twisting alternately the clutch discs seated on the independent parts of a torsion shaft.

The cutting properties of the heat treated and thermochemically treated high-speed HS6-5-2 steel drills were tested with constant cutting parameters. 15 mm deep blind openings were bored for this purpose in flat bars made of normalised C55 steel with the hardness of 200-220 HBW, with the cutting speed of 28.7 m/min and the shift of 0.18 mm per revolution. Cooling with the capacity of approx. 5 l/min using an emulsion made of 10% emulsifiable E oil and water was applied for boring. The wear equal to $VB_{max} = 0.5$ mm at the flank surface was adopted as a blade blunting criterion. 15 cutting ability tests were carried out for drills from each batch, and the results were elaborated in a statistical manner.

2.4. Technology roadmaps and technology information sheets

The results of the experimental and comparative research made provide source data for creating **technology roadmaps** [51-53]. The set-up of the custom technology roadmap corresponds to the first quarter of the Cartesian system of coordinates. Three time intervals for the years: 2010-11, 2020 and 2030 are provided on the axis of abscissa, and the time horizon for all the results of the research applied onto the map is 20 years. Seven main layers were applied onto the axis of coordinates of the technology roadmap answering subsequently to more and more detailed questions: When? Why? What? How? Where? Who? How much? The main technology roadmap layers hierarchised starting with the top, most general layers determining all-social and economic reasons and causes of the actions taken, through the middle layers characterising products and their manufacturing technology, to the bottom layers detailing organisational and technical matters concerning the place, contractor and costs. The middle layers of the technology roadmap are subject to two types of influence – pull from the top layers and push from the bottom layers. The relationships between the individual layers and sub-layers of the technology roadmap are presented with the different types of arrows representing, respectively, cause and effect relationships, capital ties, time correlations and two-directional data and/or resources flow.

The technology roadmaps prepared with a custom concept are a very convenient tool for a comparative analysis enabling to select the best technologies according to the criterion chosen. Besides, their undisputed advantage is flexibility and, if needed, additional sub-layers can be added or expanded for the maps according to the circumstances of the industry, size of enterprise, scale of the company's business or an entrepreneur's individual expectations.

Technology information sheets, containing technical information very helpful in implementing a specific technology in the industrial practice, especially in SMEs not having the capital allowing to conduct own research, are detailing and supplementing the technology roadmaps. The technology information sheets provide, in particular, a description of the technological process progress and a characteristic of a physiochemical phenomenon accompanying the technological processes, the advantages and disadvantages of the relevant technology, the most prospective detailed technologies and substitute / alternative technologies. A technology information sheet also contains the types of a coating / surface layer that may be deposited or the processes occurring at the substrate surface, as well as the specific properties of coatings / surface layers / substrate surfaces as a result of technological processes. A special heed was paid also to the general physiochemical conditions of technological process implementation, substrate material preparation methods, research instrument type / kind and possible specific accessories. Besides, the research results acquired with an expert research method have allowed to provide the following details in the developed sheets determined with a universal scale of relative states: the impact of technology application on the predicted and expected material properties, the efficiency of preventing the consequences of wear, industry section acc. to the PKD classification having the highest technology applicability, the applicability of computer modelling and steering methods and the development prospects of the individual analysed technologies. In addition, each technology information sheet provides a general or example diagram of the considered production process and a three-part list of the recommended references.

3. Technologies value and their strategic development directions

The results of the foresight research described in this chapter includes the assessment of potential and the attractiveness of the analysed technologies against the micro- and macro-environment performed based on the key experts' opinions expressed in a ten-degree universal scale of relative states and a recommended strategy of managing a relevant technology

resulting from the assessment together with the predicted strategic development tracks. The three homogenous groups have been separated from the analysed technologies in order to carry out experimental and comparative works including, respectively:

- (A) nitriding and its variants,
- (B) carburising and carbonitriding,
- (C) diffusion boriding.

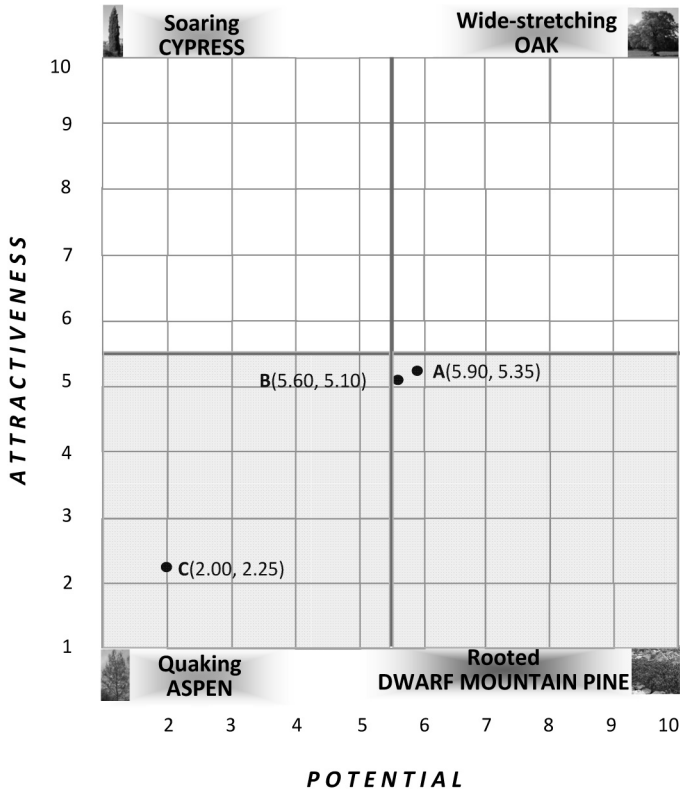


Figure 3. The dendrological matrix of technology value for the following thermochemical technologies: (A) nitriding and its variants, (B) carburising and carbonitriding, (C) diffusion boriding

The individual technology groups have been evaluated by experts using a ten-degree universal scale of relative states for their: business, economic, humane, natural and system attractiveness as well as for their: creational, applicational, qualitative, developmental and

technical potential. A weighted average for the criteria considered (attractiveness and potential) was calculated using a multi-criteria analysis, and the result received for the individual groups of technologies was entered into the dendrological matrix of technologies value (Fig. 3). The analysis showed that a group of (A) technologies including nitriding and its variants and (B), including carburising and carbonitriding in high temperature, were classified to the quarter called Rooted Dwarf Mountain Pine representing solid, proven technologies with high potential, characterised by limited attractiveness. Diffusion boriding (C) was classified to the least promising matrix quarter referred to as Quaking Aspen representing technologies with limited potential and small attractiveness.

The positive and negative environment influence on the relevant groups of technologies was evaluated with the meteorological matrix of environment influence. The results of the multi-criteria analysis were entered into the matrix evaluated in the experts process, as shown in Fig. 4. The results of the studies made show that in the case of all the tested group of technologies, the environment is predictable and stable with a neutral character. Therefore, no related spectacular opportunities should be expected from it, nor unpredictable difficulties that are definitely not supportive to the development of the technology groups in question. Very similar results (3.26, 5.25) were obtained for the technology group (A) and the technology group (B), receiving the value of (3.11, 4.91), and the technology group (C) with (4.70, 3.33) ranked lower, meaning fewer opportunities and more difficulties in the future.

At the next stage of research works, the research results presented graphically with the dendrological matrix of technology value and the meteorological matrix of environment influence were entered into the technologies strategy matrix (Fig. 5). The matrix is presenting, graphically, the place of the individual technology groups of steel thermo-chemical processing with regard to their value and the environment influence degree, indicating the relevant managing strategies. Using the pre-defined mathematical relationships, the specific numerical values provided in the dendrological and meteorological matrix dimensioned [2x2] were moved to the strategy matrix for technologies dimensioned [4x4]. For the group of technologies (A) and (B), it is recommended to use a strategy of a dwarf mountain pine in autumn that recommends deriving profits from production implementation in a stable, predictable environment using a solid technology that should be modernised and promoted intensively to strengthen its attractiveness. As regards the technology group (C), the strategy of an aspen in autumn should be applied that recommends the withdrawal of a technology from a market not providing new opportunities.

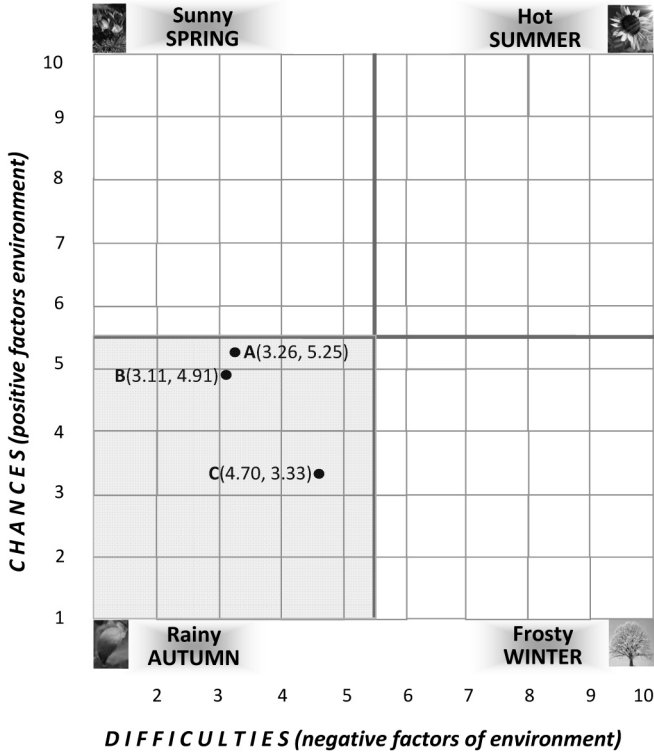


Figure 4. The meteorological matrix of environment influence for the following thermochemical technologies: (A) nitriding and its variants, (B) carburising and carbonitriding, (C) diffusion boriding

Strategic development tracks for the individual technology groups were established based on the acquired expert opinions. The tracks represent an optimistic, most probable and pessimistic forecast of their development for the relevant time intervals: 2015, 2020, 2025 and 2030. A graphical example of the strategy matrix for the technologies with strategic development tracks provided in three variants created for nitriding and its variants is shown in Fig. 6. The most probable strategic development track for this technology group assumes that neutral environment conditions will be maintained to be slowly, insignificantly improving in the next years. The technology value should also increase slightly as forecast, which is connected with the strengthening potential of technology with attractiveness maintaining at the existing level. The optimistic strategic development track assumes more dynamic, positive changes taking place in the environment related to the decreasing number of external difficulties accompanied by the strengthening technology potential. This, on the other hand,

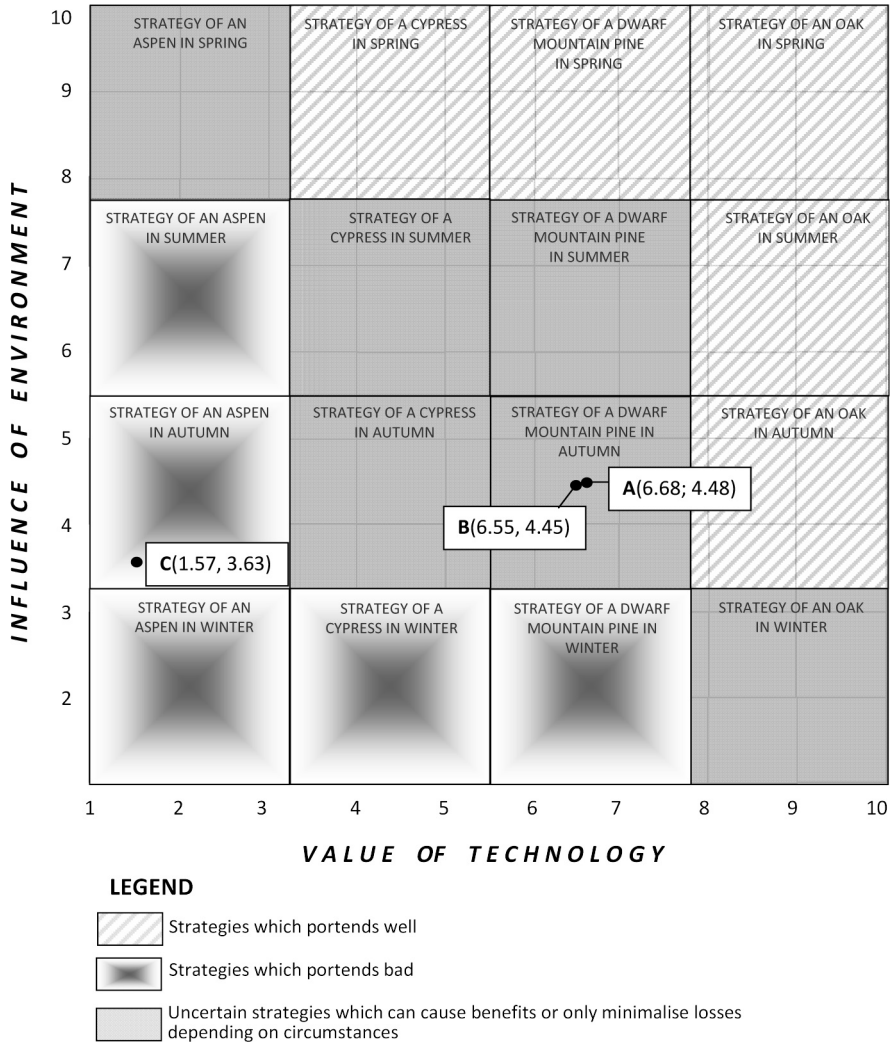


Figure 5. The matrix of strategies for technologies prepared for selected thermochemical technologies, as follows: (A) nitriding and its variants, (B) carburising and carbonitriding, (C) diffusion boriding

allows to move the technology group (A) from the strategy field of dwarf mountain pine in autumn to the strategy field of dwarf mountain pine in spring. This means that the key objective should be strengthening, modernising, automating, computerising and promoting technologies with high potential based on good economic conditions at the market. The optimistic variant of events is mainly related to the vision of fast development of the most prospective (ion, glowing) plasma nitriding and hybrid technologies with nitriding (e.g. in

connection with the technology of physical deposition from gaseous phase – PVD) with the development of nitriding at the existing level with decreased pressure and the smaller importance of conventional gas nitriding. The development of nitriding and its variants must be also accompanied by an improved ecological aspect of the discussed technologies to minimise the harmful substances emitted to the environment.

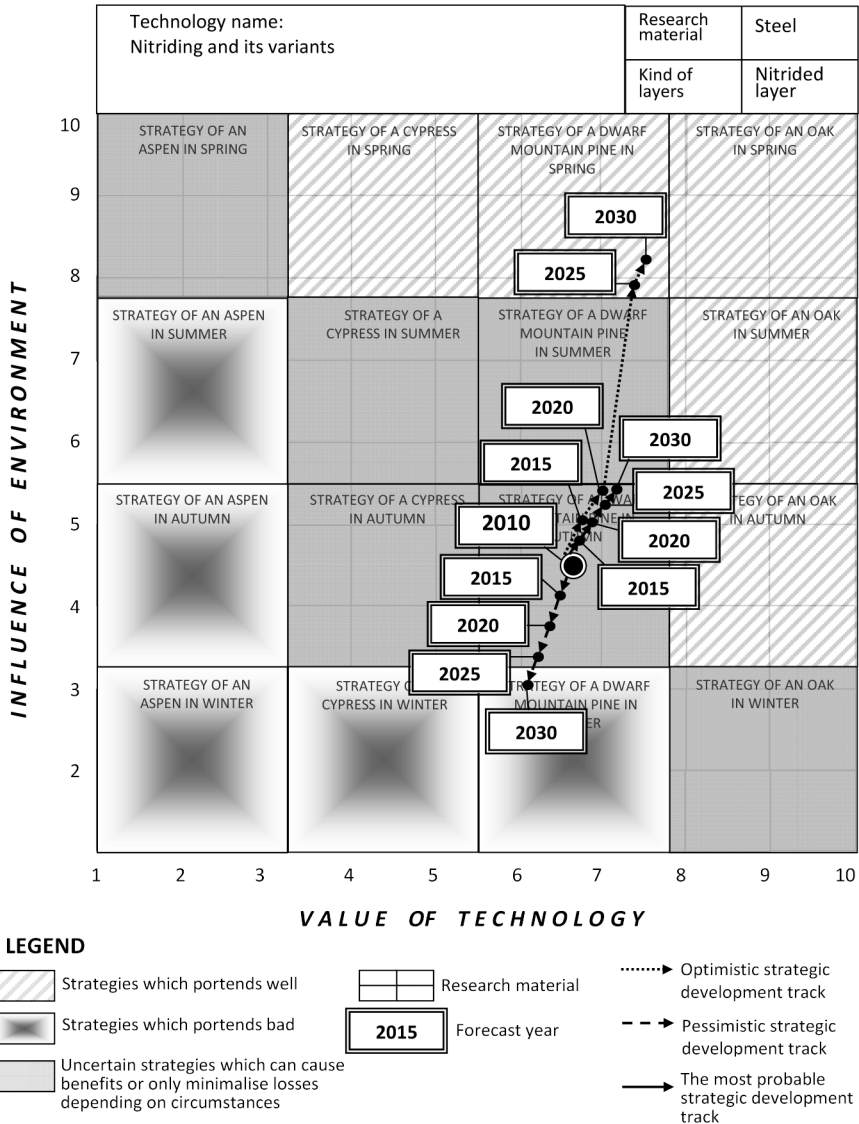


Figure 6. The strategic development tracks created for the (A) demonstration technology group: nitriding and its variants

The analysis made has shown that that the development forecast of the technology group (B) including carburising and carbonitriding is very similar to the development forecast of the technology (A), reaching slightly smaller, very similar values. An optimistic development variant of this technology group is conditioned by the strengthening and growing importance of the most promising technologies such as: glowing carbonitriding, carburising in a controlled atmosphere of natural gas and the carbonitriding variants enabling direct quenching and low-temperature tempering of the treated parts.

Table 4. The strategic development tracks of selected thermochemical treatment. Types of strategic development tracks: (O) – optimistic, (P) – pessimistic, (MP) – the most probable

No	Technology name	Steady state 2010	Type of strategic development tracks	Years			
				2015	2020	2025	2030
1.	Nitriding and its variants	Strategy of a dwarf mountain pine in autumn A (6.7, 4.5)	(O)	(6.8, 4.9)	(7.0, 5.4)	(7.5, 7.9)	(7.7, 8.3)
			(P)	(6.5, 4.1)	(6.4, 3.8)	(6.2, 3.4)	(6.1, 3.1)
			(MP)	(6.8, 4.7)	(6.9, 4.9)	(7.1, 5.2)	(7.3, 5.4)
2.	Carburising and carbonitriding	Strategy of a dwarf mountain pine in autumn B (6.6, 4.5)	(O)	(6.7, 4.7)	(6.8, 5.1)	(7.2, 7.8)	(7.4, 8.1)
			(P)	(6.4, 3.9)	(6.2, 3.6)	(6.0, 3.2)	(5.8, 2.8)
			(MP)	(6.7, 4.5)	(6.8, 4.6)	(6.9, 4.8)	(7.1, 5.1)
3.	Diffusion boriding	Strategy of an aspen in autumn C (1.6, 3.6)	(O)	(1.8, 4.0)	(2.0, 4.3)	(2.3, 5.6)	(2.6, 5.9)
			(P)	(1.5, 3.1)	(1.4, 2.5)	(1.3, 2.1)	(1.2, 1.7)
			(MP)	(1.5, 3.5)	(1.4, 3.4)	(1.3, 3.4)	(1.2, 3.3)

The weakest development prospects are exhibited by the technology group (C) including diffusion boriding with its significance most likely declining within the nearest 20 years. This stems from limited effectiveness, high costs and the unfavourable environmental impact of the existing boriding technologies. The pessimistic variant of events assumes that already in 2015 the technology group (C) moves from the field of matrix corresponding to the strategy of aspen in winter, where it is recommended to withdraw a weak technology from the market with difficulties predominant. An optimistic variant provides gradual, moderate improvement in the value of the technology group (C) with more favourable conditions of the environment over the

next 20 years, which would allow to move it in 2025 to the matrix field corresponding to the strategy of aspen in summer. The strategy allows to run a risk and to make an attempt to exploit the new emerging external circumstances. This, however, is possible only if there is a major breakthrough by finding a new, wide range of industrial applications and a spectacular improvement in the currently used solutions, especially for environmental protection.

The numerical values resulting from all the research performed for the three analysed group of technologies are presented in Table 4.

4. Research results concerning the structure and properties of thermochemically treated steels

4.1. Structure and properties of surface layers of steel after nitriding

Nitriding and its variants are very popular methods of thermochemical treatment for machine and tool steels. They are performed as the final operation after prior quenching and high tempering at a temperature slightly higher than the assumed nitriding temperature. A layer of nitrides is forming at the surface of the tested steels as a result of gas nitriding carried out in an atmosphere of partially dissociated ammonia at a temperature of 540°C. The hardness of the layer is up to approx. 1500 HV 0.05 and the layer is transiting into the diffusion zone to the core. The hardness of the zone depends on the chemical composition and on the steel heat treatment conditions (Fig. 7). The largest thickness for the continuous zone of nitrides and for the entire diffusion zone was obtained on 38CrAlMo6-10 machine steel for nitriding (Fig. 8) whereas high-speed HS6-5-2 and HS12-0-2+C (Fig. 7) steels exhibit the highest surface hardness. If the nitriding temperature of high-speed steels is raised to 570°C, the thickness of the hardened layer is higher by approx. 20-25%. The continuous zone of nitrides by the steel surface contains most of all a phase with the $Fe_{2,3}N$ lattice structure and also phases with CrN and Mo_2N lattices in individual steels. Such nitrides also occur as precipitates distributed at the boundaries of grains in the diffusion zone of a nitrated layer (Fig. 9). The dispersive precipitates of $Fe_{16}N_2$ nitride are also produced in martensite in this layer and the precipitates maintain their privileged crystallographic orientation with the matrix (Fig. 10).

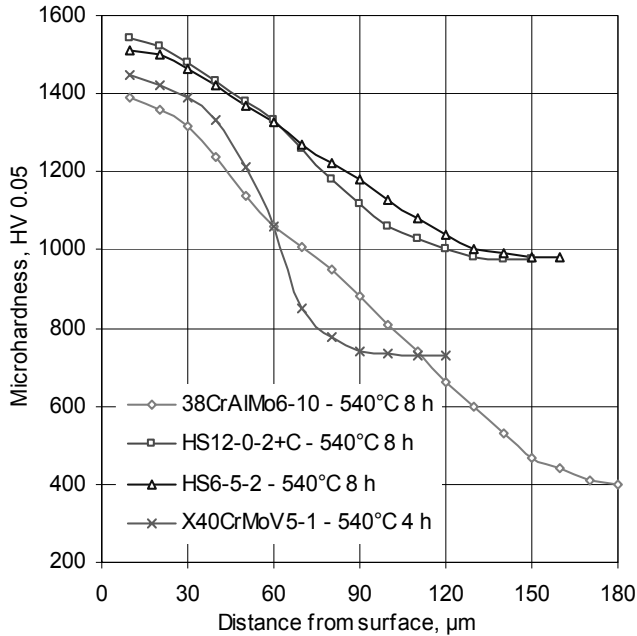


Figure 7. Microhardness distribution in the surface layer of the selected steels subject to quenching and tempering gas nitriding at 540°C



Figure 8. Surface layer microstructure of 38CrAlMo6-10 steel quenched from 920°C, tempered at 575°C and gas-nitrided at 570°C for 8 hrs in an ammonia atmosphere

The continuous layers of hard brittle nitrides produced at the steel surface reduce the strength and ductility of steel. Nitriding in the atmosphere of an ammonia and technical nitrogen mixture has a favourable effect on maintaining ductility at high strength and slightly

limited surface hardness. This is because the continuous zone of nitrides is produced on the surface to a limited extent only. If 50% of inert N_2 molecular nitrogen is added to the nitriding atmosphere, the hardness and thickness of the hardened layer is lowered, and this becomes clear after nitriding for a short time. Hardness variations in the surface layer are similar to those achieved after nitriding in an atmosphere of 100% NH_3 for a twice shorter time (Fig. 11). After nitriding in an atmosphere containing 25% NH_3 and 75% N_2 , a diffusion zone is created only at the steel surface (Fig. 12), even after long-term nitriding. The thickness of surface layers and their hardness and abrasion resistance is lower, however.

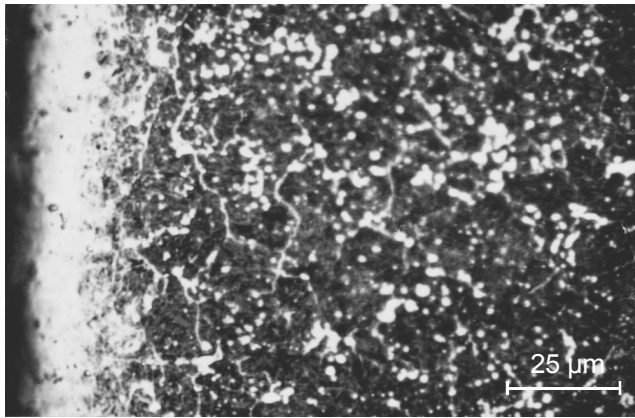


Figure 9. Surface layer microstructure of HS6-5-2 steel quenched, tempered and gas-nitrided at 570°C for 4 hrs in an ammonia atmosphere

If a surface layer with high hardness is formed, this causes the bending strength of the tested steels to change with impact load and static load. Impact strength is usually significantly reduced, especially the impact strength of the steel featuring small crack resistance, and static bending strength increases if layer thickness is low as compared to part dimensions. The tested 4 mm thick specimens made of high-speed HS6-5-2 steel quenched from 1230°C and tempered once at 550°C have their bending strength R_g of approx. 2460 MPa. The strength increases by approx. 20% after tempering again at the same temperature. This is certainly a result of dispersion alloy carbides being released in the martensite formed as a result of retained austenite transformation during steel cooling after the first tempering. Steel nitriding at 540°C in an atmosphere of 100% NH_3 is reducing R_g resistance to approx. 1640 MPa (Fig. 13). R_g rises slightly under the tested conditions only after nitriding the high-speed HS6-5-2 steel for 0.5 h in an atmosphere containing 25% NH_3 and 75% N_2 . The plastic properties of steel can

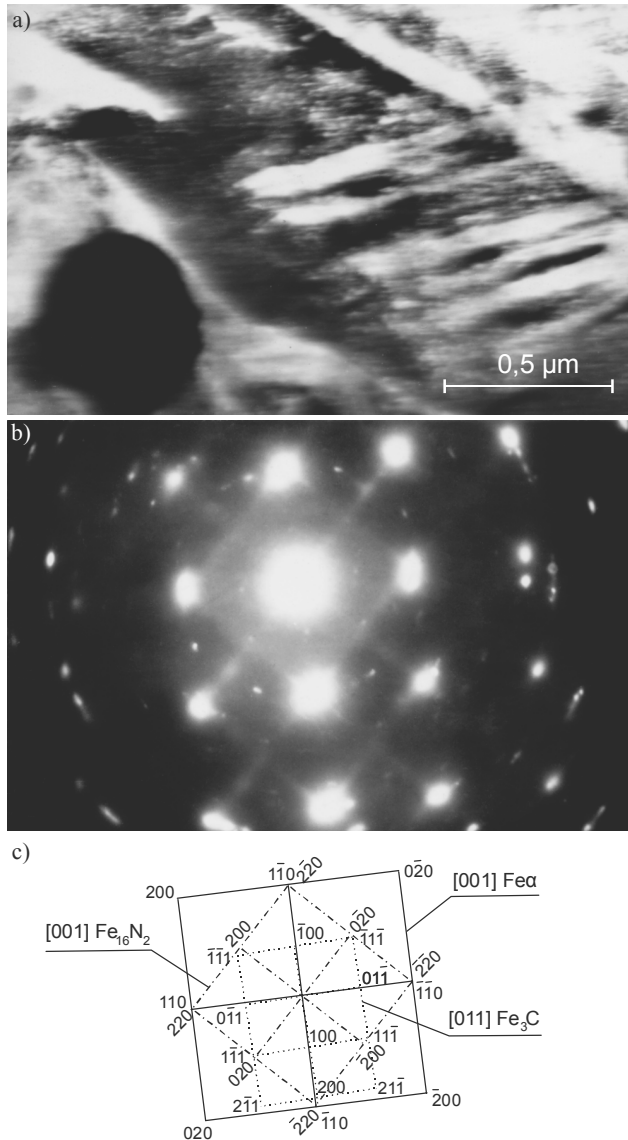


Figure 10. Surface layer microstructure of HS6-5-2 steel quenched, tempered and gas-nitrided at 540°C for 3 hrs; thin foil, a – bright field image, b – diffraction pattern from the area as in Fig. a, c – diffraction pattern solution from Fig. b

be characterised to some extent by the total deflection value f_g that decreases from 1.95 mm for the heat treated steels to 0.84 mm after nitriding the specimens at 540°C for 4 hrs (Fig. 13). The plastic deflection value f_{pl} for the heat treated high-speed steel specimens is very low – 0.05 mm, and becomes practically immeasurable after nitriding.

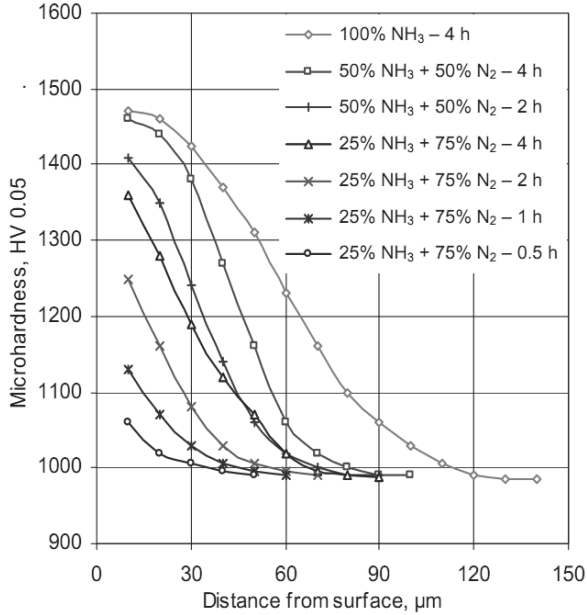


Figure 11. Microhardness distribution in the surface layer of HS6-5-2 steel quenched from 1230°C, tempered at 550°C and gas-nitrided at 540°C in an atmosphere of ammonia with addition of nitrogen

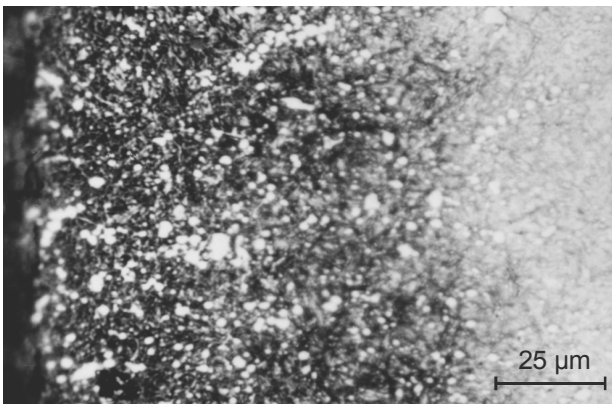


Figure 12. Surface layer microstructure of HS6-5-2 steel gas-nitrided at 540°C for 4 hrs in an atmosphere containing 25% NH₃ and 75% N₂

The structure of the hot-work X40CrMoV5-1 tool steel surface layer after gas nitriding in an atmosphere of dissociated ammonia at a temperature of 570°C consists of a continuous zone of alloy nitrides and of a diffusion zone lying underneath (Fig. 14). The zone of continuous nitrides with the hardness of approx. 1340 HV 0.05 consists of ϵ -Fe_{2,3}N and CrN phase.

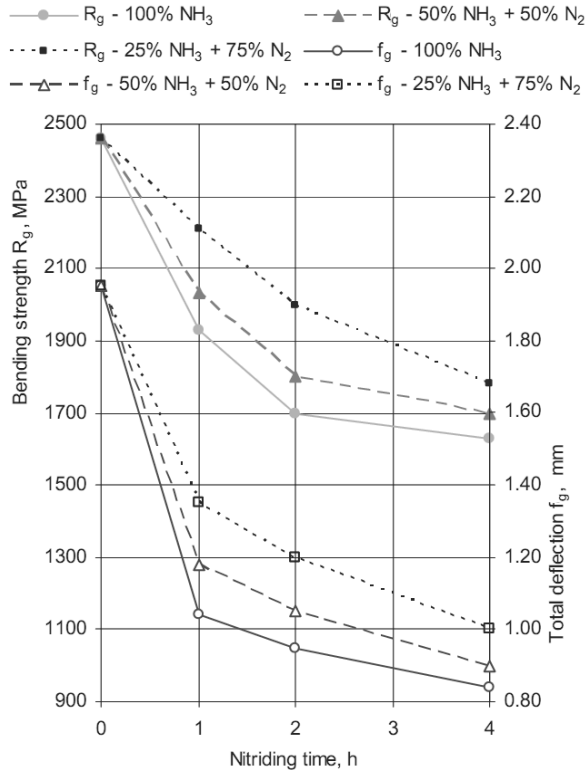


Figure 13. Influence of nitriding conditions on the properties identified in the static bending test of the specimens made of HS6-5-2 steel quenched, tempered and gas-nitrided at 540°C

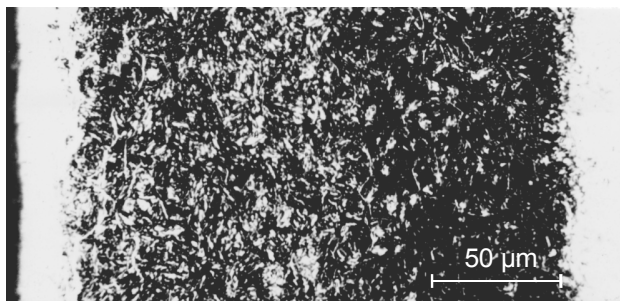


Figure 14. Microstructure of the X40CrMoV5-1 steel surface layer gas-nitrided at 570°C for 6 hrs

The nitrogen concentration and the layer hardness are declining constantly in the diffusion zone and reach the value of approx. 550 HV 0.05 in the core (Figs. 14, 15). The diffusion zone has a tempered martensite structure with the dispersion precipitates of carbides and nitrides of $Fe_{16}N_2$ type and the grainy nitrides of CrN and $Fe_{2-3}N$ type. In the core of the nitrided

specimens, X40CrMoV5-1 steel has a tempered martensite structure with the M_7C_3 , M_4C_3 and M_3C dispersion alloy carbides. The structure is formed during heat treatment including quenching from 1030°C and tempering at 600°C.

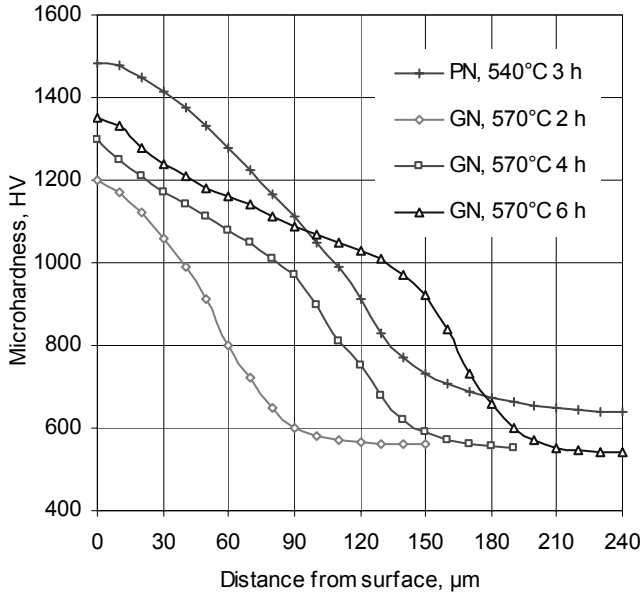


Figure 15. Microhardness distribution in the surface layer of gas-nitrided X40CrMoV5-1 steel (GN) and plasma-nitrided X37CrMoV5-1 steel (PN)

Some functional properties of the nitrided layer strongly depend upon its thickness and the fraction of structure components. Hence, it may be more advantageous to perform nitriding with a method allowing greater control over the structure of the produced surface layer as compared to normal gas nitriding. The plasma nitriding technology (also known as ion nitriding, plasma-ion nitriding or glow-discharge nitriding) progressing using glow discharge, has been dynamically entering the global industry and is successfully replacing the traditional process. This technology is so successful because of the following advantages distinctive for the plasma nitriding process as compared to traditional technologies [4-7]:

- the four basic types of nitrided layers structures can be achieved in a controlled manner: a diffusion zone only, a diffusion and iron nitride zone $\gamma\text{-Fe}_4\text{N}$, a diffusion and iron carbonitride zone $\epsilon\text{-Fe}_{2.3}(\text{C},\text{N})_{1-x}$ and a diffusion zone with the surface layer of $\epsilon + \gamma'$ components; this allows to choose the type of the nitrided layer structure for the specific operating conditions of a given part,

- parts with complicated shapes can be treated,
- a shorter process duration as a charge is heated faster to the treatment temperature and the faster activation of the environment and the treated charge surface,
- controllable increase of dimensions for the parts subject to treatment,
- considerable electricity savings, a batch alone is heated only and no heat-resisting retorts are required, etc.; energy consumption with a specific charge represents 30-40% as compared to gas nitriding,
- the need of using ammonia as a reactive atmosphere is eliminated.

The plasma nitriding of X37CrMoV5-1 steel can be provided as an example. It is revealed with the metallographic observations of the microstructure of steel plasma-nitrided at a temperature of 550°C for 3 hrs that the nitrided layer is characterised by its homogenous, compact and zonal structure. The thickness of the layer that is plasma-nitrided in such conditions is 148 μm . Nitride precipitates are present at the boundaries of steel grains (Fig. 16) that were identified with an X-ray phase analysis method as $\epsilon\text{-Fe}_3\text{N}$ and $\gamma'\text{-Fe}_4\text{N}$ phases. Fe α reflections coming from martensite were also recorded (Fig. 17), with martensite being the matrix of the surface layer and the substrate.

A GDOES analysis performed for hot-work heat treated and plasma nitrided X37CrMoV5-1 tool steel (Fig. 18) shows, apart from the elements present in steel, i.e. Fe, Si, C, Mo, V, Mn, Mo, also the presence of nitrogen introduced into the surface layer in nitriding.

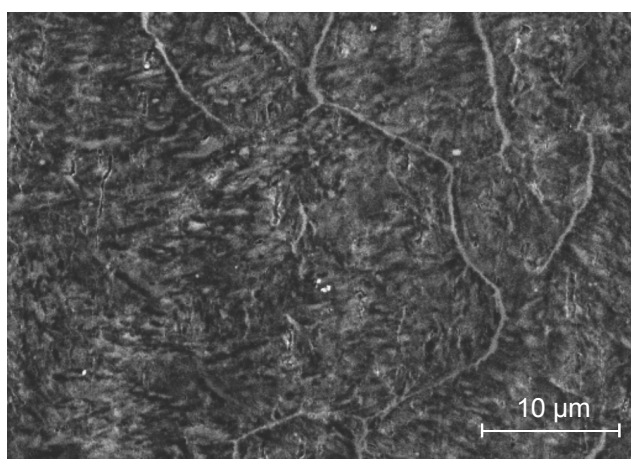


Figure 16. Microstructure of the plasma-nitrided surface layer of X37CrMoV5-1 steel, SE image

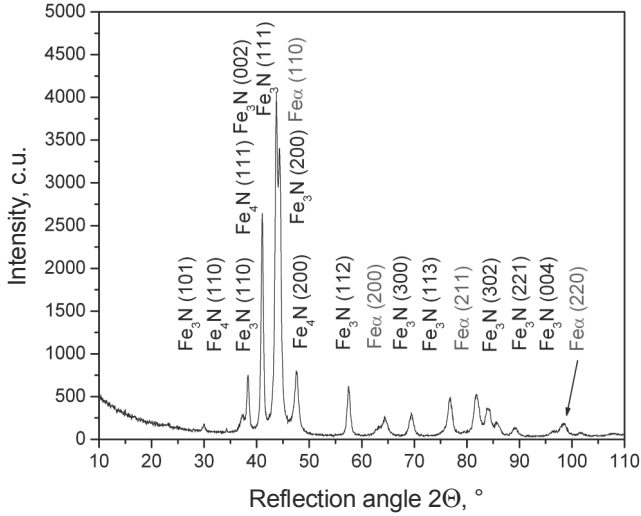


Figure 17. X-ray diffraction pattern of the plasma-nitrided surface layer of X37CrMoV5-1 steel

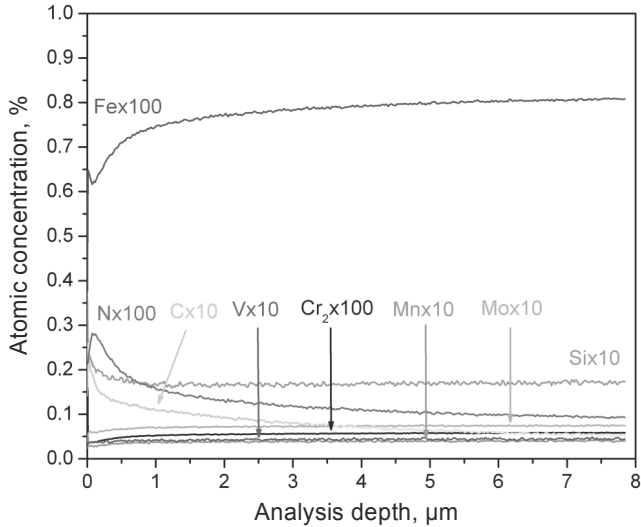


Figure 18. Variations in the concentration of elements in plasma-nitrided X37CrMoV5-1 steel analysed with a GDOES spectrometer

The maximum hardness of the plasma-nitrided layer is approx. 1480 HV 0.1. As distance from the surface increases, the micro-hardness of the tested nitrided layer is slowly decreasing to approx. 610 HV 0.1, which is adequate for the core (Fig. 15).

The tested hot-work heat treated X37CrMoV5-1 tool steel specimens prepared for depositing a plasma-nitrided layer exhibit the roughness of $R_a = 0.008 \mu\text{m}$. Roughness after plasma nitriding rises to $0.08 \mu\text{m}$, i.e. typical for this process [54, 55]. An abrasive resistance test with the pin-on-disc was carried out to create a functional and operating characteristic of the tested plasma-nitrided layer. As the tested layers are intended for work at higher temperatures, the test was made at a room temperature and a temperature increased to 500°C . The friction coefficient variations tests during a test for heat treated steel and for a plasma-nitrided layer allow to conclude that the highest friction coefficient of approx. 0.5 to 0.7, respectively, for 20°C and 500°C , is exhibited in the tested conditions by the heat treated steel (Fig. 19a). If temperature is raised to 500°C , both for heat treated steel and for plasma-nitrided steel, the friction coefficient grows. This is a consequence of higher width and depth of the wear track at an increased temperature and an increased volume of the material worn. The high friction coefficient values for this steel may relate to its relatively low hardness. If a nitride layer is produced on this substrate, the friction coefficient falls to some 0.4 to 0.6 for 20°C and 500°C (Fig. 19b) along with smaller friction width (Fig. 20). The width of the wear tracks is correlated with their depth, thus the volumetric wear of the material removed during the abrasion resistance test was calculated on such basis. The largest material loss was identified for heat treated steel and, e.g. wear at 500°C after 7500 revolutions is 1.31 mm^3 , whereas the volumetric wear of steel with a nitrided layer represents 1.03 mm^3 in such conditions (Fig. 21).

One may conclude based on the tests performed that the highest material wear in the conditions of a pin-on-disc test is seen at a temperature of 500°C . As a result of the plasma nitriding of X37CrMoV5-1 hot-work tool steel, the abrasion resistance of the steel improves substantially as compared to the heat treated steel. A nitrided layer improves the anti-wear properties mainly by reducing a friction coefficient. The layers nitrided in the conditions making it impossible to create a continuous zone of nitrides at the steel surface may also represent a substrate for multizonal hybrid layers [32, 33, 45, 56, 57] with the better functional properties than those achieved after thermochemical treatment with the methods used to date.

Nitriding is one of thermochemical treatment methods enhancing the wear-resistant of many tools, including those exposed to cyclical temperature variations. The substrate of the layers produced through thermochemical treatment should therefore be resistant to thermal fatigue. It was found as a result of the tests that the steels austenitised at a temperature ensuring the fine-grain structure of primary austenite and relatively high hardness after quenching and double

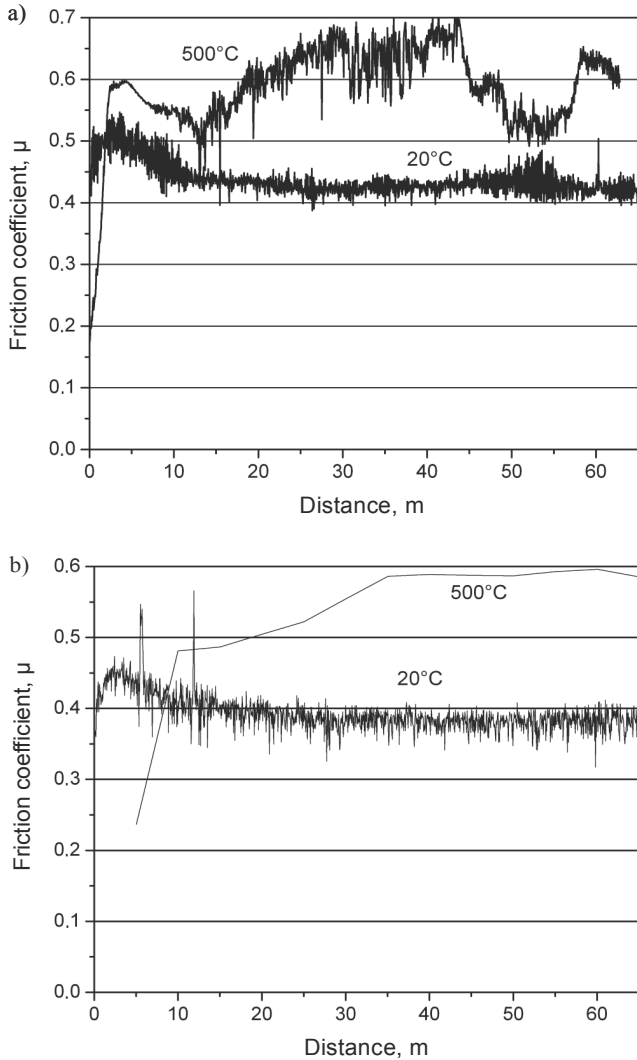


Figure 19. Variation curve of the friction coefficient according to the friction path length for a) thermal treated and b) plasma-nitrided X37CrMoV5-1 steel tested at a temperature 20°C and 500°C for 1000 revolutions

tempering at 600°C exhibit the highest resistance to thermal fatigue. The smallest depth of cracks with their density only slightly increased, are seen for X37CrMoV5-1, X40CrMoV5-1 and 40CrWMoVB17-11-16 steels tempered at 600°C (Fig. 22), i.e. at a temperature of approx. 50 to 100°C higher than this ensuring the secondary hardness effect. If tempering temperature is increased to 650°C, steel hardness is reduced and resistance to thermal fatigue deteriorated.

Low-alloy 38CrMoVB10-4 steel features much lower resistance to thermal fatigue as compared to the steels described above. This results from a high thermal expansion factor, low hardness and a large fraction of non-metallic inclusions. The cracks caused by thermal cycles nucleate at the surface of specimens and are distributed perpendicular to the core direction. The boundaries of primary austenite grains and non-metallic inclusions are the initiators of such cracks most frequently. The cracks are propagated mainly along the boundaries of primary austenite grains (Fig. 23) thus chipping off steel particles from the specimens surface.

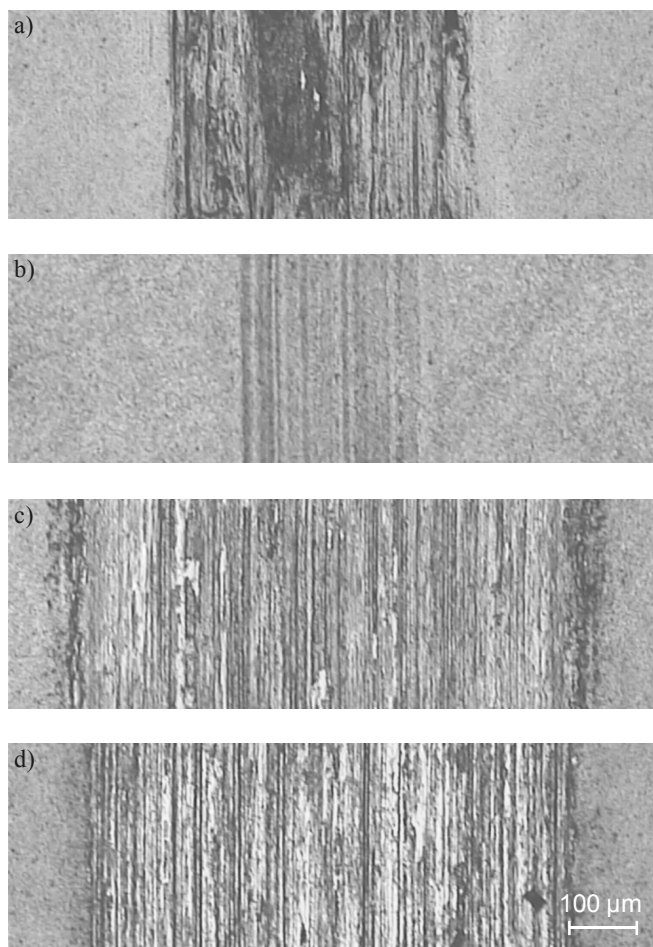


Figure 20. Wear tracks formed in a pin-on-disc test on X37CrMoV5-1 steel: a) and c) heat treated steel, b) and d) plasma-nitrided steel; a test for 7500 revolutions at a temperature of a) and b) 20°C, and c) and d) 500°C

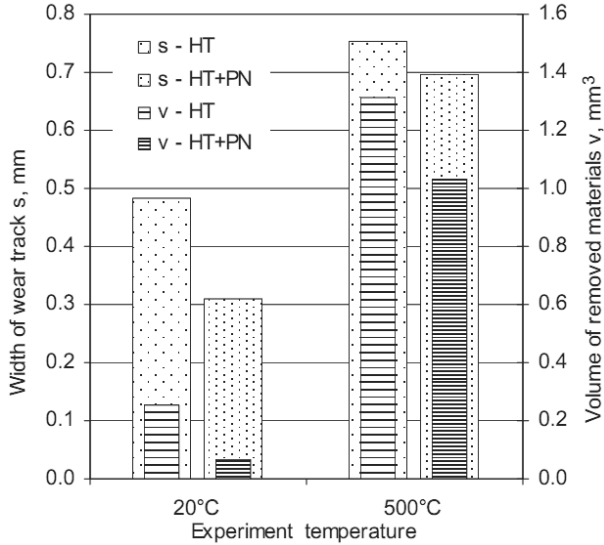


Figure 21. Width of wear tracks and the volume of the removed material for heat treated (HT) and plasma-nitrided X37CrMoV5-1 steel (PN), subject to a pin-on-disc test (after 7500 revolutions)

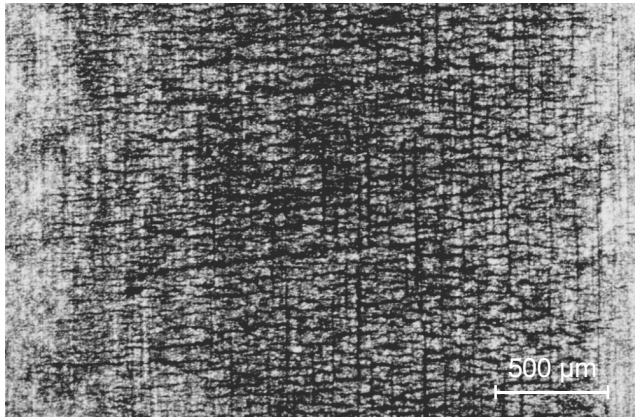


Figure 22. Cracks at the surface of the X40CrMoV5-1(vac) steel specimen quenched from 1030°C and tempered at 600°C, formed during 5000 thermal cycles within 600-100°C with induction heating

Thermal cycles cause structure changes in a steel surface layer. It was found that the steels quenched and tempered in the conditions ensuring maximum resistance to cracking at cyclical temperature variations show a structure of tempered martensite with dispersion alloy carbides, and in particular for: Cr-Mo steels of 5-1 type – M_7C_3 , M_4C_3 and M_3C (Fig. 24), in

40CrWMoVB17-11-16 steel – M_4C_3 , M_2C and M_3C , and in 37CrMoB10-4 steel – M_3C . Cyclical heating and cooling during a thermal fatigue test causes martensite to decompose further with the intensity rising along with a higher maximum temperature of a cycle. Alloy cementite is partially dissolved in the tested high-alloy steels and there are more precipitates of more stable carbides, i.e. MC and M_2C type, and the coagulation of M_3C precipitates is experienced for low-alloy 37CrMoB10-4 steel. Steel matrix recovery is taking place along with phase transitions and the growth of carbides. The structural changes caused by cyclical temperature variations reduce the hardness of the surface layer and support the propagation of cracks.

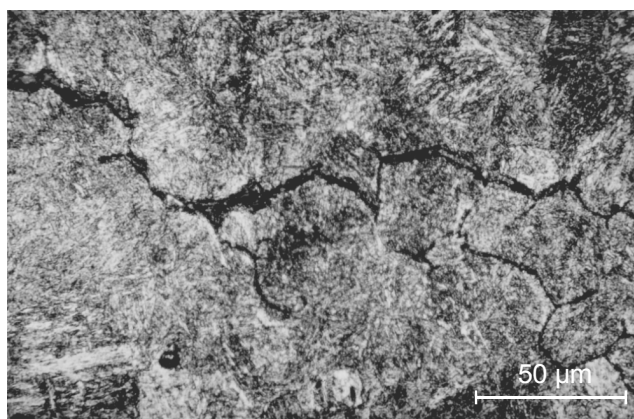


Figure 23. Microstructure within approx. 0.5 mm from the 38CrMoVB10-4 steel specimen quenched from 890°C and tempered at 500°C, after 3000 thermal cycles within 600-100°C

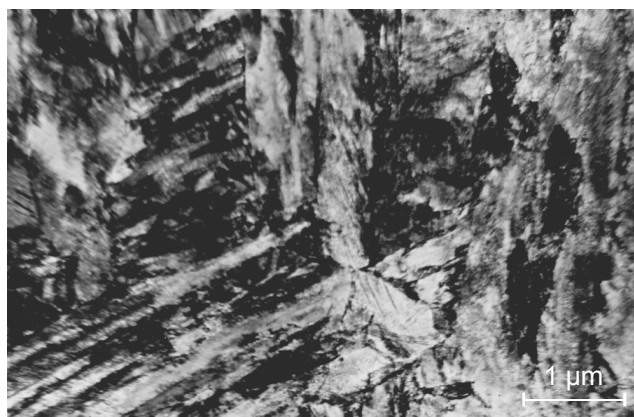


Figure 24. Microstructure of X37CrMoV5-1 steel quenched from 1030°C and tempered at 600°C; thin foil

The studies made reveal that X40CrMoV5-1 steel is most resistant to the formation of a surface cracks lattice during thermal cycles within 700-100°C. 40CrWMoVB17-11-16 steel shows cracks that are somewhat less deeper after thermal cycles at 600-100°C. The steel, however, contains a considerable concentration alloy elements (Table 2) reducing susceptibility to diffusion boriding. As it has been confirmed that a smaller portion of non-metallic inclusions leads to enhanced resistance of steel to cyclic temperature variations, hence further studies after thermochemical treatment were carried out on the specimens made of X40CrMoV5-1 steel after vacuum or electroslag remelting.

A nitrided layer accelerates the nucleation and propagation of cracks during cyclic temperature variations within 600-20°C performed with direct-contact heating at a rate of approx. 85°C/s and cooling in water at a rate of approx. 180°C/s. The depth of cracks is approx. 0.12 mm for steel with a nitrided approx. 0.23 mm thick layer subjected to 25000 thermal cycles. Surface layer hardness in the nitrided specimens declines during thermal cycles because the continuous zone of nitrides is dissolving and because nitride is diffusing deep inside the steel. Diffusion layer hardness is lowering in such conditions causing also the coherent precipitates of Fe₁₆N₂ phase to fade. Mass losses for the nitrided specimens and the specimens subjected to thermal fatigue tests with the corrosive impact of air and water are much smaller than for the heat treated specimens. The corrosive destruction processes are present within the surface cracks and the depth increases along with more thermal cycles. Some of the thermal fatigue resistance tests were carried out with a device where specimens were separated from the activity of the atmosphere and the cooling medium by placing them in air-tight heat-resisting steel capsules. Studies into the effect of thermal cycles with the heating rate of approx. 8.5°C/s and cooling speed of approx. 15.5°C/s within 600-100°C on the progress of surface layer cracks point out that cracks in the nitrided specimens are nucleated and propagated much slower than in the borided specimens and only dozen or so % faster than in those quenched and tempered.

4.2. Structure and properties of surface layers of 18CrMnTi4-4 machine steel subject to carburising and carbonitriding

The surface layer of steel after carburising or carbonitriding should contain near its surface approx. 0.8% of C. This was ensured for the tested 18CrMnTi4-4 machine steel through thermochemical treatment in the conditions stated in sub-chapter 2. The depth largely of the

surface layer depends on NH_3 addition in the atmosphere in carbonitriding – it increases from approx. 0.51 mm after carburising to 0.65 mm after carbonitriding with the addition of 6% NH_3 . This permits, in particular, to produce a surface layer with the required thickness during carbonitriding by approx. 20% faster than during carburising.

The structure of the 18CrMnTi4-4 steel surface layer after carburising at a temperature of 880°C and quenching is composed of partially twinned lath martensite with a high dislocation density (Fig. 25) and of retained austenite with its volume fraction by the surface of approx. 22%. If ammonia is added to the carburising atmosphere, major structure changes are seen in the surface layer. The changes include most of all a retained austenite fraction increased to approx. 39% after carbonitriding with an addition of 6% NH_3 in the atmosphere. This stems from the impact of nitrogen on the decreased initial and final temperature of a martensitic transformation in 18CrMnTi4-4 steel after thermochemical treatment. M_s temperature in the surface layer of carburised steel is approx. 160°C, and it drops to approx. 130°C after carbonitriding with 6% of NH_3 added, and M_f temperature in both cases is below 0°C. The fraction of partially twinned lath martensite in martensite in the surface layer of steel following carbonitriding is going up (Fig. 26), and some martensite grains are characterised by a lath morphology following carbonitriding in an atmosphere with 6% NH_3 added. The dispersion precipitates of cementite occur in the carburised and carbonitrided layer in some areas of martensite. The precipitates are formed during martensite self-tempering. A concentration of carbon in the surface layers is decreasing as the distance from the surface is rising. This, in turn, is mildly reducing hardness to approx. 380 HV 1 in the core (Fig. 27).

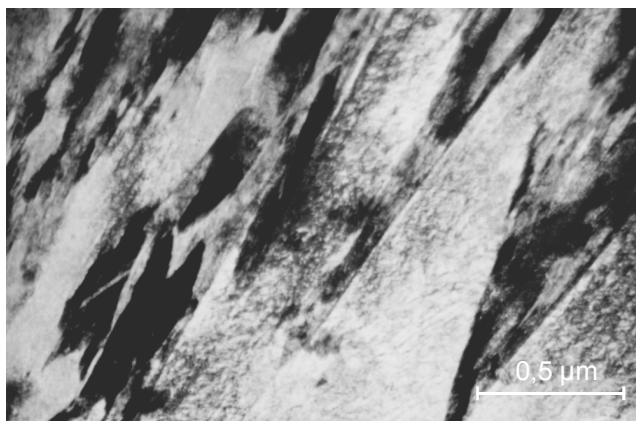


Figure 25. *Microstructure of the surface layer of 18CrMnTi4-4 steel after carburising at a temperature of 880°C and quenching from 840°C, thin foil*

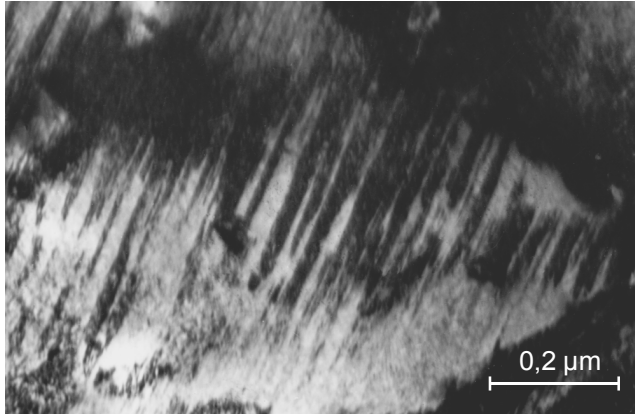


Figure 26. Microstructure of the surface layer of 18CrMnTi4-4 steel after carbonitriding with addition of 6% of NH₃ at a temperature of 880°C and quenching from 840°C, thin foil

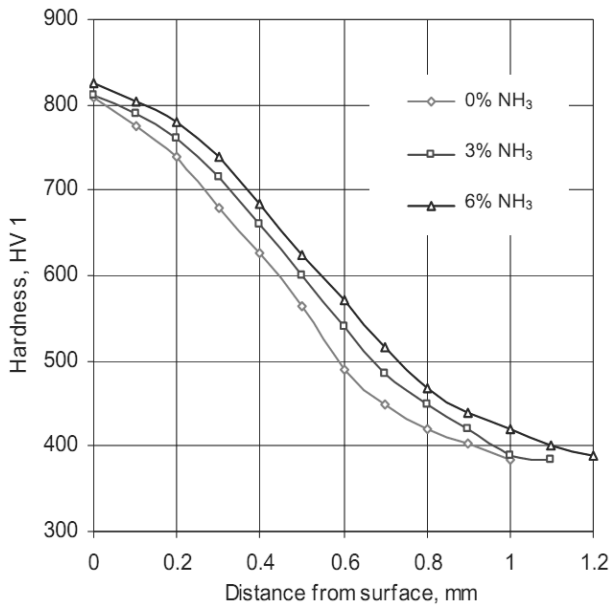


Figure 27. Hardness distribution in a surface layer of 18CrMnTi4-4 steel after carburing and carbonitriding with addition of 3 and 6% of NH₃, at temperature of 880°C for 5 hrs and quenching from 840°C

The final properties of carburised or carbonitrided steel are achieved in quenching and low tempering. As a tempering temperature increases, a concentration of carbon in martensite lowers stemming from cementite precipitation and retained austenite transition. Cementite precipitates are formed predominantly at the boundaries of laths and microtwins in martensite (Fig. 28).

Such processes are developing intensively after tempering at a temperature of above. 200°C thus considerably reducing surface layer hardness. Carbonitrided layers are more resistant to tempering however, i.e. structural changes and hardness reduction occur in them after tempering at a slightly higher temperature as compared to carburised layers.

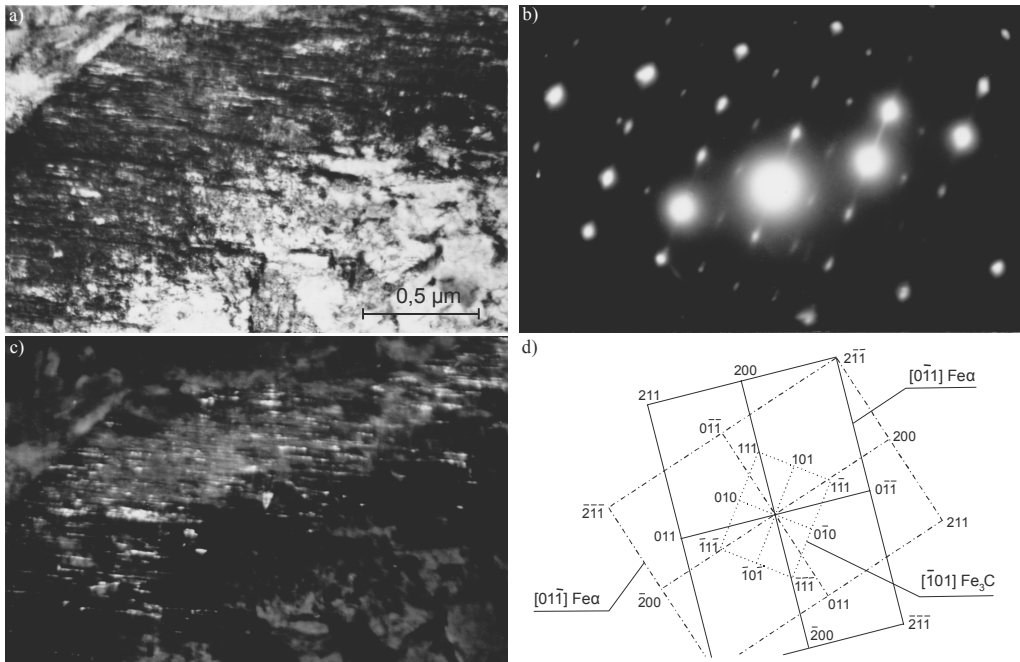


Figure 28. Surface layer microstructure of 18CrMnTi4-4 steel after carburising at temperature of 880°C, quenching from 840°C and tempering at 300°C, thin foil, a – bright field image, b – diffraction pattern from the area as in Fig. a, c – dark field image from 111 M_3C reflection, d – diffraction pattern solution from Fig. b

The tests results for 18CrMnTi4-4 steel specimens with a surface layer produced in carburising or carbonitriding show that fatigue strength Z_{gj} has improved and the best properties are ensured by layers approx. 0.4 mm thick containing approx. 27% of retained austenite at the surface. Thicker layers do not ensure improved functional properties important for the strength of toothed gears, similar as a tempering temperature increased above 200°C causing a decreased fraction of retained austenite and the progressing cementite precipitation from martensite.

The surface layers formed during carburising and carbonitriding contribute to improved fatigue strength properties Z_{gj} and the strength of toothed gears. A prerequisite for achieving

the most advantageous effect of such thermochemical treatment is identifying the impact of multiple factors on the functional properties of specific parts, including in particular atmosphere composition, carburising temperature, quenching and tempering temperature, which are decisive for layer thickness and structure (especially for a fraction of retained austenite) and properties.

4.3. Cutting ability of high-speed HS6-5-2 steel drills subject to thermochemical treatment

The improvement of operating properties of cutting tools with thermochemical treatment has been known from the scientific and technical literature [4, 6]. The low-temperature methods of such treatment are used most often for high-speed steels, carried out for pre-heat treated tools. The tools are usually subjected to nitriding in different atmospheres; oxynitriding, passivation and more and more often to ion implantation. The numerous studies have shown that the most advantageous operating properties for nitrided cutting tools are ensured by a surface layer with a tempered martensite structure with the dispersion precipitates of Fe_{16}N_2 , $\gamma\text{-Fe}_4\text{N}$, $\epsilon\text{-Fe}_{2,3}\text{N}$ nitrides being arranged uniformly in the matrix. The formation of a continuous zone of nitrides and carbonitrides of $\epsilon\text{-Fe}_{2,3}(\text{C},\text{N})$ type at the surface of cutting tools should be prevented during such thermochemical treatment as it increases blade brittleness. Different nitriding methods are used for producing the appropriate surface layer of the tool, especially in the conditions of a limited nitride potential, e.g. in an ammonia atmosphere with addition of nitrogen, nitriding with prior oxidising or plasma nitriding [4, 7, 24, 39]. The life of blades in tools also ameliorates due to a thin layer of spinels being formed on the surface, e.g. Fe_3O_4 . The tools are passivated for this purpose in a water vapour atmosphere or oxynitrided. This is done by introducing a water vapour into the nitriding atmosphere when saturating the surface layer with nitride or after finishing this process. The results of works [4, 30, 58] show that oxynitriding is a very effective method of improving the life of tool blades. Considering the different technologies, types of tools and conditions of operating tests used, the results of such tests do not provide a clear answer concerning the efficiency of different thermochemical treatment methods on the life of tools.

To determine, by comparison, the impact of the selected thermochemical treatment methods on the cutting ability of some tools, tests were carried out on twist drills made of the same

HS6-5-2 steel melting. The drills were heat treated in one batch and subjected to the selected thermochemical treatment processes (see sub-chapter 2). The thermochemical treatment applied has an important effect on the life of high-speed HS6-5-2 steel drills (Fig. 29). The drills made of heat treated steel not subjected to any additional thermochemical treatment are wearing fastest in the tested conditions. The average number of openings bored with such drills is 69, and the blade useful life until next sharpening is approx. 3.2 min. Wearing is done by abrasion from the flank and margin side. Scratches and grooves are formed on the flank face, whereas the chamfered corner is worn out only slightly. Local chipping at the cutting blades occurs when using the drills, both, near the margin and near the chamfered corner. The blades of the plasma-nitrided drills show smaller wear from the flank face as compared to the plasma-nitrided drills, but are more brittle.

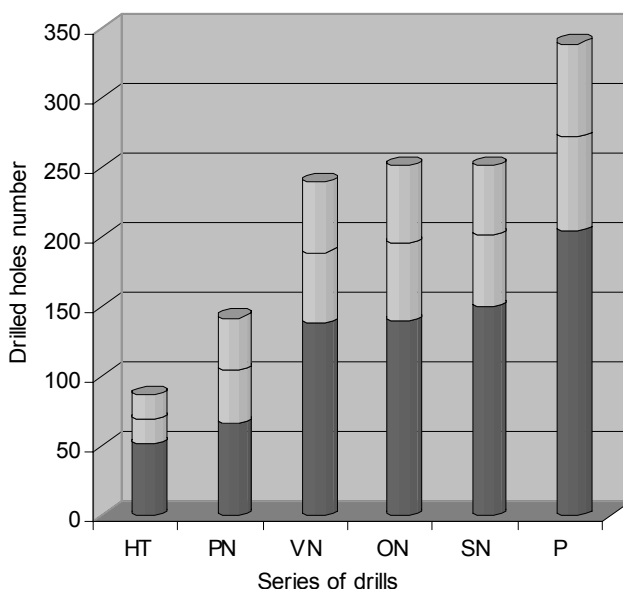


Figure 29. Cutting ability tests results for drills made of HS6-5-2 steel that was heat treated (HT) and plasma nitrided (PN), sulphonitrided and vacuum nitrided (VN), oxynitrided in fluidised bed (ON), nitrided selectively (SN) and passivated in water vapour (P)

Important statistical differences were found between the life of the heat treated drills and the drills subjected to other thermochemical treatment methods. The drills that are sulphonitrided and then vacuum nitrided, oxynitrided in a fluidised bed and nitrided selectively

feature similar durability (Fig. 29). The average number of openings bored with the drills subject to the above types of thermochemical treatment is, respectively, ca. 189, 196 and 201, and the blade life, respectively, approx. 8.6, 8.9 and 9.2 min. The blade life indices given for the thermochemically treated drills do not differ much, but their life build-up is approx. 170 to 190% against the heat treated drills. The blades of vacuum nitrided, selectively nitrided and oxynitrided drills show the similar symptoms of wear such as material losses at the cutting blade, especially close to the margin and the chamfered corner and also the wear of the surface layer at the flank and face surface. Besides, the sulphonitrided and vacuum nitrided drills show minor blade chipping along the cutting blade and chamfered corner.

The passivation of drills in a water vapour atmosphere ensures much longer blade life with the average number of openings bored with such drills being about 272 (Fig. 29). This corresponds to the blade life of approx. 12.4 min. If we take into consideration the average number of openings, passivation ensures the life increase of approx. 290% for the drills as compared to those heat treated. The relative difference between the average number of openings drilled with such drills and the first blade blunting represents approx. 35-39%. Cutting blades become blunt when using passivated drills, especially near the margin and chamfered corner and the oxides layer on the flank and on the face is being destroyed.

The tests carried out show that the presence of an oxides layer on the surface of 5 mm drills has a very positive effect on their life. The largest number of openings until the first blade blunting was bored with the tools having their oxides surface layer, i.e. passivated, nitrided selectively and oxynitrided. The beneficial effect of passivation on the improved life of a drill blade shows that it is reasonable to use such treatment after sharpening the tool each time and allows to implement this technology at some industrial plants, especially when we realise that the process does not require costly equipment.

4.4. Structure and properties of surface layers of X40CrMoV5-1 steels after boriding

Diffusion boriding is used to a limited extent, however, research is still held to modify and optimise the technological process conditions and improve the quality and the properties for the surface layers produced [59-65]. Boriding is considerably improving the strength of some

parts of hot-working machines and tools. Tool steel highly resistant to cyclic temperature variations and with a high austenitisation temperature was chosen as the test material enabling direct quenching from a boriding temperature. A dual-zone layer of borides is forming at the X40CrMoV5-1 steel surface subject to diffusion boriding, i.e. an outer FeB zone with multiple pores and an Fe₂B zone bordering the substrate Fe₂B (Fig. 30). The total thickness of the borides layer is increasing as the boriding time is extending. However, an increase in FeB zone thickness is smaller than the total layer thickness (Fig. 31). Thickness growth for the FeB borides zone is also significantly reduced if a boriding temperature rises above 1000°C. The limited fraction of the FeB phase causes the smaller density of pores and cracks in the surface layer that are forming when cooling the specimens from the boriding temperature. Stresses are produced at the interphase boundary of FeB and Fe₂B borides. The borides are characterised by their high hardness and high elasticity modulus values and different thermal expansion coefficients. The stresses cause cracks perpendicular and parallel to the surface. The cracks perpendicular to the surface are also formed due to the different properties of borides and matrix. During cooling, however, it is possible to partially relax the structural stresses at the interphase boundary of Fe₂B borides with the matrix by deforming austenite or ferrite plastically. The density of surface cracks is rising in heat treatment performed after boriding so that the steel is endowed with its required strength parameters.

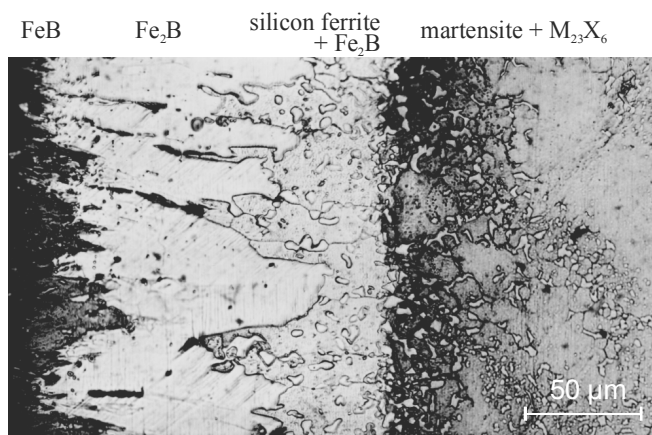


Figure 30. Elongation of FeB and Fe₂B boride grains in the surface layer of X40CrMoV5-1 steel borided at 1030°C for 6 hrs

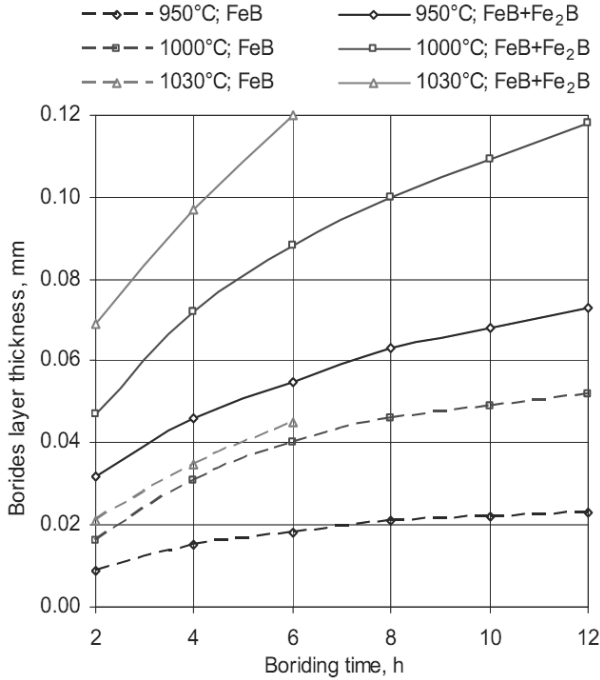


Figure 31. Effect of boriding temperature and duration on borides layer thickness on X40CrMoV5-1 steel

Advantageous conditions are achieved when boriding X40CrMoV5-1 steel at a temperature of 1030°C that is equal to the optimum austenitisation temperature. Considering the high hardenability of the tested steel, the hardening operation can be performed when cooling from boriding temperature. It permits to shorten heat treatment duration, reduce the thickness of the FeB phase zone that is usually porous and decrease the density of surface layer cracks. Hardness and resistance to the wear of the borided layer is enhanced at the same time. The hardness of FeB borides measured on the specimens having compact surface layers with sufficient thickness is ca. 1900-2000 HV 0.05. The values, for the significance level of $\alpha = 0.05$, are substantially higher than the hardness of Fe₂B borides of approx. 1800-1950 HV 0.05 (Fig. 32).

FeB and Fe₂B borides have an elongated shape in the direction perpendicular to the surface, i.e. according to the boron concentration gradient diffusing to steel during thermochemical treatment. The orientation of such crystals' phases, and also a relative intensity of X-ray radiation deflected from the individual families of lattice planes different than the intensity for

powder preparations imply that boride textures exist in the surface layer. This fact was confirmed with an X-ray texture analysis method by showing that both FeB borides and Fe₂B borides have their axial structure of {001} type. The formation degree of this texture increases along with a higher temperature and longer boriding time. The structure tests of thin foils in a transmission electron microscope indicate that dislocations and other lattice defects occur in borides, probably packing errors created as the diffusion layer grows. Dislocations in some Fe₂B grains are distributed in the planes {100} (Fig. 33).

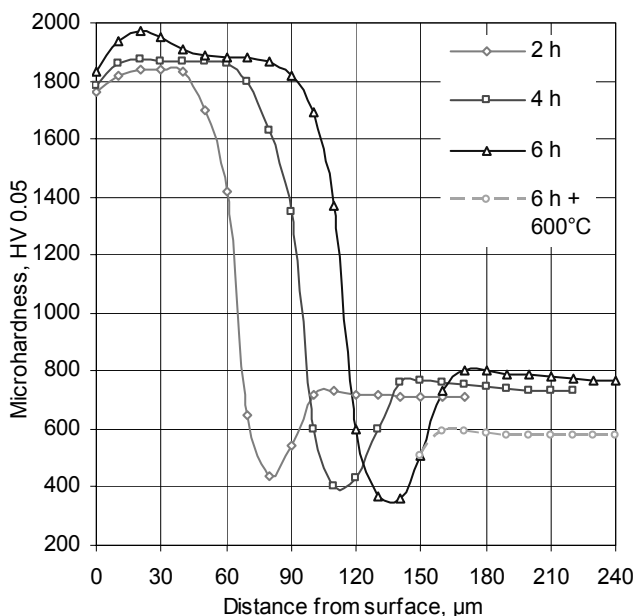


Figure 32. Microhardness distribution in the surface layer of X40CrMoV5-1 steel borided at temperature of 1030°C for 2 to 6 hrs and directly quenched and tempered twice at 600°C

Small, elongated areas exist between Fe₂B phase grains with hardness much smaller than the hardness of borides (Fig. 30). These are ferrite grains probably rich in silicon dislodged from the borides layer. The areas show a limited concentration of boron and chromium and other alloy elements in steel, and the carbon concentration does not vary much compared to this existing in Fe₂B borides. The largest concentration of boron in the borided layer occurs, as expected, near the surface, i.e. in a FeB zone. A lower concentration of boron in this zone occurs in the place of cracks and pores by the surface. The boron concentration in the Fe₂B phase

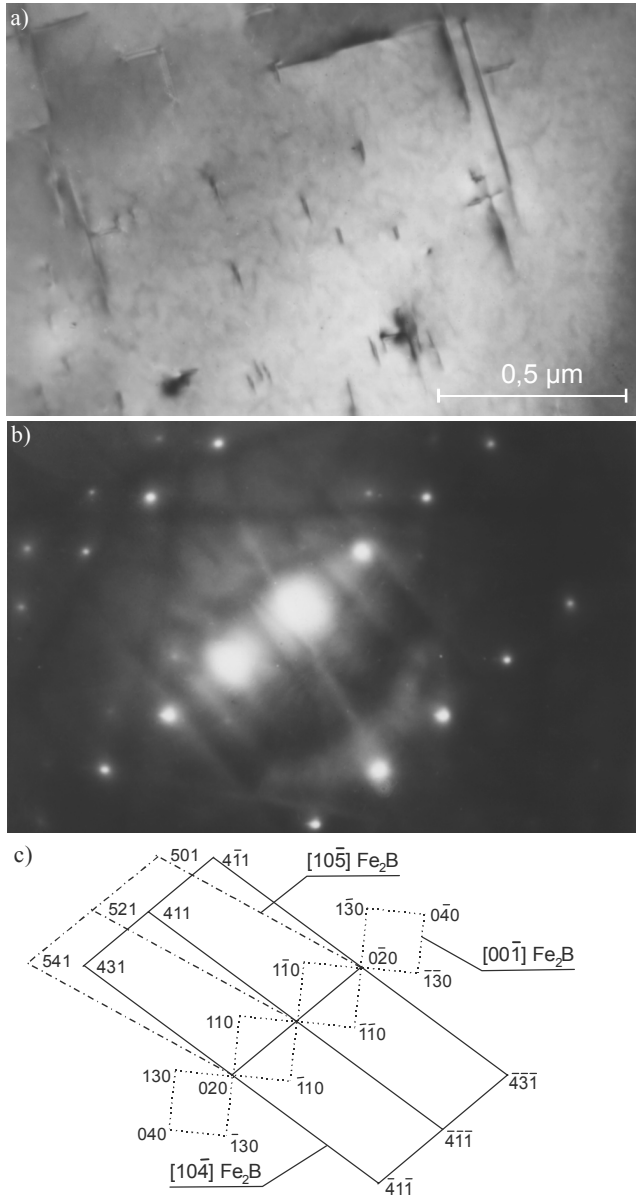


Figure 33. Dislocation in a Fe_2B boride grain within approx. 0.08 mm from the surface of X40CrMoV5-1 steel borided at 1030°C for 6 hrs; thin foil, a – bright field image, b – diffraction pattern from the area as in Fig. a, c – diffraction pattern solution from Fig. b

zone maintains at a constant level, and it is sharply reduced underneath the borides layer. Chromium and other carbide-forming elements introduced into steel, i.e. Mo, V and Mn are Evaluation of selected steel thermochemical treatment technologies using foresight methods

partly dissolving in Fe_2B borides. The large solubility of chromium in Fe_2B borides is a result of chromium and boron forming an isomorphous Cr_2B phase with Fe_2B with similar lattice parameters. Carbide-forming alloy elements occur in the tested steel in a concentration that is too small to produce separate phases with boron. Silicon and carbon do not dissolve in borides, however, hence the elements are dislodged deep inside the steel.

A silicon ferrite zone is situated immediately underneath the borides layer with the grainy precipitates of Fe_2B , and M_{23}X_6 exists slightly deeper (Figs. 30, 34). The silicone concentration increased to approx. 3.5-4.0% exists in the silicone ferrite areas. The quantitative microanalysis method revealed that the grainy precipitates of Fe_2B phase contain, apart from boron, approx. 80% Fe, 8% Cr, 1.5% V and 1% Mo. The zone hardness immediately beneath the borides layer is approx. 340-450 HV 0.05, i.e. much less than the hardness of the specimens core (Fig. 32).

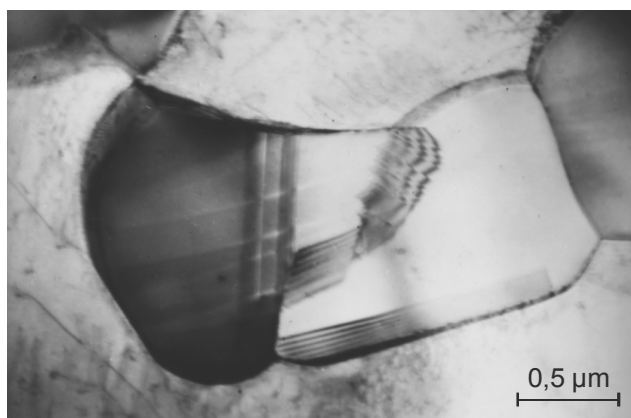


Figure 34. Microstructure within approx. 0.15 mm from the X40CrMoV5-1 steel surface borided at 1030°C for 4 hrs; thin foil

Another martensite zone occurs underneath silicone ferrite with retained austenite and multiple, grainy precipitates of a phase with its lattice structure appropriate for Cr_{23}C_6 carbide (Fig. 30, 34). These are boron carbides that can be assigned an M_{23}X_6 formula where M – Fe, Cr, Mo, V and Mn, and X – C and B. It was found with the X-ray quantitative microanalysis method that $\text{Fe}_{17.6}\text{Cr}_{4.3}\text{V}_{0.7}\text{Mo}_{0.3}\text{Mn}_{0.1}\text{C}_{3.5}\text{B}_{2.5}$ formula is corresponding to one of the analysed boron carbides. Hardness in the martensite zone with grainy precipitates $\text{M}_{23}(\text{C},\text{B})_6$ is about 600 to 800 HV 0.05 depending on the boriding temperature and the cooling method after boriding. Transition to the core with the hardness of approx. 760 HV 0.05 in steel borided

at 1030°C and quenched directly (Fig. 32) occurs only outside that zone. The width of silicone ferrite zones from Fe₂B precipitates and of martensite zones with M₂₃X₆ precipitates extends as temperature is rising and boriding time is extending (Fig. 31). Apart from the phases mentioned, a small fraction of VC and M₇C₃ carbide precipitates (Fig. 30) not dissolved in austenite during boriding is present across the section of the entire diffusion zone.

When austenitising steel that was borided in prior at 950°C, the concentration of alloy and carbon elements is partially homogenised underneath a borides layer, thus contributing to small growth in hardness after quenching by approx. 30 HV 0.05 in the silicon ferrite zone and to growth in core hardness to approx. 760 HV 0.05. The tested steel, that in prior was borided and quenched, is quenched without causing structural changes in the borides layer. However, retained austenite is transformed in the matrix and M₇C₃ and M₄C₃ carbides are precipitated from lath martensite and the recovery of a solid solution begins. This leads to the smaller matrix hardness of approx. 560 to 580 HV 0.05 (Fig. 32).

If specimens with surface layers are cyclically heated and cooled, much faster nucleation and cracks development is seen than in the case of heat treated specimens. This is caused by the structural stresses formed during thermal cycles between the diffusion surface layer and the steel matrix with different physiochemical properties. A deformation occurring as a result of such stresses can be compensated by a plastic deformation of the matrix or by the cracking of the borides layer. Stresses and deformations in the surface layer are even greater in case of rapid temperature variations in a thermal cycle. It was concluded as a result of the tests carried out in equipment with direct-contact heating that cracks are nucleated in the heat treated specimens after approx. 20000 when heating at a rate of approx. 85°C/s and water cooling at a rate of approx. 180°C/s within 600-20°C. On the other hand, the density of surface cracks in the borided specimens is much higher already after 5000 thermal cycles. Some of the cracks in the borided specimens are initiated by cracks in the surface layer after thermochemical treatment. The lattice of surface cracks is becoming more and more evident as the thickness of borides layer and the number thermal cycles grow due to the higher depth, density and width of cracks (Fig. 35). Micro-cracks are growing fastest in borides zone along the boundaries of grains and through the crystals of such phases. The rate of cracks growth is declining in the silicone ferrite zone as stresses may relax in the plastic matrix. Once the crack face passes silicone ferrite to the martensite zone tempered with a large fraction of M₂₃X₆ phase, the intensity of corrosion destruction of steel is accelerated.

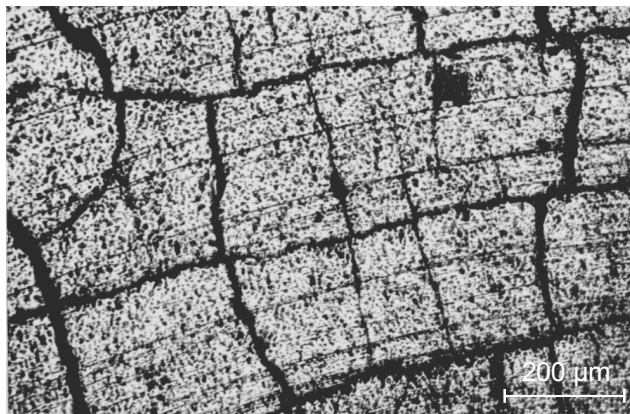


Figure 35. Cracks lattice at the surface of the X40CrMoV5-1 steel specimen borided at a temperature of 950°C for 8 hrs, quenched from 1030°C and tempered twice at 600°C, formed during 25000 thermal cycles within 600-20°C

The tests of influence of thermal cycles with the heating rate of approx. 8.5°C/s and cooling rate of approx. 15.5°C/s within the range of 600-100°C on the progress of surface layers cracks in the samples isolated from the activity of atmosphere and cooling medium and placed in airtight heat-resisting steel capsules reveal that the first cracks in the heat treated specimens are formed after approx. 5000 cycles. The number of cracks in borided samples, however, rises significantly already after 2500 cycles. The depth of maximum cracks in steel with a thick borides layer is rising insignificantly to approx. 10000 thermal cycles due to a broad silicone ferrite zone. More thermal cycles causes the propagation of cracks to the tempered martensite zone with the grainy precipitates of $M_{23}X_6$ phase having smaller cracking resistance. The tests of solid specimens heated through radiation and convection at a rate of approx. 4°C/s and cooled in water at a rate of approx. 47.5°C/s within 600-80°C enable to identify the portion of corrosion processes in the destruction of the steel surface layer. The specimens without surface layers are intensively destroyed by corrosion. In this case the surface is oxidising and an oxides layer is cracking and chipping during cooling. The fusion-borided specimens corrode much slower and higher wear resistance should also be expected until hard borides are preserved in the surface layer. This ensures enhanced resistance for many hot-work tools subjected to boriding as compared to those heat treated. Diffusion boriding has not been used broadly in industrial manufacturing due to technological reasons, however.

5. Technology Roadmapping

The results of foresight research and the results of traditional materials science research have set a basis for creating a series of roadmaps for the technology groups considered. Table 5 provides a representative technology roadmap prepared for carburising and carbonitriding, and an aggregate list containing data provided in all the roadmaps produced for this chapter for the selected steel thermochemical treatment technology groups presented in Table 6. Technology information sheets were also prepared for the research undertaken that detail out and supplement the technology roadmaps. The sheets present technical information being very helpful for the implementation of the technology in the industrial practice, especially in SMEs not having the capital allowing to conduct own research in this field. Table 7 presents selected data stated in the technology information sheets concerning the specific analysed groups of steel thermochemical treatment technologies concerning the impact of technology application on the predicted and expected material properties, the efficiency of preventing the consequences of wear, industry section acc. to the PKD classification having the highest technology applicability. The level of the individual analysis factors has been expressed in relative values using a universal scale of relative states presented in 2.1. of the chapter (Table 1).

6. Summary

Thermochemical treatment methods, especially the different variants of carburising and nitriding, are still being extensively applied to produce surface layers ensuring the enhanced functional properties of machine and tool parts. This mainly relates to surface layers with their thickness between several decimals of mm to over 1 mm, with the mild transition of properties from the part surface to the part core. Investigations are still being conducted aimed at improving the functional properties of the thermochemically treated parts by modifying the conditions during diffusion saturation (temperature variations, saturating medium composition, activating factors) and during heat treatment prior to nitriding or after carburising.

The foresight-materials science research undertaken as part of the work, being part of a wider project aimed at selecting the priority, innovative material surface engineering technologies [66-70], has revealed the stable and certain development outlooks for nitriding as well as

Table 5. An example technology roadmap made for carburising and carbonitriding

TECHNOLOGY ROADMAP		Technology name: Carburising and carbonitriding		Catalogue No. M/4-11-2010/11	
Research scope: Thermochemical technologies		2010-11		2020	
Time intervals		2010-11		2020	
When?		Creating the Critical Technologies Book		Development of priority innovation technologies	
All society and economic perspectives		Creating future events scenarios		Using chances and avoiding difficulties	
Strategy for technology environment influence		Development of information society and intellectual capital		Wide education and effective intensive cooperation between Science and industry representatives	
Technology value		Rainy autumn		Strategy of a dwarf mountain pine in autumn. "To milk this cow" as long as possible strengthening technology attractiveness. To profit the realisation of production in a safe, practicable environment using solid technology which should be implemented and intensively promoted in order to strengthen its attractiveness	
Product		Rooted dwarf mountain pine		Toothed gears, worms, pinions, crankshafts and camshaft, piston rings, shafts of large rolling bearings, pins of slide bearings, sleeves of diesel engine cylinders for trucks and others	
Product quality at the background of foreign competitors		Moderate (6)		Moderate (6)	
Substrate		Low-carbon non-alloy and alloy steels for carburising, e.g.: C10E, C15R, 17Cr3, 12CrMo4, 14NiCrMo13-4, alloy steels for carburising for rolling bearings, e.g.: 20Cr3, 13MoCrN42-16-14, alloy machine steels with C contents between 0.07 to 0.24%			
Kind of surface coatings layers/ processes on substrate surface		Diffusion carburised layer hardened by quenching and low-temperature tempering			
Improved material properties		Hardness, resistance to strain wear, adhesive wear and abrasive wear, resistance to pitting and spalling, contact strength (to fretting and scuffing), erosion strength			
Diagnostic-research equipment		Light microscope, hardness and microhardness tester, or optional transmission and scanning electron microscopes, X-ray diffractometer, work-stand for testing of thermo-mechanical fatigue strength, abrasion and corrosion resistance			
Technology		Carburising and carbonitriding			
Life cycle period		Late mature (4)		Base (3)	
Production type		Serial and mass production		Serial and mass production	
Production organisation form		Non-direct-line production at line and in cells		Non-direct-line p., at line, synch, direct-line p.	
Machine park modernity		Medium (5)		Low (3)	
Automation & robotisation		Moderate (6)		Medium (5)	
Quality and reliability		Moderate (6)		Medium (5)	
Proecology		Quite low (4)		Medium (5)	
Organisation type		Small-, medium- and large-sized enterprises, microenterprises, R&S centres		Large-sized as well as small- and medium-sized enterprises, microenterprises	
Represented industry		Automotive, machine (for mining sector, agriculture, aviation and electrical ones)			
Where?		Quite low (4)		Quite low (4)	
Who?		Quite low (4)		Quite low (4)	
How much?		Moderate (6)		Medium (5)	
		High (8)		Moderate (6)	
		Very high (9)		Moderate (6)	
LEGEND:		Cause and effect connections		Time correlations	
		Capital connections		Two-way transfer of data and/or resources	

carburising and carbonitriding. The technology groups referred to above are characterised by high potential and a neutral environment enabling slow but steady progress. In the future, after having eliminated the difficulties originating from the environment, it may become even more supportive. Such development of events, however, is conditioned, in case of nitriding, by the swift development of the most prospective of its variant, i.e. plasma nitriding (ion, glowing nitriding) and hybrid technologies with nitriding (e.g. in combination with Physical Vapour Deposition – PVD) with the growth of low-pressure nitriding maintaining at the current level and the declining importance of conventional gas nitriding. The optimistic variant of carburising and carbonitriding development requires that such technologies strengthen and grow as: carburising in a controlled atmosphere and variants of carbonitriding, enabling direct quenching and low-temperature tempering of the treated parts. The development of nitriding and carburising and carbonitriding must be also accompanied by an improved ecological aspect of the discussed technologies to minimise the harmful substances emitted to the environment. The weakest development prospects are exhibited by diffusion boriding with its significance most likely declining within the nearest 20 years. This stems from limited effectiveness, high costs and the unfavourable environmental impact of the existing boriding technologies. Another scenario is only possible if there is a major breakthrough by finding a new, wide range of industrial applications and a spectacular improvement in the currently used solutions, especially for environmental protection.

Table 6. Selected main source data used for preparation of technology roadmaps for selected groups of thermochemical treatment, as follows: (A) nitriding and its variants, (B) carburising and carbonitriding, (C) diffusion boriding

No.	Analysed factor		Time interval	Analysed technology		
				A	B	C
1.	All-society and economic perspectives	1 st trend	2010	Creating the Critical Technologies Book		
			2020	Development of priority innovation technologies		
			2030	Statistically high quality of technologies implemented in industry		
		2 nd trend	2010	Creating future events scenarios		
			2020	Using chances and avoiding difficulties		
			2030	Sustainable development		

No.	Analysed factor	Time interval	Analysed technology		
			A	B	C
	3 rd trend	2010	Development of information society and intellectual capital		
		2020	Wide education and effective intensive cooperation between Science and Industry representatives		
		2030	Knowledge-based economy		
2.	Strategy for technology (the most probable one)	2010-2030	Strategy of a dwarf mountain pine in autumn	Strategy of a dwarf mountain pine in autumn	Strategy of an aspen in autumn
3.	Environment influence	2010-2030	Rainy autumn		
4.	Technology value	2010	Rooted dwarf mountain pine	Rooted dwarf mountain pine	Quaking aspen
5.	Product	2010-2030	Forging dies, drawing dies, mouldings for plastics, parts of injection moulders and extruding machines, crankshafts, shafts, piston rings and pins, parts of engines and pumps, cutting tools (milling cutters, drills, screw taps), tools for precision die cutting, medical technology tools, parts of worm gears, of electromagnetic clutches, part of sensor technology and others	Toothed gears, worms, pinions, crankshafts and camshaft, piston pins, piston rings, shafts of large rolling bearings, pins of slide bearings, sleeves of diesel engine cylinders for tracks and others	Mining / drilling tools, working parts of road machines and special machines, including caterpillars, casting equipment, parts of pumps and valves, tools not subjected to dynamic loads (drawing dies, plugs for drawing pipes), parts of weapon, parts of clothing industry machines and others
6.	Product quality at the background of foreign competitors	2010	Quite high (7) ^(*) or Medium (5) ^(**)	Moderate (6)	Quite low (4)
		2020	Quite high (7) ^(*) or Medium (5) ^(**)	Moderate (6)	Quite low (4)
		2030	Quite high (7) ^(*) or Quite low (4) ^(**)	Medium (5)	Quite low (4)
7.	Improved material properties	2010-2030	Fatigue strength (mainly to pitting), hardness, wear resistance, resistance to erosion, corrosion, contact strength (to fretting and scuffing)	Hardness, resistance to strain wear, adhesive wear and abrasive wear, resistance to pitting and spalling, contact strength (to fretting and scuffing), erosion strength	Hardness, resistance to high temperature, wear resistance, resistance to erosion and corrosion

No.	Analysed factor	Time interval	Analysed technology		
			A	B	C
8.	Diagnostic-research equipment	2010-2030	Light microscope, hardness and microhardness tester, optionally: scanning and transmission electron microscopes, X-ray diffractometer, work-stand for testing of thermo-mechanical fatigue strength, abrasion and corrosion resistance		
9.	Life cycle period	2010	Early mature (6)-plasma nitriding Growth (7)- low pressure nitriding Late mature (4)- gas nitriding	Late mature (4)	Late mature (4)
		2020	Early mature (6)-plasma nitriding Growth (7)- low pressure nitriding Base (3)- gas nitriding	Base (3)	Late mature (4)
		2030	Early mature (6)-plasma nitriding Growth (7)- low pressure nitriding Base (3)- gas nitriding	Base (3)	Late mature (4)
10.	Production type	2010	Small- and medium-scale serial Large-scale serial and mass- only *)	Serial and mass	Small- and medium-scale serial
		2020		Serial and mass	Small- and medium-scale serial
		2030		Serial and mass	Small- and medium-scale serial
11.	Production organisation form	2010	Non-direct-line production in cells and at line	Non-direct-line production in cells and at line	Non-direct-line production in process cells
		2020	Non-direct-line production in cells and at line, synchronic direct-line production	Non-direct-line production at line, synchronic direct-line production	Non-direct-line production in process cells
		2030	Non-direct-line production in cells and at line, synchronic and automated direct-line production	Non-direct-line production at line, synchronic and automated direct-line production	Non-direct-line production in process cells
12.	Machine park modernity	2010	Quite high (7) ^{*)} or Medium (5) ^{**)}	Medium (5)	Quite low (4)
		2020	Quite high (7) ^{*)} or Quite low (4) ^{**)}	Quite low (4)	Low (3)
		2030	High (8) ^{*)} or Quite low (4) ^{**)}	Very high (9)	Low (3)

No.	Analysed factor	Time interval	Analysed technology		
			A	B	C
13.	Automation and robotisation	2010	Moderate (6)	Moderate (6)	Low (3)
		2020	Moderate (6)	Medium (5)	Low (3)
		2030	Moderate (6)	Medium (5)	Low (3)
14.	Quality and reliability	2010	Moderate (6)	Moderate (6)	Quite low (4)
		2020	Quite high (7) ^{*)} or Quite low (4) ^{**))}	Medium (5)	Low (3)
		2030	Quite high (7) ^{*)} or Quite low (4) ^{**))}	Medium (5)	Low (3)
15.	Proecology	2010	Quite high (7) ^{*)} or Quite low (4) ^{**))}	Quite low (4)	Low (3)
		2020	Quite high (7) ^{*)} or Quite low (4) ^{**))}	Quite low (4)	Low (3)
		2030	Quite high (7) ^{*)} or Quite low (4) ^{**))}	Medium (5)	Low (3)
16.	Organisation type	2010	Higher education institutions, research institutes, small- and medium-sized enterprises	Small-, medium- and large sized enterprises, microenterprises, R&S centers	Small-, medium- and large sized enterprises
		2020	Higher education institutions, research institutes, small- and medium-sized enterprises	Large-sized as well as small- and medium-sized enterprises, microenterprises	Small-, medium- and large sized enterprises
		2030	Higher education institutions, research institutes, small- and medium-sized enterprises	Large-sized as well as small- and medium-sized enterprises, microenterprises	Small-, medium- and large sized enterprises, microenterprises
17.	Represented industrial branches	2010-2030	Automotive industry, machine industry, tool industry, aviation industry, ship industry	Automotive industry, machine industry (for mining sector, agriculture, motor industry), aviation industry, electrical industry	Machine industry (especially for road and mining sector), electrical machine industry, electrical industry
18.	Staff education level	2010	High (8) ^{*)} or Quite low (4) ^{**))}	Quite low (4)	Quite low (4)
		2020	High (8) ^{*)} or Quite low (4) ^{**))}	Quite low (4)	Quite low (4)

No.	Analysed factor	Time interval	Analysed technology		
			A	B	C
		2030	High (8) ^{*)} or Quite low (4) ^{**)}	Quite low (4)	Quite low (4)
19.	Engagement of scientific-research staff	2010	Quite high (7) ^{*)} or Quite low (4) ^{**)}	Quite low (4)	Medium (5)
		2020	Quite high (7) ^{*)} or Quite low (4) ^{**)}	Quite low (4)	Medium (5)
		2030	Quite high (7) ^{*)} or Low (3) ^{**)}	Quite low (4)	Medium (5)
20.	Capital requirements	2010	Quite high (7) ^{*)} or Quite low (4) ^{**)}	High (8)	Quite low (4)
		2020	Quite high (7) ^{*)} or Medium (5) ^{**)}	Moderate (6)	Quite low (4)
		2030	Quite high (7) ^{*)} or Medium (5) ^{**)}	Moderate (6)	Quite low (4)
21.	Production size determining profitability in firm	2010	Moderate (6)	Medium (5)	Quite low (4)
		2020	Moderate (6)	Quite high (7)	Low (3)
		2030	Moderate (6)	Moderate (6)	Low (3)
22.	Production size in the country	2010	Moderate (6)	Very high (9)	Quite low (4)
		2020	Moderate (6)	High (8)	Low (3)
		2030	Moderate (6)	Moderate (6)	Low (3)

^{*)} for plasma nitriding and for low-pressure nitriding
^{**)} for gas nitriding

Table 7. The selected data provided in the technology information sheets concerning the relevant, analysed groups of thermochemical steel treatment, as follows: (A) nitriding and its variants, (B) carburising and carbonitriding, (C) diffusion boriding

No.	Analysed factor	Analysed technology group					
		A		B		C	
		Properties	Level	Properties	Level	Properties	Level
1.	Impact of technology application on the predicted and expected material properties	Fatigue strength	Quite high (7)	Fatigue strength	Medium (5)	Hardness	Quite high (7)
		Erosion resistance	Quite high (7)	Hardness	Medium (5)	Resistance to high temperature	Quite high (7)
		Hardness	Quite high (7)	Ductility	Medium (5)	Wear resistance	Quite high (7)

No.	Analysed factor	Analysed technology group					
		A		B		C	
		Wear resistance	Quite high (7)	Wear resistance	Medium (5)	Erosion resistance	Moderate (6)
		Corrosion resistance	Medium (5)	Erosion resistance	Medium (5)	Corrosion resistance	Quite low (4)
2.	Efficiency of preventing the consequences of wear	Wear mechanisms	Level	Wear mechanisms	Level	Wear mechanisms	Level
		Strain and fatigue corrosion	Quite high (7)	Strain wear	Moderate (6)	Abrasive wear	High (8)
		Attrition wear	Quite high (7)	Pitting	Moderate (6)	Attrition wear	Quite high (7)
		Fretting	Quite high (7)	Spalling	Moderate (6)	Corrosion determined by contact with liquid Zn or Al	Quite high (7)
		Pitting	Quite high (6)	Abrasive wear	Medium (5)	Uniform corrosion	Medium (6)
		Erosion	Moderate (6)	Fretting	Medium (5)	Local and pitting corrosion	Medium (5)
3.	Industry section acc. to the PKD nationwide classification with the highest technology applicability	Industry sections	Level	Industry sections	Level	Industry sections	Level
		Scientific research and development works	High (8)	Production of metal ready products excluding machinery and equipment	High (8)	Production of metal ready products excluding machinery and equipment	Quite low (4)
		Manufacture of vehicles, semi-trailers and trailers	Quite high (7)	Manufacture of vehicles, semi-trailers and trailers	High (8)	Scientific research and development works	Quite low (4)
		Manufacture of other transport equipment	Moderate (6)	Production of machinery and equipment not elsewhere classified	Quite high (7)	Production of machinery and equipment not elsewhere classified	Medium (5)
		Production of metal ready products excluding machinery and equipment	Moderate (6)	Scientific research and development works	Quite high (7)	Manufacture of vehicles, semi-trailers and trailers	Quite low (4)
		Production of machinery and equipment not elsewhere classified	Quite low (4)	Manufacture of other transport equipment	Moderate (6)	Architectural and engineering activity; technical testing and analyses	Low (3)

When evaluating the importance of the selected groups of steel thermochemical technologies presented in the chapter, their broad scale of contemporary applications in the industry should be emphasised, and in many cases the fact that they cannot be replaced with reasonable alternatives having similar costs. Hence, they will certainly still be important in the nearest 20 years amongst other technologies of engineer materials surface engineering, which justifies their position in The Critical Technologies Book.

References

1. A.D. Dobrzańska-Danikiewicz, E-foresight of materials surface engineering, *Archives of Materials Science Engineering* 44/1 (2010) 43-50.
2. A.D. Dobrzańska-Danikiewicz, Foresight methods for technology validation, roadmapping and development in the surface engineering area, *Archives of Materials Science Engineering* 44/2 (2010) 69-86.
3. A.D. Dobrzańska-Danikiewicz, Main assumptions of the foresight of surface properties formation leading technologies of engineering materials and biomaterials, *Journal of Achievements in Materials and Manufacturing Engineering* 34/2 (2009) 165-171.
4. L.A. Dobrzański, E. Hajduczek, J. Marciniak, R. Nowosielski, *Physical metallurgy and heat treatment of tool materials*, WNT, Warsaw, 1990 (in Polish).
5. L.A. Dobrzański, *Engineering materials and materials design. Fundamentals of materials science and physical metallurgy*, WNT, Warsaw, 2006 (in Polish).
6. T. Burakowski, T. Wierchoń, *Surface Engineering of Metals*, WNT, Warsaw, 1995 (in Polish).
7. P. Kula, *Surface Layer Engineering*, Monographs No. 983, Publishing House of Technical University of Lodz, Lodz, 2000 (in Polish).
8. F.A.P. Fernandes, S.C. Heck, R.G. Pereira, A. Lombardi-Neto, G.E. Totten, L.C. Casteletti, Wear of plasma nitrided and nitrocarburised AISI 316L austenitic stainless steel, *Journal of Achievements in Materials and Manufacturing Engineering* 40/2 (2010) 175-179.
9. Z. Gawroński, B. Kruszyński, P. Kula, Synergistic effects of thermo-chemical treatment and super abrasive grinding in gears' manufacturing, *Journal of Materials Processing Technology* 159/2 (2005) 249-256.
10. P. Kula, R. Pietrasik, K. Dybowski, Vacuum carburizing – process optimization, *Journal of Materials Processing Technology* 164-165 (2005) 876-881.
11. A. Sugianto, M. Narazaki, M. Kogawara, A. Shirayori, S.-Y. Kim, S. Kubota, Numerical simulation and experimental verification of carburizing-quenching process of SCr420H steel helical gear, *Journal of Materials Processing Technology* 209/7 (2009) 3597-3609.

12. R.L. Liu, M.F. Yan, D.L. Wu, Microstructure and mechanical properties of 17-4PH steel plasma nitrocarburized with and without rare earths addition, *Journal of Materials Processing Technology* 210/5 (2010) 784-790.
13. G.-J. Li, J. Wang, Q. Peng, C. Li, Y. Wang, B.-L. Shen, Influence of salt bath nitrocarburizing and post-oxidation process on surface microstructure evolution of 17-4PH stainless steel, *Journal of Materials Processing Technology* 207/1-3 (2008) 187-192.
14. J. Ratajski, T. Suszko, Modelling of the nitriding process, *Journal of Materials Processing Technology* 195/1-3 (2008) 212-217.
15. K. Genel, Estimation method for the fatigue limit of case hardened steels, *Surface & Coatings Technology* 194 (2005) 91-95.
16. D.-W. Kim, B.-S. Lim, Plasma and Vacuum Carburizing Processes and Mechanical Properties of SCM 415 Steel, *KSME International Journal* 13/8 (1999) 634-641.
17. S.-K. Lyu, K. Inoue, G. Deng, M. Kato, Effect of Surface Treatments on the Strength of Carburized Gears – An Application of Fracture Mechanics, *KSME International Journal* 12/2 (1998) 206-214.
18. I.N. Roslyakov, V.I. Kolmykov, Influence of Nitrocementation on the Increase in Fatigue Strength and Wear Resistance of Galvanic Iron Coatings, *Russian Engineering Research* 29/9 (2009) 903-904.
19. M. Fujii, M. Seki, A. Yoshida, Surface durability of WC/C-coated case-hardened steel gear, *Journal of Mechanical Science and Technology* 24 (2010) 103-106.
20. P. Kula, J. Olejnik, J. Kowalewski, New vacuum carburizing technology, *Heat Treating Progress* 1 (2001) 57-60.
21. M. Szota, J. Jasiński, Modelling of carburising parameters, *Materials Engineering* 1 (2010) 614-618 (in Polish).
22. J. Walkowicz, J. Smolik, C. Bertrand, A. Ioncea, Thermochemical treatment and operating life of hot forging dies, *Materials Engineering* 5 (2005) 214-218 (in Polish).
23. P. Kochmański, J. Nowacki, Initial growth phase of gas-nitrided layer on 17-4PH precipitation hardening stainless steel, *Materials Engineering* 5 (2005) 314-318 (in Polish).
24. K. Maruśić, H. Otmačić, D. Landek, F. Cajner, Modification of carbon steel surface by the Tenifer® process of nitrocarburizing and post-oxidation, *Surface & Coatings Technology* 201 (2006) 3415-3421.
25. Z. Gawroński, A. Malasiński, J. Sawicki, A selection of the protective atmosphere eliminating the inter-operational copper plating step in the processing of gear wheels, *Archives of Materials Science and Engineering* 44/1 (2010) 51-57.
26. G.H. Farrahi, H. Ghadbeigi, An investigation into the effect of various surface treatments on fatigue life of a tool steel, *Journal of Materials Processing Technology* 174/1-3 (2006) 318-324.
27. R.L.O. Basso, R.J. Candal, C.A. Figueroa, D. Wisnivesky, F. Alvarez, Influence of microstructure on the corrosion behavior of nitrocarburized AISI H13 tool steel obtained by pulsed DC plasma, *Surface & Coatings Technology* 203 /10-11 (2009) 1293-1297.

28. D.-C. Wen, Erosion and wear behavior of nitrocarburized DC53 tool steel, *Wear* 268/3-4 (2010) 629-636.
29. W. Gräfen, B. Edenhofer, New developments in thermo-chemical diffusion processes, *Surface & Coatings Technology* 200/5-6 (2005) 1830-1836.
30. T. Babul, Z. Obuchowicz, W. Grzelecki, Nitro-Oxidation of Tools Manufactured from High-Speed Steel, *Materials and Manufacturing Processes* 24/7-8 (2009) 842-846.
31. K.-T. Youn, Y.-M. Rhyim, J.-H. Lee, C.-G. Lee, Y.-C. Jung, An Evaluation of Thermal Fatigue Cracking and Chemical Reaction in Die Casting Mould, *Key Engineering Materials* 345-346 (2007) 701-704.
32. J. Smolik, J. Walkowicz, J. Tacikowski, Influence of the structure of the composite: 'nitrided layer/PVD coating' on the durability of tools for hot working, *Surface & Coatings Technology* 125/1-3 (2000) 134-140.
33. J. Smolik, M. Gulde, J. Walkowicz, J. Suchanek, Influence of the structure of the composite: 'nitrided layer/PVD coating' on the durability of forging dies made of steel DIN-1.2367, *Surface & Coatings Technology* 180-181 (2004) 506-511.
34. J. Adamczyk, M. Przybył, Effect of nitriding on structure and properties of high-speed steels, *Works by the Institute for Ferrous Metallurgy* 33/34 (1978) 109-114 (in Polish).
35. J. Adamczyk, M. Przybył, Effect of nitriding conditions on mechanical properties of selected tool steel grades, *Proceedings of the Conference on Carbides–nitrides–borides*, Poznań, 1981, 260-272 (in Polish).
36. J. Adamczyk, M. Przybył, E. Hajduczek, Structure of nitrides layers on selected tool steels, *Proceedings of the 6th Conference on Electron Microscopy of Solids*, Kraków – Krynica, 1981, 266-270 (in Polish).
37. J. Adamczyk, E. Hajduczek, Effect of surface diffusion layers on thermal fatigue of hot work tool X40CrMoV5-1 steel, *Metal Science and Heat Treatment* 66 (1983) 9-14 (in Polish).
38. J. Adamczyk, E. Hajduczek, Phase composition of surface layer of diffusion borided X40CrMoV5-1 steel, *Proceedings of the 3rd International Conference "Carbides, nitrides, borides"*, Poznań – Kołobrzeg, 1984, 272-278 (in Polish).
39. J. Adamczyk, E. Hajduczek, L.A. Dobrzański, M. Czech, H. Słupik, Cutting ability tests for thermochemically treated HS6-5-2 steel drills, *Works by the Centre for Technical Development* 64 (1986) 211-216 (in Polish).
40. J. Adamczyk, K. Adamaszek, E. Hajduczek, H. Szymura, Effect of carbonitriding on the structure and properties of 18CrMnTi4-4 steel surface layers, *Proceedings of the Scientific and Technical Conference on Issues of Modern Thermochemical Treatment*, Warsaw, 1984, Vol. 1, 16-23 (in Polish).
41. J. Adamczyk, K. Adamaszek, E. Hajduczek, Effect of carbonitriding on the structure of surface layers and fatigue resistance of 18CrMnTi4-4 steel, *Proceedings of the 5th International Congress on Heat Treatment of Materials*, Budapest, Hungary, 1986, Vol. II, 759-766 (in Russian).

42. J. Adamczyk, E. Hajduczek, Microstructure of borided layer of Cr-Mo-V die steel, Proceedings of the 5th International Congress on Heat Treatment of Materials, Budapest, Hungary, 1986, Vol. II, 798-805 (in Russian).
43. L.A. Dobrzański, J. Adamczyk, E. Hajduczek, M. Czech, H. Słupik, Cutting ability tests of the drills after thermochemical treatments, Proceedings of the 1st International Scientific Conference "Achievements in the Mechanical and Material Engineering", Gliwice, 1992, Vol. 1, 29-34 (in German).
44. L.A. Dobrzański, J. Mazurkiewicz, E. Hajduczek, J. Madejski, Comparison of the thermal fatigue resistance and structure of the 47CrMoWVTiCeZr16-26-8 hot-work tool steel with X40CrMoV5-1 type one, Journal of Materials Processing Technology 113 (2001) 527-538.
45. M. Polok-Rubinić, L.A. Dobrzański, M. Adamiak, Comparison of the PVD coatings deposited onto plasma nitrided steel, Journal of Achievements in Materials and Manufacturing Engineering 42 (2010) 172-179.
46. L. Georghiou, J.C. Harper, M. Keenan, I. Miles, R. Popper (eds.), The Handbook of Technology Foresight. Concepts and Practice, Edward Elgar Publishing Ltd., UK, 2008.
47. L.A. Costanzo, R.B. Mackay, Handbook of Research on Strategy and Foresight, Edward Elgar Publishing, UK, 2009.
48. A.D. Dobrzańska-Danikiewicz, The methodological fundamentals of development state analysis of surface engineering technologies, Journal of Achievements in Materials and Manufacturing Engineering 40/2 (2010) 203-210.
49. A.D. Dobrzańska-Danikiewicz, Foresight of materials surface engineering as a tool stimulating sustainable development and to increase the quality of technology, Journal of Machine Engineering 10/3 (2010) 48-59.
50. The Boston Consulting Group, The Product Portfolio, Perspectives 66 (1970).
51. N. Gerdşri, R.S. Vatananan, S. Dansamasatid, Dealing with the dynamics of technology road-mapping implementation: A case study, Technical Forecasting & Social Change 76 (2009) 50-60.
52. Y. Yasunaga, M. Watanabe, M. Korenaga, Application of technology roadmaps to governmental innovation Policy for promoting technology convergence, Technical Forecasting & Social Change 76 (2009) 61-79.
53. R. Phaal, G. Muller, An architectural framework for roadmapping: Towards visual strategy, Technological Forecasting & Social Change 76 (2009) 39-49.
54. J.C.A. Batista, C. Godoy, V.T.L. Buono, A. Matthews, Characterisation of duplex and non-duplex (Ti, Al)N and Cr-N PVD coatings, Materials Science and Engineering A 336 (2002) 39-51.
55. I. Lee, I. Park, Microstructures and mechanical properties of surface-hardened layer produced on SKD 61 steel by plasma radical nitriding, Materials Science and Engineering A 449-451 (2007) 890-893.

56. K. Dybowski, Ł. Kaczmarek, R. Pietrasik, J. Smolik, Ł. Kołodziejczyk, D. Batory, M. Gzik, M. Stegliński, Influence of chemical heat treatment on the mechanical properties of paper knife-edge die, *Journal of Achievements in Materials and Manufacturing Engineering* 37/2 (2009) 422-427.
57. B. Podgornik, S. Hogmark, O. Sandberg, V. Leskovsek, Wear resistance and anti-sticking properties of duplex treated forming tool steel, *Wear* 254/11 (2003) 113-1121.
58. V.I. Shemegon, Surface hardening of twist drills, *Metal Science and Heat Treatment* 40/6 (1998) 243-249.
59. K. Genel, Boriding kinetics of H13 steel, *Vacuum* 80/5 (2006) 451-457.
60. B.S. Mann, Boronizing of cast martensitic chromium nickel stainless steel and its abrasion and cavitation-erosion behaviour, *Wear* 208/1-2 (1997) 125-131.
61. C. Martini, G. Palombarini, G. Poli, D. Prandstraller, Sliding and abrasive wear behaviour of boride coatings, *Wear* 256/6 (2004) 608-613.
62. S. Taktak, Tribological behaviour of borided bearing steels at elevated temperatures, *Surface & Coatings Technology* 201/6 (2006) 2230-2239.
63. M. Kulka, A. Pertek, Gradient formation of boride layers by borocarburing, *Applied Surface Science* 254/16 (2008) 5281-5290.
64. I. Gunes, S. Ulker, S. Taktak, Plasma paste boronizing of AISI 8620, 52100 and 440C steels, *Materials and Design* 32/4 (2011) 2380-2386.
65. M. Mathew, P.K. Rajendrakumar, Optimization of process parameters of boro-carburized low carbon steel for tensile strength by Taquchi method with grey relational analysis, *Materials and Design* 32/6 (2011) 3637-3644.
66. A.D. Dobrzańska-Danikiewicz, T. Tański, S. Malara, J. Domagała-Dubiel, Assessment of strategic development perspectives of laser treatment of casting magnesium alloys, *Archives of Materials Science Engineering* 45/1 (2010) 5-39.
67. A.D. Dobrzańska-Danikiewicz, E. Jonda, K. Labisz, Foresight methods application for evaluating laser treatment of hot-work steels, *Journal of Achievements in Materials and Manufacturing Engineering* 43/2 (2010) 750-773.
68. A.D. Dobrzańska-Danikiewicz, K. Lukaszewicz, Technology validation of coatings deposition onto the brass substrate, *Archives of Materials Science Engineering* 46/1 (2010) 5-38.
69. A.D. Dobrzańska-Danikiewicz, A. Drygała, Foresight methodology application for laser texturing of silicon surface, *Proceedings of Polish-Ukrainian Scientific Conference – Mechanics and Computer Science*, Chmielnicki, Ukraine, 2011, 156-157.
70. FORSURF. Structural project in realisation, www.forsurf.pl 2009-2012 (in Polish).