POLITEHNICA BUCHAREST NATIONAL UNIVERSITY FOR SCIENCE AND TECHNOLOGY

DOCTORAL SCHOOL MATERIALS SCIENCE AND ENGINEERING

DOCTORAL THESIS

Summary

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SULPHO-NITROCARBURIZING THERMOCHEMICAL TREATMENT IN SOLID POWDERY ENVIRONMENTS APPLIED TO CUTTING TOOLS MADE FROM LEDEBURITIC STEELS

SUMMARY

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Key word: sulpho-nitrocarburizing, cutting tools, high speed steels, solid powdery environments, carbamide, present stress in cutting tools working, testing the performance of cutting tools, experimental programming, second-order non-compositional programming method – active experiment, effects quantification by varying the components percentage of solid powdery environments, compositional analysis of the resulting gases from the foils combustion

ABSTRACT

The present paper present how behaves carbamide during heating and at the same time about its capacity to provide carbon and nitrogen in solid powdery environments on matrices of Armco iron in thermochemical treatment of sulphonitrocarburizing, without generating toxic components or if these occur are in very small quantities. It has been demonstrated experimentally that up to temperature 750°C increases its ability to supply nitrogen at the expense of carbon and at higher temperatures up to T=950°C these two reports are reversed. The second-order non-compositional programming method – active experiment was used with a view to quantify the effects by varying the components percentage of solid powdery environments used for sulpho-nitrocarburizing. The resulting conditions of previous experimental work determined as to be optim were extrapolated to metallic matrix made from high speed steel of HS18-0-1. Throughout the duration of experimental research, Fe-ARMCO foils were sulpho-nitrocarburized in solid powdery environments which by medium component combustion and analysis of the resulting gases leads to the completion and validation of the results obtained on massive metal matrices. At the same time, it was checked the functionality during exploitation of some removable tools which were thermochemical processed in different variants, including thermochemical treatment of sulphonitrocarburing in solid powdery environments where carbamide can be found.

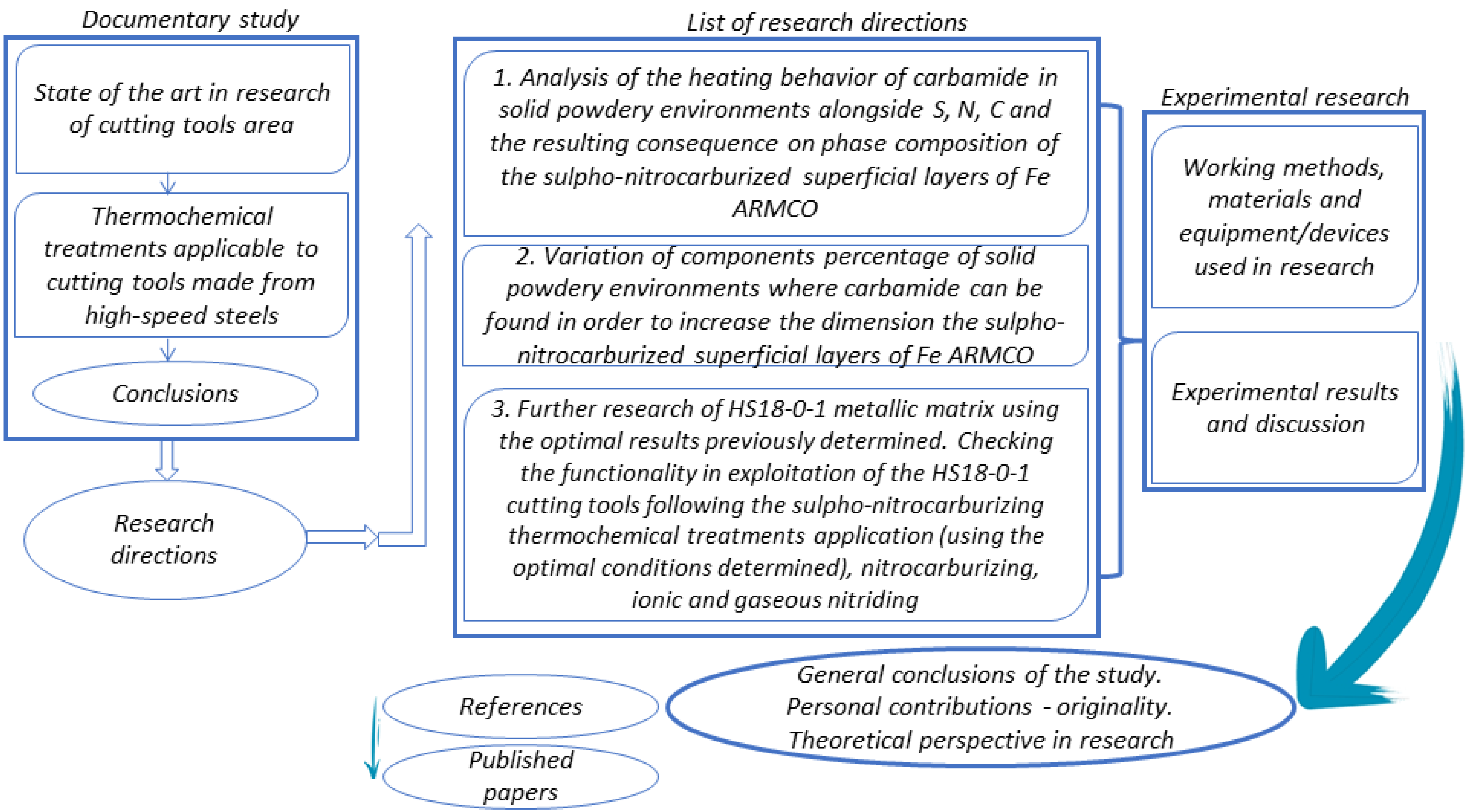


Figure 1. *Structure of doctoral thesis*

INTRODUCTION

Cutting tools play an important role in mechanical processing industry and are often limited by their performance over time. Numerous researchers have pursued over time to develop and improve the performance of cutting tools to extend their service life as much as possible.

There are several methods by which the performance of cutting tools can be improved, and the choice of the right method depends on the specific application and the type of cutting tool used. Thermochemical treatments applied to cutting tools start to be used in the early 20^{th} century, but the technology has developed tremendously over recent decades, so the thermochemical treatments are now much advanced. Over the years, various methods of thermochemical treatments have been developed, and researchers continue to discover new technologies and methods to improve the performance of cutting tools by applying thermochemical treatments. The application of thermochemical treatment methods depends on the metallic material from which the cutting tools are made. A variety of steels are used for manufacturing cutting tools, but the high-speed steels are chosen regularly due to their thermal and mechanical properties.

These steels present a high concentration of carbon and also another chemical components, such as tungsten, molybdenum, cobalt and vanadium, ensuring high hardness, wear resistance and thermal stability. High-speed steels were developed at the beginning of the 20^{th} century and were used in mechanical processing industry of metallic materials since the beginning.

Generally, manufacturing the cutting tools by using the high-speed steels, in particular, the ledeburitic steels, represents an important stage, allowing the users to obtain high performance in mechanical processing.

There are several types of thermochemical treatments which can be applied successfully to cutting tools in order to improve the performance, namely carbonitriding at low temperature or nitrocarburizing, nitriding, sulphating and sulpho-nitrocarburizing.

Present work aims to analyze how the performance of cutting tools made from ledeburitic steels sulpho-nitrocarburized in solid media powder containing carbamide can be improved.

PART I: DOCUMENTARY STUDY

CHAPTER 1: State of the art in research of cutting tools area

1.1. Theoretical considerations on cutting tools – recommended steels for production, requests to which the cutting tools are subjected and evaluation of the performance of cutting tools during working

Cutting tools represents manual or mechanic working tools used to remove the material from the workpiece by cutting, milling, drilling, chip removal following mechanical processing [1]. Cutting tools present following components:

- cutting edge (active part);
- fastening-positioning component on machine tool;
- tool body.

Mechanical processing represents an important stage in manufacturing cycle consisting in changing geometric shapes, the shapes, the dimensions and the quality of the semi-product surfaces and thus obtaining finished part.

The technological process of mechanical machining can be classified as follows:

- metal-cutting processes;
- mechanical processing by plastic deformation;
- fast production of prototypes by mechanical process.

Metal cutting process is represented by technological operations through which the removal of a layer from the surface of a metallic semi-product is carried out in chips form, in order to obtain surfaces with remarkable dimensional accuracy.

The removal of the required material layer from the surface of a workpiece is obtained by making a cutting movement on a certain direction and at a certain speed [2]. Technological system needed for metal cutting process it is composed of the following components (*figure 1.1)*:

- machine tool with the help of which mechanical processing is performed (MU);
- the cutting tool used for mechanical processing process(S)
- retaining device of prefabricated part (D);
- retaining device of cutting tool (DS);
- prefabricated part to be processed (P) [3].

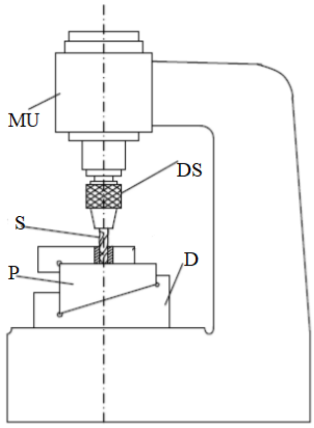


Figure 1.1 *Components of a technological system used in the mechanical cutting process [4]*

A metal material can be easily machined by cutting when high cutting speeds can be used but with minimal expenses, limited energy consumption and low mechanical stress, obtaining optimal roughness of the processed surfaces [2].

The cutting tools must have the following characteristics to achieve quality mechanical processing:

- the high temperature hardness of cutting tools represents the metalic materials property from which the abrasion resistance preservation is made under high temperature conditions;
- tenacity is the ability of a cutting tool to withstand mechanical machining operations without breaking partially or totally (fracture);
- wear resistance refers to the ability of cutting tools to have a satisfactory service life before they are replaced or re-sharpened due to degradations occurring on the surface of the active component following the machining mechanicals [5].

Mechanical machining by cutting has many aspects that require constant analysis due to the continuous evolution of the materials being processed, the geometry and the materials from which the cutting tools are made and the type of their coating [6].

Significant factors influencing the choice of materials for the manufacture of cutting tools are the material from which the workpieces, the tool pattern and the operating conditions are made [7].

1.1.3. Requests to which cutting tools are subjected in operation and types of frequent wears. Assessment of cutting tool performance

The main problems that can arise in the process of cutting tools are mainly caused by the phenomenon of their wear. The wear of tools seriously affects the efficiency of mechanical processing and the quality of the chip surfaces [13].

According to the research of Jiang and Xu [14], it was concluded that the process of wear of a cutting tool can be divided into five stages: the initial phase of use, which is, the usual phase of use, the micro-rupture stage, the stage of rapid wear and fracture of the tool.

Depending on the nature of the factors affecting the properties of the surfaces of cutting tools, the following specific mechanisms of use may appear:

- abrasive wear refers to the process of damaging cutting tools due to their friction, cutting or scratching with other hard and abrasive materials used in mechanical processing. Abrasive wear depends by the carbide content in the composition of the metal material from which the cutting tool it is made.[15];
- diffusion wear is determined by the migration of a chemical element from the composition of high speed steels from which cutting tools are made to the cutting material. This mechanism reduces the strength of cutting tools and favors the appearance of wear craters [16];
- oxidation wear leads to the appearance of gaps in the surface layers of the coating and results in their loss at high temperatures;
- adhesion wear occurs at low processing temperatures of the active component of the cutting tool and leads to the continuous division of the edge of the tool itself;
- fatigue wear (static or dynamic) is a thermo-mechanical effect that causes fatigue of the metallic material from which the cutting tool is made and subsequently leads to its gradual destruction [15].

Figure 1.2 shows areas of use on the surface of a cutting tool resulting from the formation of chips:

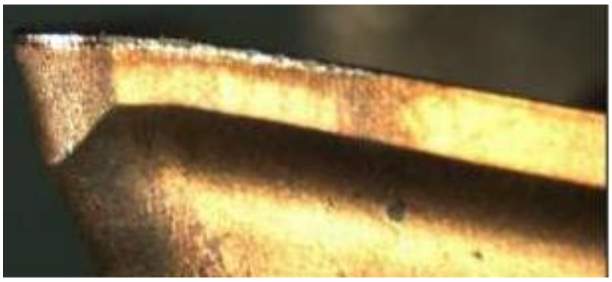


Figure 1.2. *The wear present on the flank of turning tool [17]*

The wear can be observed on the surface of the flank and it is mainly caused by its abrasion when it comes into contact with the hard part of the constituents of the workpiece. This breakdown mechanism can be observed, in particular, during the processing of cast iron and steels [15].

These types of wear can lead to fractures (*figure 1.3*). Fracture is one of the least desired ways of breakdown of cutting tools [18].

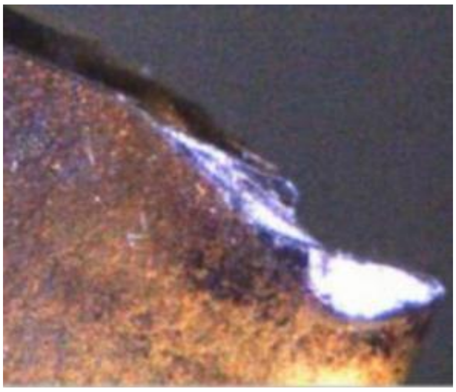


Figure 1.3. *Fracture of a turning tool [19]*

An important parameter by which the performance of cutting tools can be evaluated is to evaluate the durability of cutting tools. The durability of cutting tools is influenced by the following factors:

- the maximum permissible cutting speed (determined by the moment when catastrophic wear occurs) can be determined by the means of front cutting [20]. The maximum permissible cutting speed represents the maximum speed which can be obtained by the cutting tool during working until the moment of catastrophic wear occurs. The front cutting consists in setting a certain speed with which the cutting tool moves from the center of the metal material to its periphery and repeating these movements until the moment of the catastrophic use of the tool cutting. Thus, the maximum permissible cutting speed it is determined [21];
- the maximum cutting length with the maximum permissible cutting speed (until the tool wears out completely, meaning the maximum cut length between two resharpenings) can be determined by the means of longitudinal cutting [20]. The longitudinal cutting consists of the cutting of the working surface having the same working parameters (cutting speed, cutting depth) throughout the entire working until the catastrophic surface destruction occurs [21].

The durability of cutting tools refers to lifetime for which a tool can be used between two resharpenings or until tool replacement; by the means of durability of cutting tools the behavior of cutting tool can be appreciated [3].

Other factors that may influence the durability of the cutting tool are the material from which the cutting tool is made, the cutting speed, geometry, micro-geometry, assembly consisting of cutting tool and cutting material, and tribological system, the existence of cooling during the cutting process, the cross-section specific to the chip, the types of thermochemical treatments applied to improve performance.

The types of thermochemical treatments applied to improve performance play an extremely important role in the final durability of cutting tools [22].

Prior to this stage, thermal treatments are carried out on the semi-product in order to modify the structural state and the internal stress of the metal matrix.

CHAPTER 2: Thermochemical treatments applicable to cutting tools made of high speed steels

Thermochemical treatments are based on thermal diffusion to incorporate metallic or non-metallic atoms into the superficial layers of metallic materials or alloys in order to modify their chemical composition and microstructure.

The process of introducing atoms into the superficial layers of some metallic materials is named cementation. The atoms introduced following the thermochemical cementation treatments have the role of ensuring the metal parts a good surface hardness, resistance to contact pressure, etc, wear resistance and fatigue resistance [25].

Thermochemical treatments can be performed in solid, liquid, gaseous or plasma environments with at least one active chemical element.

2.4. Sulpho-nitrocarburizing

Simultaneous cementation of a surface with sulph, nitrogen and carbon it is named sulpho-nitrocarburizing [60]. This process can be performed in some media capable of providing the chemical elements of interest in the native state, which differ depending on the state of aggregation or the composition of the phase. Most often, powdery or gaseous solid media are used, and from the point of view of environmental composition, cyanide-generating compounds are used. The thermochemical treatment media used contain or are capable of generating components with high toxicity (cyanides) during the heating process following reactions occurring between the media components (for example, reactions occurring between carbamide and the carbonates in the solid powder mixtures used). The carbonates present in the composition of solid powder media used for nitrocarburizing can be replaced by chlorides [25] and thus to reduce or block the tendency of formation of toxic components, without affecting the activity of environments.

Another common method it is sulpho-nitrocarburizing in liquid media – in this case high toxicity components are predominantly:

- salts which can ensure cementation with nitrogen and carbon: sodium cyanide, sodium cyanate, potassium cyanate, potassium ferrocyanide;
- salts which can ensure cementation with sulph, nitrogen and carbon or only with sulph: potassium thiocyanate, sodium thiocyanate, sodium suphide, sodium sulphate;
- neutral salts that accelerate chemical reactions through which cyanates are formed and increase the depth of superficial layers.

Along with these, can be found non-toxic components that are extremely active during processing and act as an accelerator in chemical reactions to produce cyanide in the salt bath and, therefore, in the kinetics of layer generation.

Ionic and gaseous media are often used in sulpho-nitrocarburizing processes; these media consist in gaseous mixt (ammonia+sulphide carbon) [25, 63].

Regarding the solid powdery media, the information related to this type of thermochemical treatment are quite rare; one of these it is related to use of the potassium ferricyanide [55] and another one related to a patent application [64], based on carbamide using an an active element, which represents the primary source of nitrogen and carbon.

Sulpho-nitrocarburizing can be realized at a temperature ranging from T=560÷580°C. At these temperatures, within a time interval between t=1,5÷2 h, sulfur, nitrogen and carbon-enriched layers with dimensions between 0,05÷0,10 mm can be obtained. The microstructure of the sulpho-nitrocarburized layer can be compared to that of the layers obtained at low temperatures by thermochemical nitrocarburizing treatment.

By sulpho-nitrocarburizing, fatigue resistance and wear resistance are increased. The anti-friction properties obtained following sulpho-nitrocarburizing application remain even after the destruction of the sulph-rich layer. The explanation of this behaviors is given by the sulphur diffusion resulting from the temperature rised of the metal product during the operating process [29].

PART II: EXPERIMENTAL RESEARCH

CHAPTER 5. Experimental results and discussion

5.1. Determination of carbamide heating behaviour

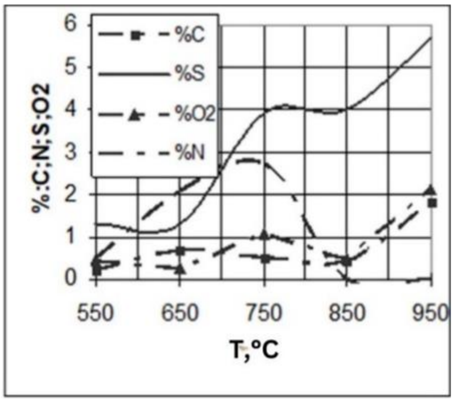
Experimental research was performed in the temperature range of 550°C and 950°C and maintained for $t_{menț}$=1h, thus covering the subcritical processing (sulpho-nitrocarburizing), respectively, overcritical (sulpho-carbonitriding); the composition of solid powdery media remained permanently the same throughout the investigations corresponding to this stage: 10% native sulph, 35% carbamide, 5% ammonium chloride, 50% carbon graphite. Sulpho-nitrocarburizing thermochemical processing were performed using Fe Armco foils with thickness of 100 μm, respectively massive samples with dimensions of 10x10x15mm of pure technical iron (iron ARMCO).

The processing of the data resulting from the compositional analysis of the combustion gases using Armco-Fe SNC foils sulpho-nitrocarburized in solid media powdery which contain carbamide at different temperature levels in the range of temperature T=550–950°C (*figura 5.1* ***-a)***, ***-b)***), revealed few interesting aspects.

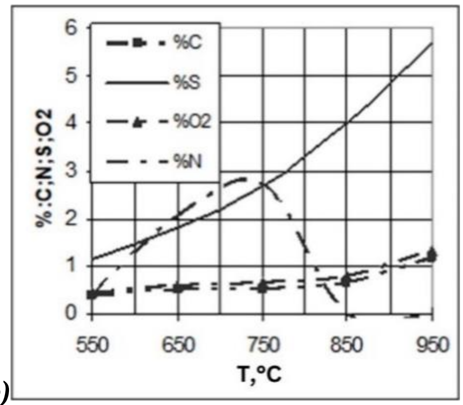
- the potential sulphur Spot level in the sulpho-nitrocarburizing environment increases continuously, concurrently with the increase of the temperature;
- the potential nitrogen Npot level in the same environment, strongly increases in the temperature range 550–725 (730)°C, after which it drops sharply; at 820°C reaching lower levels compared to carbon;
- the potential levels of carbon Cpot and oxygen Opot increase continuously throughout the temperature range taken into consideration; at approximately 820°C the carbon potential level is higher compared to that of nitrogen.

The X-ray diffraction analysis of the sulpho-nitrocarburizing Fe-ARMCO foils (*figura 5.3-**a)***) using different types of solid media powdery carried out at different temperatures confirms the anticipated evolution of the phase proportions containing sulphur, nitrogen and carbon.

Using X-ray microanalysis (EDS spectrometry), iron sulphides (iron sulphide – FeS), nitrides (Fe3N and Fe2N0.5), and iron carbides (Fe2C, FeC0.045) were identified, increasing the sulpho-nitrocarburizing temperature above 820°C determined a change in the ratio of nitride/carbide, with an increase in the ratio of carbide due to a decrease in nitrides (*figure 5.1 **-a)**, **-b)**, figura 5.3 **-b)***).



a)



b)

Figure 5.1. *Activity modification versus temperature variation of the powdery solid environment specific elements used for SNC, (a) unprocessed (real) values of the elements in question (b) processed values representing the evolutionary trends according to the temperature variation*

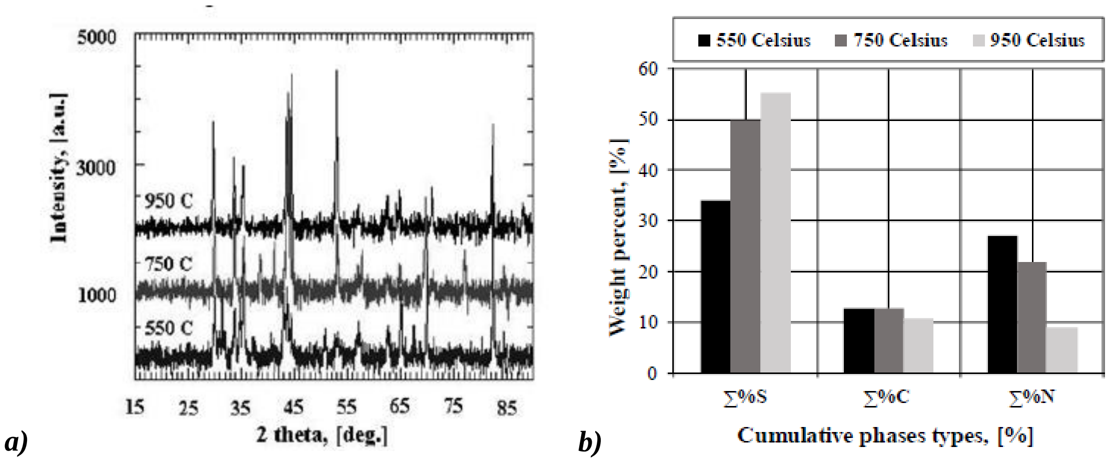


Figure 5.3. *Nitride/carbide variation ratio with sulpho-nitrocarburizing temperature rise (550-750- 950°C), (a) X-ray patterns (b) the percentage cumulative phases (Σ%) that contain sulphur, carbon and nitrogen*

Also with the help of optical and electronic microscopy (*figura 5.4÷5.7*) can be characterized superficial layers of the metallic matrix of Fe ARMCO highlighting typical aspects of the ferritic and austenitic nitrocarburised layers, across different temperature ranges (550°C, 650°C, 750°C and 950°C), in the specified solid powdery media composition. Depending on the processing temperature, the layer will consist of a thin area (dimensions starting at 13 µm) of oxycarbonitrides and iron sulphides followed the diffusion area itself.

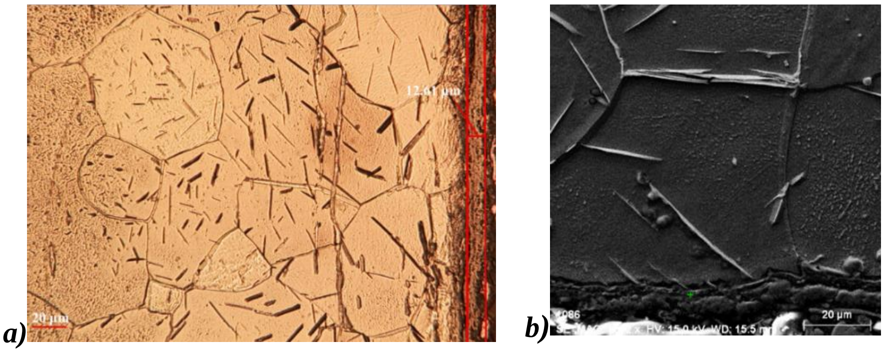


Figure 5.4. *Optical metallography -**a)**; electronic -**b)** of technical pure iron sulpho-nitrocarburized at temperature T=550°C, t_{ment}=1h in solid powdery media containing carbamide (35%)*

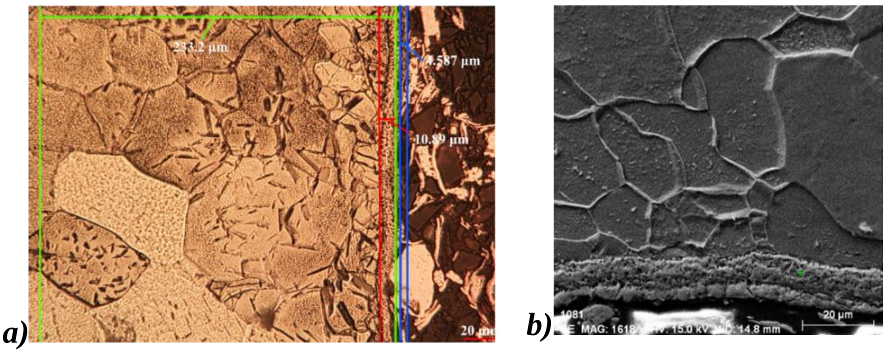
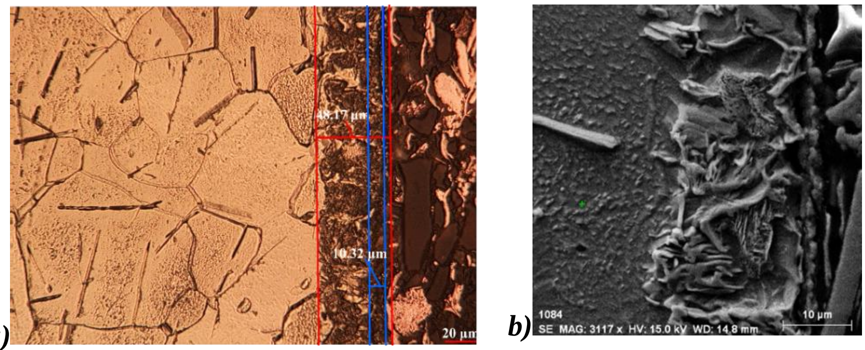
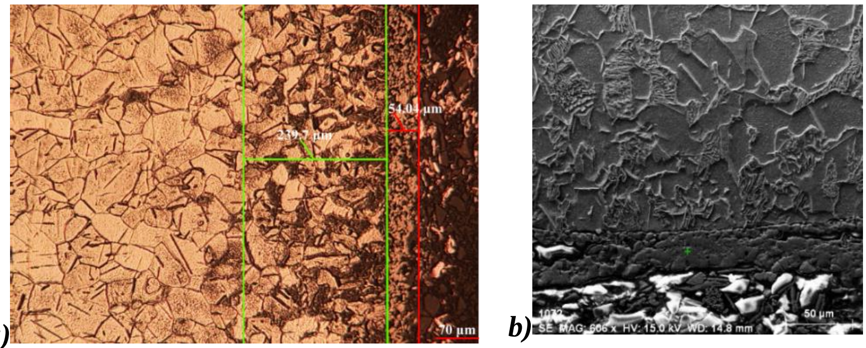


Figure 5.5. *Optical metallography -**a)**; electronic -**b)** of technical pure iron sulpho-nitrocarburized at temperature T=650°C, t_{ment}=1h in solid powdery media containing carbamide (35%)*



a) *b)*

Figure 5.6. *Optical metallography **-a)**; electronic **-b)** of technical pure iron sulpho-nitrocarburized at temperature T=750°C, $t_{menț}$=1h in solid powdery media containing carbamide (35%)*



a) *b)*

Figure 5.7. *Optical metallography **-a)**; electronic **-b)** of technical pure iron sulpho-nitrocarburized at temperature T=950°C, $t_{menț}$=1h in solid powdery media containing carbamide (35%)*

The kinetics growth analysis of the sulphonitrocarburized layer as a function of temperature, at a constant maintenance time of one hour (*figura 5.9*) certified that the carbamide used as the main source of carbon and nitrogen is particularly active even for relatively short processing periods.

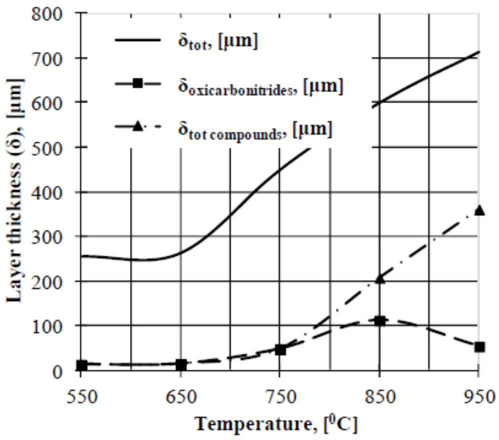


Figure 5.9. *The structural evolution tendency of the SNC layer components obtained by using a Fe-ARMCO matrix maintained for one hour in a solid powdery environment containing 35% carbamide and 10% sulph*

5.2. The quantification by using experimental programming of variation of carbamide and native sulphur in the composition of the solid powdery media, on kinetics of the formation sulpho-nitrocarburized layers and phase composition

Effects quantification by varying the phase composition of the solid powdery media used to carry out the sulpho-nitrocarburizing process was made possible through experimental programming. It was used a second-order non-compositional programming method based on X_1 as sulphur native (%), X_2 as carbamide (%), X_3 as ammonium chloride (%) in role of independent variable and a powder carbon, which represent the difference to 100 % corresponding to each experiment (*table 5.1*). As variable dependents were chosen Y_1 as total thickness of the sulpho-nitrocarburized layer and Y_2 as compound zone thickness.

Table 5.1. The second-order non-compositional programming method *(k=3) and operating conditions of the experiments and results*

No.exp	Independent variable (X_i)										**Y,μm**	
	X_0	**X_1 %S**	**X_2 %CON_2H_4**	**X_3 %NH_4Cl**	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2	**δ_{tot}**	**δ_{comp}**
1	+1	+1	+1	0	+1	0	0	+1	+1	0	**195**	**4,034**
2	+1	+1	-1	0	-1	0	0	+1	+1	0	**59,9**	**8,5**
3	+1	-1	+1	0	-1	0	0	+1	+1	0	**202,9**	**5,099**
4	+1	-1	-1	0	+1	0	0	+1	+1	0	**22,5**	**4,8**
5	+1	+1	0	+1	0	+1	0	+1	0	+1	**62,3**	**3,8**
6	+1	+1	0	-1	0	-1	0	+1	0	+1	**196**	**2,664**
7	+1	-1	0	+1	0	-1	0	+1	0	+1	**245,1**	**1,98**
8	+1	-1	0	-1	0	+1	0	+1	0	+1	**33**	**0,99**
9	+1	0	+1	+1	0	0	+1	0	+1	+1	**235,8**	**1,752**
10	+1	0	+1	-1	0	0	-1	0	+1	+1	**188,6**	**1,0**
11	+1	0	-1	+1	0	0	-1	0	+1	+1	**66,81**	**0,8**
12	+1	0	-1	-1	0	0	+1	0	+1	+1	**165,5**	**1,45**
13	+1	0	0	0	0	0	0	0	0	0	**127,7**	**0,99**
14	+1	0	0	0	0	0	0	0	0	0	**131,4**	**1,52**
15	+1	0	0	0	0	0	0	0	0	0	**144,4**	**1,068**

Following the statically processing of the information obtained as a consequence of experimental cycle, according to the previously presented methodology has led to the next coded particular forms of the regression equations, respectively the decoded forms:

- Total thickness of sulpho-nitrocarburized layer, (coded) -, Y_1:

$$Y_1 = \delta_{tot} = 134{,}5 + 64{,}8X_1 - 11{,}3X_1X_2 - 86{,}4X_1X_3 + 36{,}47X_2X_3 - 22{,}2X_{12} + 21{,}8X_{32} \quad (5.25)$$

- Compound zone thickness, (coded) -, Y_2:

$$Y_2 = \delta_{comp} = 1{,}192 + 0{,}766X_1 - 0{,}458X_2 + 0{,}275X_3 - 1{,}191X_1X_2 + 2{,}762X_1^2 + 1{,}654X_2^2 - 1{,}595X_3^2 \quad (5.26)$$

respectively decoded forms of these:

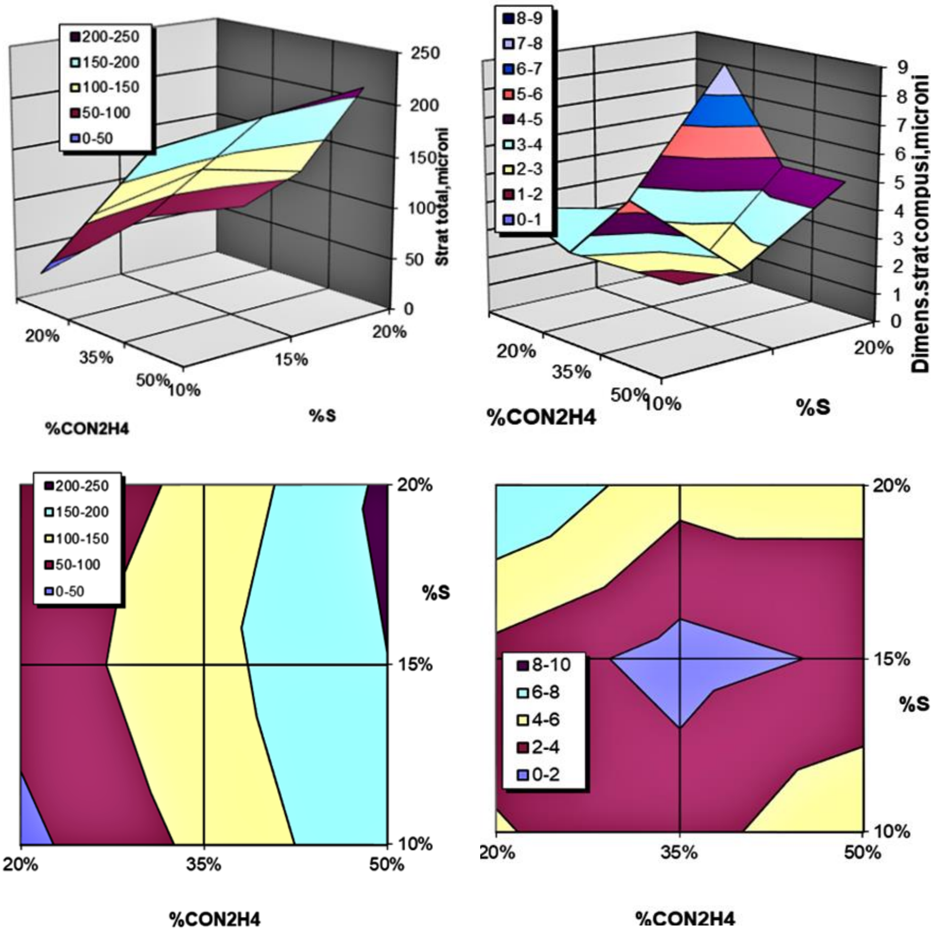
- Total thickness of sulpho-nitrocarburized layer, (decoded), δ_{tot}:

$$\delta_{tot} = -580{,}1 + \%S(71{,}9 - 0{,}88\%S) + \%CON_2H_4(0{,}9 + 1{,}62\%NH_4Cl) + \%NH_4Cl(48{,}1 + 9{,}68\%NH_4Cl) - \%S(11{,}5\%NH_4Cl + 0{,}15\%CON_2H_4) \quad (5.27)$$

☙ Compound zone thickness, (decoded) - δ_{comp}:

$$\delta_{comp} = 16{,}1 + \%S(0{,}11\%S - 2{,}59) + \%CON_2H_4(0{,}00735\%CON_2H_4 - 0{,}307) + \%NH_4Cl(5{,}13 - 0{,}708\%NH_4Cl) - 0{,}0158\%S\%CON_2H_4 \quad (5.28)$$

Graphical expression of the regression, coded or decoded forms (*figure 5.11*) are presented below and allow to determine the sense that it is possible to modify the composition solid powder mixture used in sulpho-nitrocarburizing, in order to obtain a certain ratio regarding the thickness of the interest areas of the layers simultaneous saturated with those three components.



a) ***b)***

Figure 5.11. *Graphical expressions of regression equations corresponding to the total layer size* ***a)****, respectively compound zone* ***-b)****; above - response surfaces of equations; below-isoproperty area; %NH_4Cl=ct=3,5% (base level)*

Optical microscopy (*figure 5.12-5.13*) and electronic images (*figure 5.14*) highlight the specific aspects of the sulpho-nitrocarburized layers observed on iron matrices - adjacent areas to the surface in which are found Fe and S carbo-nitrides, sulphides - especially FeS, and diffusion zone with the nitrides like Fe4N - γ'.

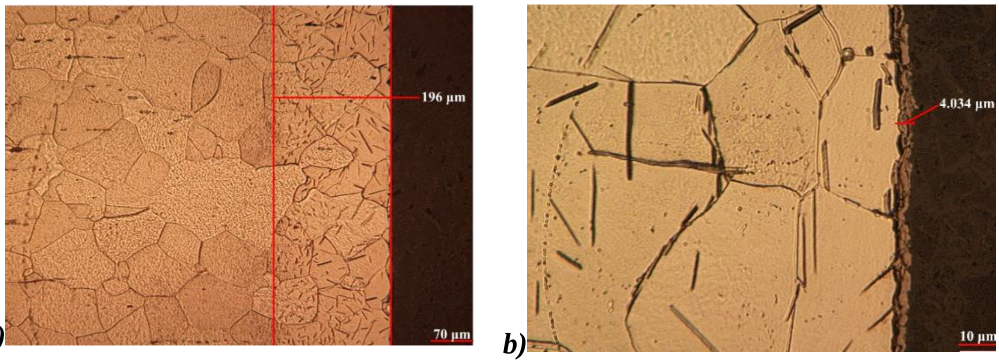


Figure 5.12. *Fe-ARMCO subjected to sulpho-nitrocarburizing in solid powdery media having the following composition S/CON$_2$H$_4$/NH$_4$Cl/Cgr=20%/50%/3,5%/26,5%, at T=560°C, t=1h*

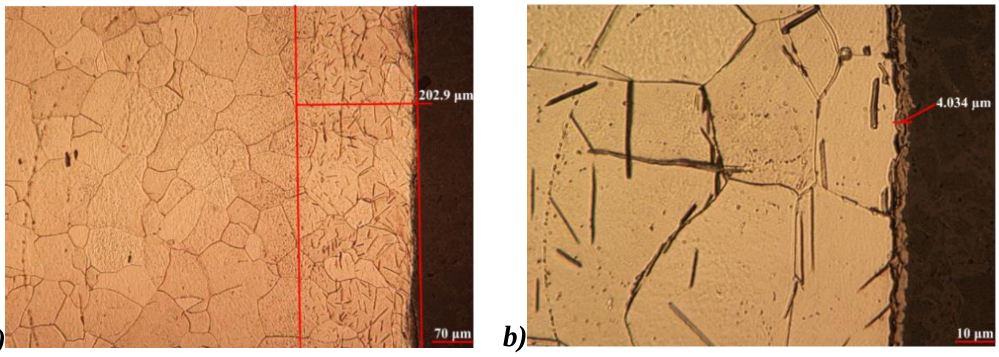


Figure 5.13. *Fe-ARMCO subjected to sulpho-nitrocarburizing in solid powdery media having the following composition S/CON$_2$H$_4$/NH$_4$Cl/Cgr=10%/50%/3,5%/36,5%, at T=560^{o}C, t=1h;*

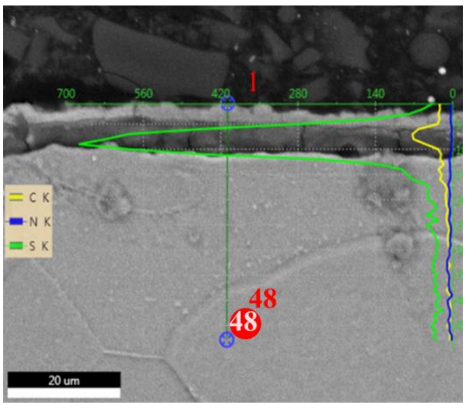


Figura 5.14. *Fe-ARMCO subjected to sulpho-nitrocarburizing in solid powdery media having the following composition S/CON$_2$H$_4$ /NH$_4$Cl/Cgr=20%/35%/5%/40% at T=560°C, t=1h*

Following the results of the optical metallography investigations it is found that for constant proportions of carbamide and ammonium chloride in the medium used for sulpho-nitrocarburizing, at an increase in the proportion of native sulfur there is an increase in the proportion of sulfur in the form of iron sulphides in the compound layer and a decrease in nitrogen; by increasing the carbamide percent in powdery media (the rest components maintaining constant), the adsorbed sulphur percentage will be diminish and that of nitrogen will be increased.

The change in the ratio of the proportions of the components of the solid powdery media used in sulfonitrocarburization obviously affects the kinetics of the formation of the total layer and the size of the compound area (*figure 5.15*).

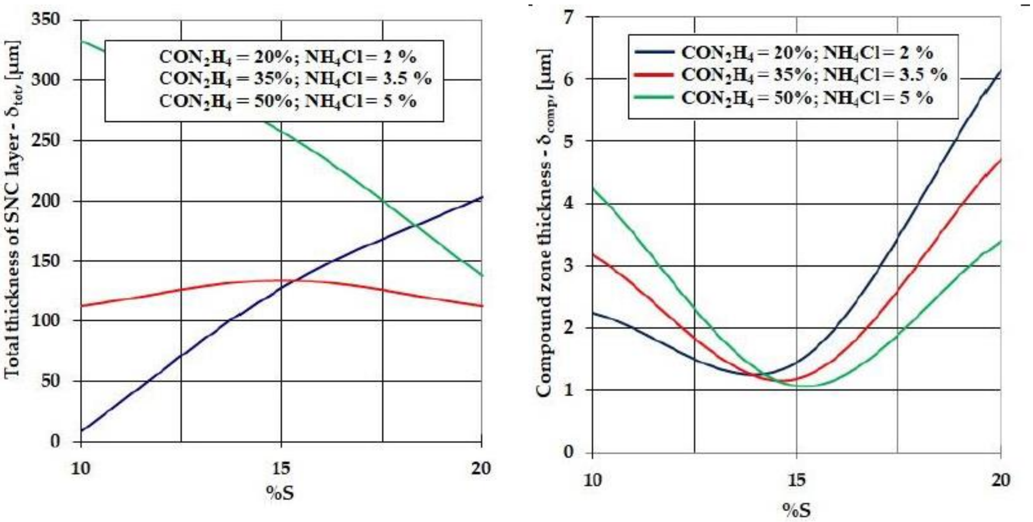


Figure 5.15. *Variation of total thickness of sulpho-nitrocarburized layer (a) and compound zone (b) determined by the change in the ratio of the percentages of the powdered solids components used for the thermo-chemical processing,* $T=560^{o}C$, $t_{menț}=1h$

5.3.2-(a) The extrapolation on metallic matrix of high-speed steels of HS18-0-1 of previously obtained results, with highlighting the effects of applying this type of thermochemical treatment to these types of matrices

High speed steels matrices of HS18-0-1 type were subjected to thermochemical treatments of sulpho-nitrocarburizing in solid powdery environments under conditions established as optimal in previous experimental research.

The high-speed steels of HS18-0-1 type were placed in steel boxes and packed in solid powder mixture. All experiments were performed in identical condition regarding the temperature and maintaining time, respectively: 500°C for 1 hour following by air cooling of the boxes containing the samples packed in solid powder media.

The results obtained from optic metallography (*figure 5.18* ***-a)***, ***b)***) highlight interesting aspects, the thickness of superficial layers it is large, but these tend to exfoliate.

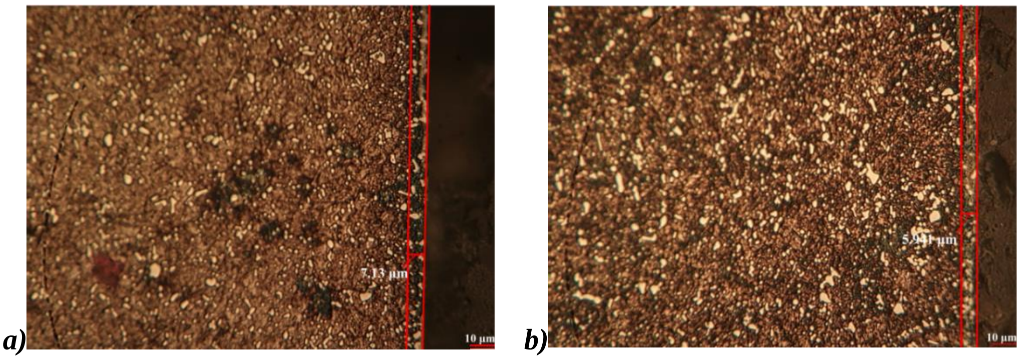


Figure 5.18. *Optical metallography of high-speed steel HS18-0-1 sulpho-nitrocarburizing in solid powdery media containing* ***a)*** *C_{grafit} -66,5%,* ***b)*** *C_{grafit} -50%*

To decrease the activity of carbon present in the media used for sulpho-nitrocarburizing, it was established to use to use alumina – a chemically inert component that has the role of limiting/removes the tendency of sintering the components of the solid powdery media.

Experimental research continued by using solid powdery environments consisting of carbamide+ammonium chloride+sulph+graphite carbon+alumina, the proportion variation of carbamide within 10-30% being compensated by the proportion variation of alumina at various temperatures in the range of T=450÷550°C for 1 h. Experimental research has concluded that a variation in the proportion of carbamide within 10-30% in powdered solid mixtures containing carbamide along with 10% sulph, 3.5% ammonium chloride, 40% carbon graphite and alumina - balance, are directly reflected in the growth kinetics of the layer (*figure 5.20*) and are in strict correlation with the processing temperature.

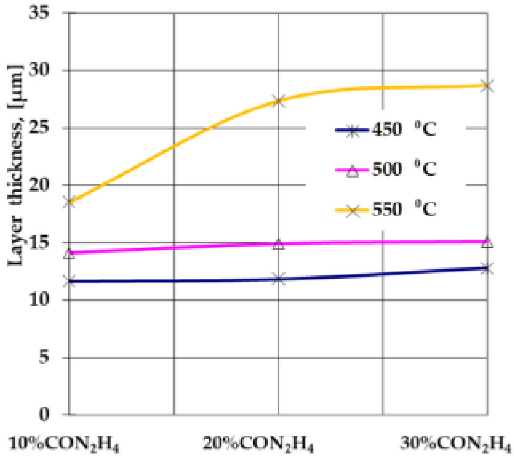


Figure 5.20. *Dependence of the sulpho-nitrocarburized layer thickness on the proportion of carbamide in the powdered solid mixture: carbamide - 10% sulph native - 3.5% ammonium chloride- 40% carbon graphite – alumina (balance) and processing temperature: HS18-0-1 steel; annealing time of 1 h.*

The results obtained from optic metallography performed on sulpho-nitrocarburized HS18-0-1 high-speed steel (*figura 5.21÷5.22*) highlight the presence of a clearly delineated diffusion zone (thickness - 10÷27µm), the range of 10÷27 µm, as determined by a temperature variation between 450°C and 550°C and a proportion of carbamide within the limits of 10÷30%.

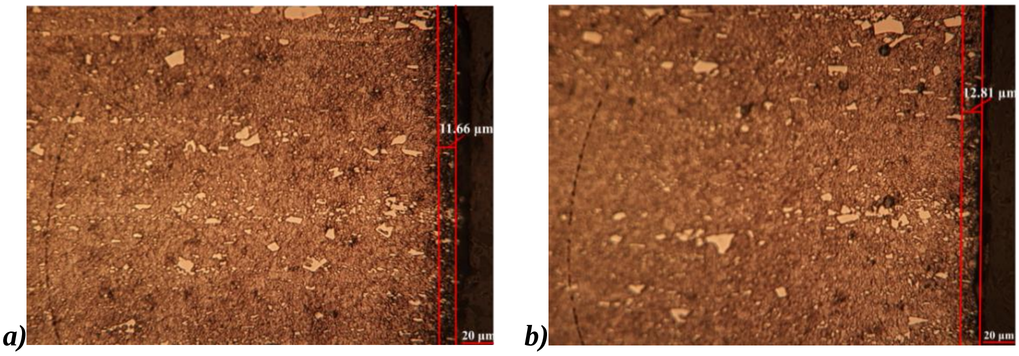


Figure 5.21. *Microstructures of sulpho-nitrocarburized layers in solid powdery media S-CON_2H_4-NH4Cl-Cgrafit-Al_2O_3 with different proportions of carbamide,* ***a)****-10%, respectively* ***b)****-30%, at T=450°C, t=1 h; metallic matrix (HS18-0-1)*

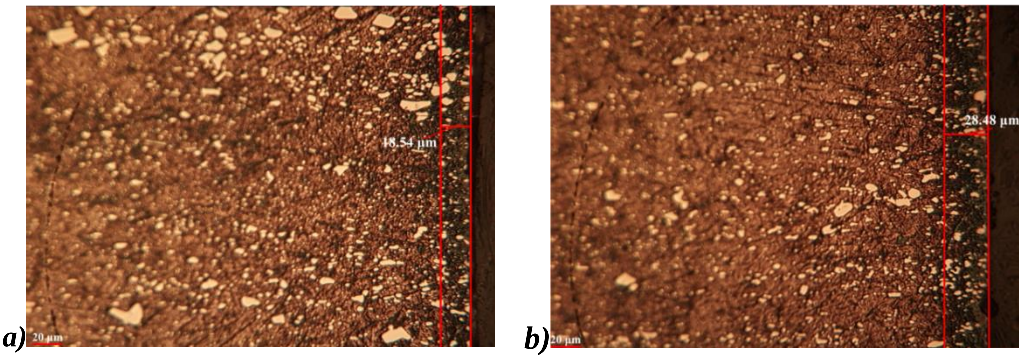
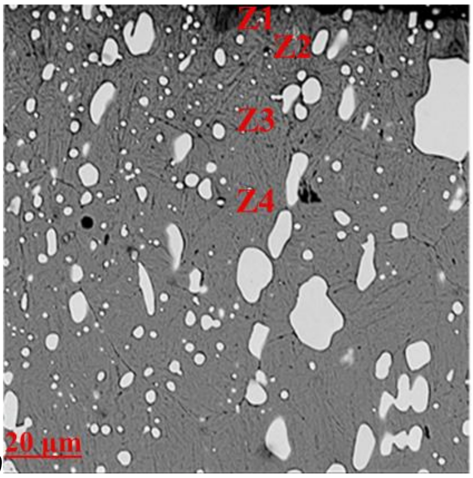


Figure 5.22. *Microstructures of sulpho-nitrocarburized layers in solid powdery media S-CON_2H_4-NH_4Cl-Cgrafit-Al_2O_3 with different proportion of carbamide,* ***a)****-10%, respectively* ***b)****-20%, at T=550°C, t=1 h; metallic matrix (HS18-0-1)*

Microhardness measurements of the sulfonitrocarburized layer (*figura 5.22 -**b)***) showed values up to 1027 $HV_{0.02}$ at distances of the order of about 12µm microns from the surface.

The verification of the solid powder media activity containing various proportions of carbamide intended for sulfonitrocarburizing (*figure 5.24*), was made on 100-micrometer thick Fe-ARMCO foils, substantiating the conclusions regarding the global growth of the sulpho-nitrocarburized layers (*figure 5.20*).



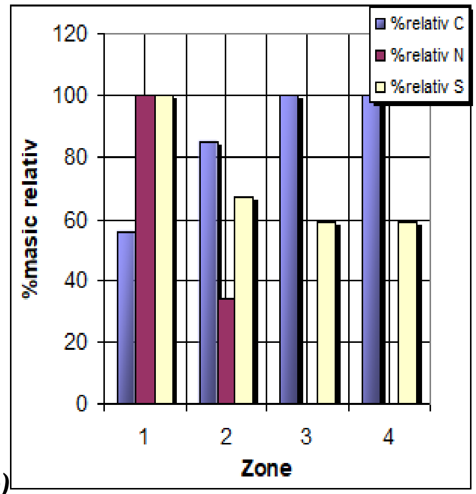


Figure 5.24. *SEM image (**a**) sulfonitrocarburized at 550 °C for 1 h in a powdered mixture of 20% CON2H4-NH4Cl-S-Cgraphite–Al2O3 with specifications of changes in relative mass proportions (**b**) of the elements of interest in the different investigated zones*

As the temperature increased by 100°C, from 450 to 550°C, together with an increase in the proportion of carbamide by 20%, from 10% to 30%, the foil average concentration of carbon increased by 400%, sulfur increased by about 156%, and nitrogen increased by 116% (*figure 5.25*).

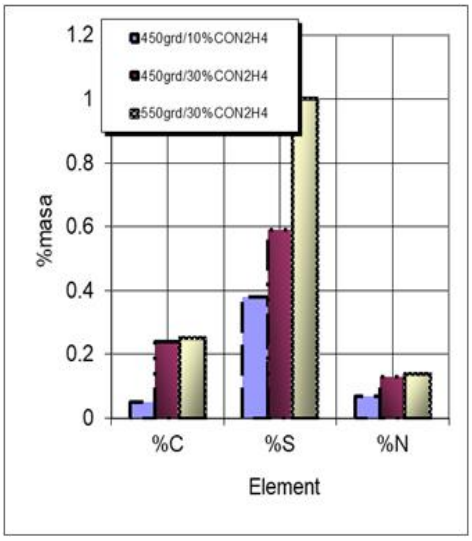


Figure 5.25. *Variations of the average mass proportions of carbon, sulfur, and nitrogen in Fe-ARMCO sulfonitrocarburized foils in the powdered solid medium at various temperatures in the range of 450–550°C for 1 h, in medium containing various proportions of carbamide (between 10 and 30%)*

Taking into account the aim of applying thermochemical treatments to high-speed steels, namely to ensure their surface hardening without affecting the core characteristics, experimental research was attempted using sulpho-nitrocarburizing mixtures with specific characteristics of the thermite composition (*figure 5.26* ***-a), -b)***).

For a mixture composition (14%carbamide+41%magnetit+14%titanium dioxide+4%magnesium+13%aluminium+14%sulph) reactions between components are very likely to happen, releasing a sufficiently large amount of energy to ensure carbamide breakdown.

In order to initiate the interaction between the components, an activation energy is required, thus the temperature of the process was T=750°C and maintaing time t=1,5 minutes.

The chemical interaction between components it is very short so that the hardness of metallic matrix it is not affected (61HRC – *figure 5.26-**b)***).

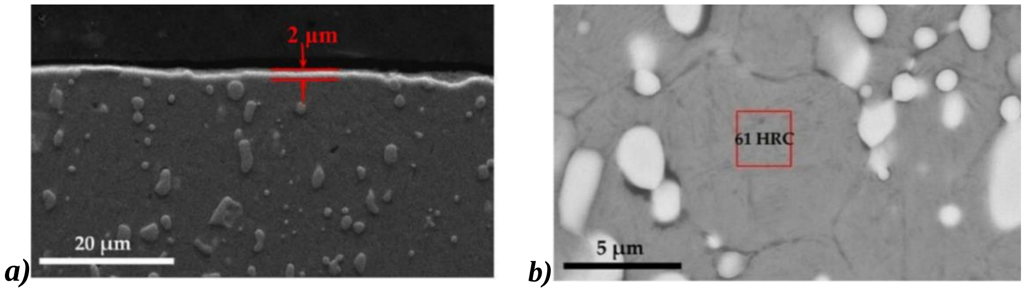


Figure 5.26. *SEM images of the HS18-0-1 sulfonitrocarburized HSS sample in paste, after 1.5 min in the furnace at a temperature of T=750 °C and being cut off. Paste composition: 14%CON_2H_4 -41%Fe_3O_4-14%TiO_2-13%Al-4%Mg-14%S; polysaccharide resin binder;* ***a)*** *layer area;* ***b)*** *central area of the sample*

One may conclude that the use of the pastes in order to achieve the sulfonitrocarburization of some areas of interest on the tools made of high-alloy steel tools surface is a method worthy of consideration.

5.3.2-(b) Specification regarding the results of applying the thermochemical treatment of ionic nitriding removable tools made of high speed steel HS18-0-1 quenched and triple tempered

The performances of sulpho-nitrocarburized tools in a solid powdery medium containing carbamide were assessed with the help of two indicators: the maximum permissible cutting speed and the maximum cut length at a certain cutting speed [88]. Small removable triangular plates were used in order to achieve this goal.

Removable triangular plates were thermochemical treated by ionic nitriding according to condition presented in the *table 5.5*.

The results obtained from front cutting round bars made of AISI 5115/16MnCr5 steel grade (EN 1.7131—case hardening steel) in the annealed state under the conditions of a feed rate of 0.7mm/rot, with a cutting depth of 1.5 mm, without cooling, are centralized in *table 5.6*, the maximum cutting speed it ranged between 146m/min, respectively 196 m/min, the highest performance corresponds to removable tools which were ionic nitrided under the conditions mentioned for the third processing (according to the *table 5.6*).

Table 5.5. Concrete conditions of thermochemical processing by ionic nitriding

No.crt	p(NH_3+Ar)torr	Tnitr, °C	Tnitr, ore	Cooling conditions
1	1,5	350	3	In the atmosphere of argon up to T=200°C following the cooling in air
2		450	1	
3		**450**	**1,5**	
4		550	0,5	
5		550	1,5	

Table 5.6. *Results of front cutting corresponding to HS18-0-1 removable tools which were ionic nitrided under certain conditions*

No.crt	Nitriding conditions	Vmax(m/min)
1	550°C/1,5h	183,4
2	550°C/0,5h	188,4
3	**450°C/1,5h**	**196**
4	450°C/1,0h	163,3
5	350°C/3,0h	146

The results of the lateral cutting tests led to the conclusion that for the cutting speed of 75m/min (under the above mentioned cutting conditions) the maximum cutting length is 275mm time when resharpening of tool becomes necessary; such a speed, considered the maximum allowable speed, is superior to the cutting speeds recommended for cutting tools made of high speed steel HS18-0-1 thermochemically untreated, whose speeds vary between range of 50-60m/min.

3.5.2-(c) Technological variants of thermochemical processing and their effects on the performance of cutting tools made of ledeburitic steels of HS18-0-1 type

Comparative research on the performance of removable pads continued by superficial (or not) treatment through a multitude of technological variants including sulpho-nitrocarburizing in solid powdery environments:

- regime 1 – quenched and triple-tempered state;
- regime 2 (SNC) – quenched and double-tempered state at 560°C for 1h with sulpho-nitrocarburized in powdered solid media, composition 20% carbamide - 3,5% ammonium chloride - 10% sulph - 40% carbon graphite–26,5% alumina; 550°C for 1h
- regime 3 (NC)– quenched and double-tempered state at 560°C for 1h with nitrocarburized in powdered solid media, composition 20% carbamide - 3,5% ammonium chloride - 40% carbon graphite–36,5% alumina; 550°C for 1h;

- regime 4 (NC) - quenched and double-tempered state at 560°C for 1h with nitrided in gaseous medium (NH_3—degree of dissociation 35%) 550°C for 0.5 h;
- regime 5 – (N ionized)—quenched and double-tempered state at 550°C for 1 h + ion nitrided (450°C for 1.5 h in a gas mixture (NH_3 + Ar) (p (NH_3+Ar) = 2 mbar).

One may see that the thermochemical processing applied to the cutting tools when thermal, temporal, and chemical parameters are correctly chosen, ensuring a substantial increase in the maximum permissible cutting speed. (*figure 5.29*).

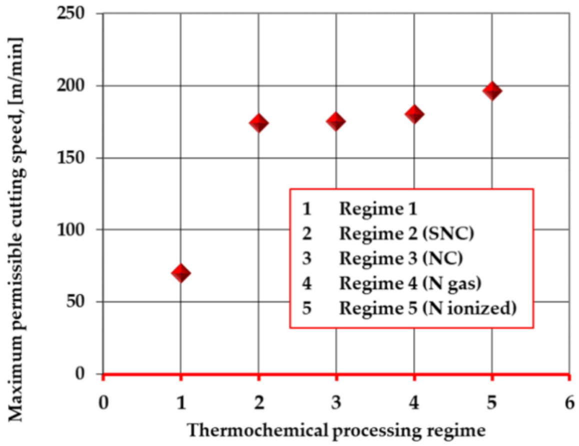


Figure 5.29. *Variation of the maximum permissible cutting speed with the thermochemical processing regime of the steel (HS18-0-1)*

The results regarding the maximum admissible cutting speed for the variants with thermochemical processing subsequent to the standard thermal processing are within the variation limits of ±15%, with a minimum of 143%, which is clearly superior to the non-thermochemically processed ones.

This results in both sulpho-nitrocarburizing and nitrocarburizing in a pulverulent solid media containing carbamide, represent particularly efficient and economically ways of increasing this indicator of the performance level of cutting tools.

Regarding the maximum cutting length at a certain cutting speed (*figura 5.31*), the longitudinal cutting tests with cutting speeds within the range of 70-195 m/min was performed. The lower limit corresponds to the high-speed steels standard heated (hardened and triple tempered), and the superior limit corresponds to the heat treated and subsequently ion-nitrided tools. The tests highlighted that while for the standard heat-treated tools the maximum cutting length was 300 mm at the maximum permissible cutting speed of 70 m/min, the subsequent thermochemical processing of the tools ensured a substantial increase in maximum cutting length by about 83%, at the maximum permissible cutting speed for thermochemically unprocessed tools.

For tools made of HS18-0-1 steel sulpho-nitrocarburized (or nitrocarburized) in powdered solid media containing 20% carbamide, both the maximum permissible cutting speed and the maximum cut length were slightly lower compared to ion-nitrided tools or those in a gaseous environment (the maximum cut length is about 5.5% lower at a cutting speed, which is equal to that of thermochemically unprocessed tools at 70 m/min) but were clearly superior to those provided by thermochemically unprocessed tools.

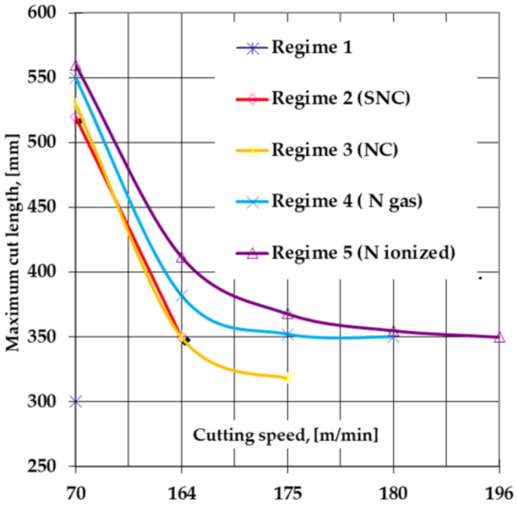


Figure 5.31. *Variation of the maximum cut length before tool resharpening, depending on the cutting speed, in strict correlation with the thermochemical processing regime of the tool made of HS18-0-1 steel. The thermochemical processing regimes are those mentioned figure 5.29*

CHAPTER 6: General conclusions of the study. Personal contributions - originality. Theoretical perspective in research

6.1. General conclusions of the study

The experimental research presented in this doctoral thesis aimed to find a viable and economical alternative of thermochemical treatment to improve the performance of cutting tools made of high-speed steels of HS18-0-1 type. Research was focused towards sulpho-nitrocarburizing performed in solid powdery media containing carbamide as the main source of carbon and nitrogen.

The main conclusions that come from the experimental research carried out within the doctoral thesis, are shown below.

1. Carbamide has the capacity to furnish nitrogen and carbon by using this in solid powdery media for sulpho-nitrocarburizing.

2. The presence of carbamide in the solid powdery medium changes the carburising or nitriding potential depending on the temperature; above 820°C the carburising tendency being prevalent.

3. The ability of carbamide to supply toxic components is diminished/eliminated following the introduction of ammonium chloride instead of carbonates (components often used

in media containing carbamide) in sulpho-nitrocarburizing in solid powdery media accomplished during this experimental research.

4. The mathematical models of the interactions between the components of solid powdery media (CON_2H_4-C-NH_4Cl-S), used in the sulpho-nitrocarburizing process, determined by the programming of experiments, are particularly useful tools for controlling the phase composition of the formed layers.

5. The kinetics of the compound area formation is accelerating substantially by the carbamide and ammonium chloride proportion decreasing in the solid powdery mixture.

6. The thickest SNC layer and that of the compound area, respectively, for mixed sulphur concentrations around 10%, while carbamide and ammonium chloride are at the maximum level adopted from the experimental research program (0% and 5% respectively) obtained.

7. A powdered solid medium containing 20% carbamide showed a considerable increase in the carbide proportion when compared to that recorded in HS18-0-1 steel in as–cast or annealed states (about 25%), quenched (about 16%), or quenched and tempered (about 18%).

8. The maximum microhardness recorded in the sulfonitrocarburized layer by HS18-0-1 steel was $1027HV_{0.02}$, at a depth of about 16÷30 µm.

9. Din punct de vedere al performanțelor sculelor așchietoare din oțeluri rapide de tipul HS18-0-1 sulfonitrocarburate în medii solide pulverulente, viteza maximă admisibilă de așchiere crește cu peste 140% comparativ cu cea a sculelor din acest tip de oțel neprocesate termochimic.

10. There was an increase of over 140% of the maximum permissible cutting speed, while the maximum cut length increased by over 80%, compared to those of thermochemically unprocessed tools working at the maximum permissible cutting speed (about 70 m/min).

11. Sulpho-nitrocarburizing in a powdered solid medium containing carbamide performs very closely with regards to the cutting tools to thermochemical processing variants such as gas nitriding or plasma nitriding.

12. The cutting condition used in order to determine performance of cutting tools were: feed rate of 0.07 mm/rot and a cutting depth of 1.5 mm, without cooling.

13. Sulpho-nitrocarburizing in a powdered solid medium containing carbamide performs very closely with regards to the cutting tools to thermochemical processing variants such as gas nitriding or plasma nitriding.

14. The use of the pastes in order to achieve the sulfonitrocarburization of some areas of interest on the tools made of high-alloy steel tools surface is a method worthy of consideration**.**

6.2. Personal contributions - originality

1. Carbamide represent an indubitably component to be used in sulpho-nitrocarburizing and act like provider of nitrogen and carbon under the thermochemical processing at low temperatures (equivalent of tempering temperature corresponding to ledeburitic steels), without generating toxic components.

2. It was determined a way for avoiding the occurrence of toxic components in solid powder media used for sulpho-nitrocarburizing by replacing carbonates (common components used in environments containing carbamide) with chlorides (ammonium chloride) during of experimental research.

3. By using a second-order non-compositional programming method – active experiment during experimental research have been established effective tools for controlling and anticipating the results of sulpho-nitrocarburizing in solid powdery environments.

4. Experimental research has led to the establishment of an optimal phasic composition of sulpho-nitrocarburizing pastes with components that under certain conditions, by initiating the metallothermic reduction reaction, they become capable of providing both the elements of interest and the amount of heat needed for the ultra-fast saturation of the metal surfaces concerned.

5. A logical scheme has been established to determine the optimal thermal processing regime of metal products so as to achieve the desired goal without the thermal tensions that occur inherently during the course warming become dangerous and jeopardize their integrity.

CHAPTER 7. Published papers

Scientific papers

1. Obtaining the Controlled Sulphonitrocarburized Layer Phase Compositions, by the Variation of the Solid Powdery Medium Components, Mihai Branzei, Mihai Ovidiu Cojocaru, Leontin Nicolae Druga, **Mariana Ion**, Rev. Chim., 71 (7), 2020, 225-233. (*https://doi.org/10.37358/RC.20.7.8240*)

2. Activity modification of a new type of carbamide-based non-polluting solid powdery medium used in the sulphonitrocarburising process, Mihai Ovidiu Cojocaru, Mihai Branzei, **Mariana Ion**, International Journal of Surface Science and Engineering 2020 14(4):307 (10.1504/IJSURFSE.2020.10034488)

3. Sulfonitrocarburizing of High-Speed Steel Cutting Tools: Kinetics and Performances, Mihai Ovidiu Cojocaru, Mihai Branzei, Sorin Ciuca, Ioana Arina Gherghescu, **Mariana Ion**, Leontin Nicolae Druga, Cosmin Mihai Cotrut, Materials 2021, 14, 7779. (https://doi.org/10.3390/ma14247779)

4. Analytical model for predicting the optimum heating conditions used in heat processing, **Mariana Ion**, Mihai Ovidiu Cojocaru, Mihai Branzei, ACTA TECHNICA NAPOCENSIS Series: Applied Mathematics, Mechanics and Engineering Vol. 64, Issue I, 2021

Project

1. PROGRAMUL OPERATIONAL CAPITAL UMAN 2014-2020 Sisteme de învăţare bazate pe muncă prin burse antreprenor pentru doctoranzi si postdoctoranzi ***SIMBA*** Axa Prioritară 6- Educație și competențe Cod *MySMIS: 124705*.

Conference:

1. Conference 26^{th} – 27^{th} November 2020 "The 8^{th} International Conference on Materials Science and Technologies – RoMat 2020" Bucharest, Romania. Online Presentation: "Analytical Model for Predicting the Optimum Heating Conditions Used in Heat Processing"

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