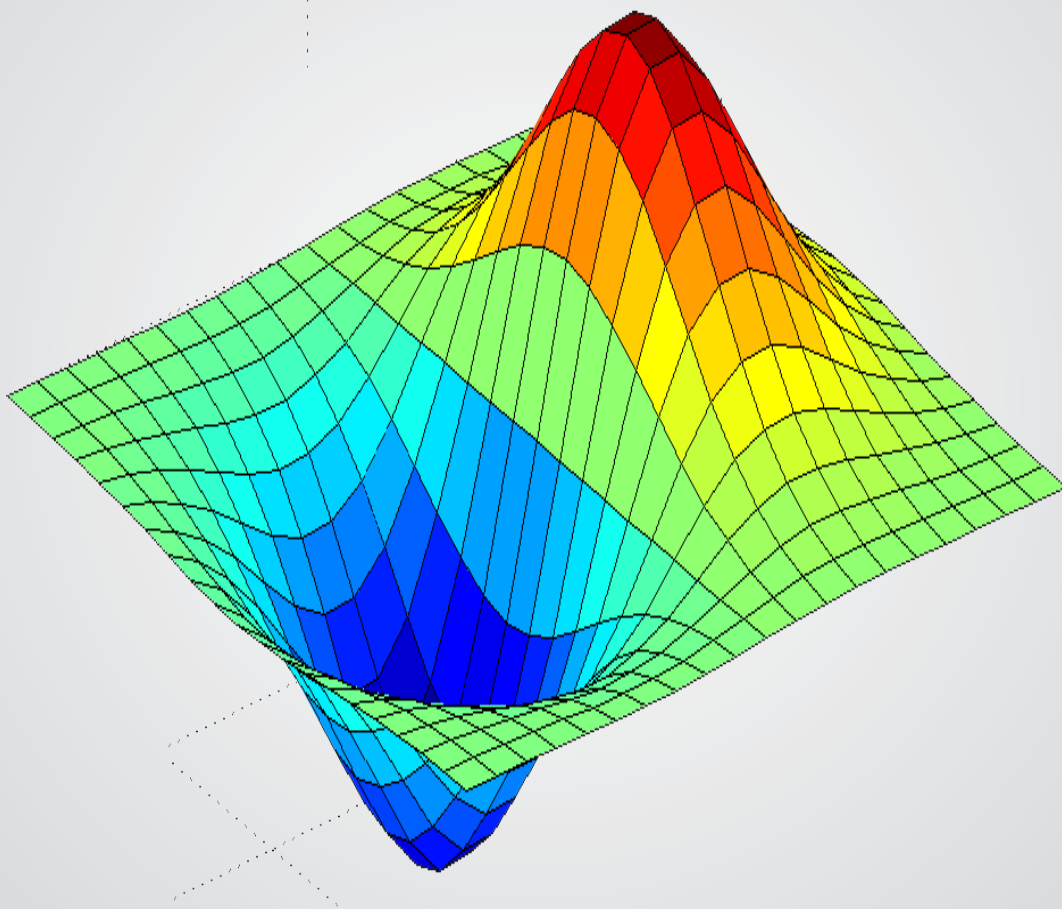




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## ABOUT THE INFLUENCE OF ION NITRIDING ON THE MECHANICAL PROPERTIES OF TOOL STEELS

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**Abstract:** The aim of the present paper is to study the influence of ion nitriding on the tensile strength ( $R_m$ ), the arbitrary yield strength ( $R_{p0.2}$ ), Young's modulus ( $E$ ), fatigue limit  $\sigma_{-1}$  and fracture toughness  $K_{IC}$ .

Two alloy tool steels – 4Cr5MoVSi (BH11, BS4659) and 3Cr2W8V (BH21, BS4659) – have been studied by subjecting them to ion nitriding at temperature  $t=530^\circ\text{C}$ , ammonia pressure  $P=300\text{ Pa}$ , time of treatment  $\tau=7\text{ h}$ . A multifactor experiment from 2 has been used in drawing the mode of nitriding. The obtained results show that ion nitriding of steel 4Cr5MoVSi at temperature  $t=530^\circ\text{C}$ , ammonia pressure  $P=300\text{ Pa}$ , and time of treatment  $\tau=7\text{ h}$  favorably influences its surface hardness  $HV_{0.1}$ , tensile strength ( $R_m$ ), arbitrary yield strength ( $R_{p0.2}$ ), fatigue limit  $\sigma_{-1}$  and fracture toughness  $K_{IC}$ . For steel 4Cr5MoVSi, this mode of nitriding influences negatively only the fracture toughness.

**Key words:** ion nitriding, properties of nitride tool steels

### I. Introduction

Tools and details, undergoing intensive exploitation, are required to have very good mechanical parameters. Therefore their surface needs modification in order to meet these demands.

Nitrided layers are characterized by high hardness and wear resistance. The values of these parameters are in direct dependence on the mode of operation and, undoubtedly, the most important parameter, influencing hardness is the temperature. In many studies on steels, intended to work in hot environments, it is observed that the increase in the temperature of nitriding leads to increase in the hardness of the nitride layers with thickness up to  $100\ \mu\text{m}$  [12, 13, 16, 17]. This is due to the fact that at temperatures over  $500^\circ\text{C}$  a thick nitride layer is formed, what considerably improves steel hardness and wear resistance [15]. These changes are observed at a smaller extent at lower working temperatures [18].

Fatigue limit of the materials can be considerably increased by means of nitriding and this is due either to improvement of the distribution of residual stresses or to locating the zone of crack generation at a bigger depth from the material surface [13, 14, 15, 16]. Studies of maraging steels, subjected to nitriding, have proved increase of their fatigue limit ( $\sigma_R$ ) by 25% [15].

Along with the positive sides, the layers possess a significant disadvantage, consisting in their brittleness [1]. The nitride (carbonitride) particles in the diffusion layer act as concentrators of stresses. These zones can be regarded as most dangerous in terms of brittleness because the cracks originate precisely in them. Since the nitrides are characterized by a high modulus of elasticity [2, 3],

the stresses, arising in these layers, are considerable, what favors the generation of microscopic cracks.

Little research has been done for defining the modulus of longitudinal elasticity ( $E$ ) and the strength characteristics  $R_m$ ,  $R_{p0.2}$  of the nitrided layers. According to some of the existing works, the modulus of longitudinal elasticity of individual types of steels is not influenced by the process of nitriding. Other works report on increased  $E$  [10]. The nitrided materials are also characterized by improved tensile strength and arbitrary yield strength. Fracture toughness ( $K_{IC}$ ) defines the resistance of materials toward propagation of cracks in them. According to certain studies the relationship between the thickness of the nitrided layer and the fracture toughness is inversely proportional, i.e., the thicker the layer, the lower the fracture toughness [11].

Coated details are multi-layer systems, consisting of a basic material and a nitrided layer. The results, obtained by tensile testing of a nitrided body, characterize the joint strength and deformation of both the coating and the base. This type of testing defines the properties of coated materials in comparison with materials without coatings [4]. It has been established in [5] that the strengthening effect of nitrogen can be used only for details up to 5 mm.

The aim of the present paper is to study the influence of ion nitriding on the tensile strength ( $R_m$ ), the arbitrary yield strength ( $R_{p0.2}$ ), Young's modulus ( $E$ ), fatigue limit  $\sigma_{-1}$  and fracture toughness  $K_{IC}$  for tool steels, intended to work in hot environments.

### II. Methodology of study

*Materials for studying and thermal treatment*

Two types of tool steels intended for work in hot environment were studied - 3Cr2W8V (BH21, BS4659) and 4Cr5MoVSi (BH11, BS4659). Samples were produced from them for the different tests. The samples were subjected to quenching and tempering at high temperature in a vacuum chamber under

modes, given in Table 1. All samples were annealed in advance at 760°C. Treated thermally this way, the samples were ion nitrided then, all under the same mode: temperature of nitriding  $t_{\text{nit.}} = 530^{\circ}\text{C}$ , ammonia pressure  $P = 300 \text{ Pa}$  and time of treatment  $\tau = 7\text{h}$ .

**Table 1. Modes and results from the thermal treatment and ion nitriding**

Material	$t_{\text{hard.}}$ °C	$t_{\text{temp.}}$ °C	HV <sub>0.1</sub>	$\delta_{\text{tot.}}$ µm	$\delta_{\text{c.z}}$ µm	Phase composition	HRC
3Cr2W8V	1110	600	1168	280	3	$\alpha - \text{Fe}, \gamma + \epsilon$	46
4Cr5MoVSi	1030	600	1206	260	4	$\alpha - \text{Fe}, \gamma$	51
3Cr2W8V	1110	650	1141	270	6	$\alpha - \text{Fe}, \gamma + \epsilon$	44
4Cr5MoVSi	1030	650	1168	250	6	$\alpha - \text{Fe}, \gamma$	46
3Cr2W8V	1110	700	1097	240	4	$\alpha - \text{Fe}, \gamma + \epsilon$	32
4Cr5MoVSi	1030	700	1100	245	5	$\alpha - \text{Fe}, \gamma$	29

#### Tensile testing

Standard cylindrical samples were used for defining the strength characteristics ( $R_m, R_{p0.2}$ ) and the modulus of longitudinal elasticity  $E$  of the studied steels. The test samples were subjected to uniaxial tension at room temperature. The test was carried out by means of the machine “INSTRON – 1343” at the following conditions: traverse speed 1mm/min; perceiver – tenso-resistive and dynamic, with sensitivity 2,5 mV/mm; base - 25mm and stroke - 2,5 mm. The calculation of the individual characteristics of the steels ( $R_m, R_{p0.2}, E$ ) was carried out based on a standard methodology [6].

#### Testing for fatigue strength

This test was carried out by means of the machine MYH-6000 under cyclic loading with a symmetric bending load. Eight standard-shaped samples from both steels were tested for defining the fatigue strength for each mode of treatment. The fatigue strength was defined based on the maximum stress, at which the sample can be subjected to an arbitrary number of cycles of load change ( $N = 10^7$ ), without destruction. A number of tests were done in the area of the supposed fatigue limit. The tests were done in the area of the multi-cyclic fatigue after a standard methodology [9].

#### Fracture toughness testing

The standard prismatic samples were tested by means of “INSTRON-1343” under the following conditions: traverse speed 0,5 mm/min; console perceiver – tenso-resistive - for opening the crack, with sensitivity 2,5 µV/mm; base 10 mm and 2 mm

stroke. The invalidation of both the machine and the perceiver for crack opening was checked before each test on a sample. The tests were conducted at room temperature with recording of the diagram load – displacement of the edges of the notch. The calculation of  $K_{IC}$  is completed based on a standard methodology [7, 8].

### III. Experimental results and analysis

*Tensile strength, arbitrary yield strength, modulus of longitudinal deformation.*

Table 1 gives the obtained results for hardness, thickness and phase composition of the nitrided layers, while Table 2 presents the results for tensile strength, yield point, and fracture toughness of the nitrided steels.

The obtained results show that after quenching and tempering at 600°C, steel 4Cr5MoVSi possesses the highest tensile strength ( $R_m = 1980\text{MPa}$ ) and yield point ( $R_{p0.2} = 1625 \text{ MPa}$  -Table2). The structure of steel 4Cr5MoVSi at this temperature of tempering contains a smaller amount of carbide particles with higher dispersion, which require bigger local stresses for their destruction than the carbide particles in steel 3Cr2W8V.

At temperature of tempering 700°C, steel 3Cr2W8V is with higher strength parameters ( $R_m = 1190 \text{ MPa}, R_{p0.2} = 1115\text{MPa}$ ) than steel 4Cr5MoVSi ( $R_m = 1000 \text{ MPa}, R_{p0.2} = 915 \text{ MPa}$ ). This is probably due to the lower diffusion mobility of tungsten at this temperature. On the other hand, the availability of tungsten and carbon in the hard solution slow down



the processes of coagulation of the carbide particles, and, in result, the hardness is higher for steel 3Cr2W8V.

After ion nitriding the tensile strength and the arbitrary yield strength of the studied steels increase by 8 ÷ 12 %. This is due to the availability of a nitrided layer on the surface with thickness  $\delta_{tot} = 220-280\mu\text{m}$  and hardness (1100-1200HV), which is higher than the one, of the base material (300-520HV). Most probably the strength of the core at this diameter of the test-tube ( $d_0 = 7.5 \text{ mm}$ ) does not influence the increase considerably, while the

strength of the nitrided layer predominantly influences it.

The results from Table 2 show that after thermal treatment, steel 3Cr2W8V has a higher modulus of elasticity ( $E=209669\text{MPa}$ ), due to the bigger amount of carbide particles with a higher modulus of elasticity in this steel[6]. The modulus of longitudinal elasticity of the nitrided sample increases by 6 ÷ 10 % (Table 2). This is probably due to the higher modulus of elasticity of the nitride phases, which predominantly influence Young's modulus for the whole multi-layer system.

**Table 2.** Results for  $R_m$ ,  $R_{p0.2}$ ,  $E$ ,  $HV$ ,  $K_{IC}$  and  $\sigma_{-1}$  of thermally treated and ion nitrided steels

Steels	Properties	$t_{temp.} = 600^\circ\text{C}$	$t_{temp.} = 650^\circ\text{C}$	$t_{temp.} = 700^\circ\text{C}$
3Cr2W8V (BH21)	$\frac{R_m}{R_m^A}$ , MPa	$\frac{1540}{1695}$	$\frac{1515}{1665}$	$\frac{1190}{1295}$
	$\frac{R_{0.2}}{R_{p0.2}^A}$ , MPa	$\frac{1490}{1680}$	$\frac{1395}{1540}$	$\frac{1115}{1270}$
	$\frac{E}{E^A}$ , MPa	$\frac{209660}{224600}$	$\frac{209640}{224600}$	$\frac{209650}{223900}$
	$\frac{HV}{HV^A}$	$\frac{460}{1168}$	$\frac{430}{1141}$	$\frac{320}{1097}$
	$\frac{K_{IC}}{K_{IC}^A}$ , $\text{MPa}\sqrt{\text{m}}$	$\frac{49}{34}$	$\frac{54}{57}$	$\frac{68^*}{46^*}$
	$\frac{\sigma_{-1}}{\sigma_{-1}^A}$ , MPa	$\frac{595}{910}$	$\frac{505}{820}$	$\frac{390}{740}$
	4Cr5MoVSi (BH11)	$\frac{R_m}{R_m^A}$ , MPa	$\frac{1920}{2083}$	$\frac{1715}{1879}$
$\frac{R_{0.2}}{R_{p0.2}^A}$ , MPa		$\frac{1610}{1770}$	$\frac{1530}{1740}$	$\frac{1000}{1120}$
$\frac{E}{E^A}$ MPa		$\frac{209370}{224000}$	$\frac{209340}{221980}$	$\frac{209350}{222000}$
$\frac{HV}{HV^A}$		$\frac{530}{1206}$	$\frac{460}{1168}$	$\frac{290}{1100}$
$\frac{K_{IC}}{K_{IC}^A}$ , $\text{MPa}\sqrt{\text{m}}$		$\frac{62}{69}$	$\frac{65}{73}$	$\frac{72^*}{86^*}$
$\frac{\sigma_{-1}}{\sigma_{-1}^A}$ , MPa		$\frac{650}{880}$	$\frac{540}{775}$	$\frac{425}{595}$
Note: *- the values of $K_{IC}$ , which don't satisfy the requirements for plane strain condition.				

For the three temperatures of tempering, the modulus of elasticity does not depend on the type of thermal treatment, i.e., it is a structurally

independent variable in the tensile tests of the nitrided details, and only qualitative assessment of E can be performed.

### *Fatigue limit*

The data in Table 2 show that with increasing the temperature of tempering, the fatigue limit ( $\sigma_{-1}$ ) decreases. This is explained by the reduction of hardness (strength) of the matrix, and, respectively, increase of ductility. From the table it can be seen that after thermal treatment, steel 4Cr5MoVSi possesses a higher fatigue limit (650-425MPa) than steel 3Cr2W8V (595-390MPa) for the three temperatures of tempering. The lower levels for steel 3Cr2W8V are due to the carbide inhomogeneity, caused by the undissolved  $\text{Fe}_3\text{W}_3\text{C}$  ( $\text{M}_6\text{C}$ ) carbide at the chosen temperature of quenching 1100°C. Because of its bigger dimensions, this carbide is a source of microscopic cracks, developing into macroscopic cracks, which leads to sample destruction at the lower values of the load.

The results in Table 2 show that after vacuum-thermal treatment and ion nitriding, both steels increase their fatigue limit. This is due to the residual compressive stresses, arising during the process of ion nitriding, which reduce the tensile stresses, arising as a result of external loads.

It can be noted that steel 3Cr2W8V has a higher fatigue limit after thermal treatment and ion nitriding, than steel 4Cr5MoVSi. This is due to the bigger compressive stresses on the surface for steel 3Cr2W8V. These stresses are caused by the bigger difference between the coefficients of thermal expansion of the obtained nitrided layer and the core of the steel.

The influence of the original hardness (strength) of the samples for increasing the fatigue limit after ion nitriding is insubstantial. The chemical composition of the studied steels is what has a great influence.

Practically the nitride layer in the samples does not take part in its own fatigue fracture. It serves as a barrier against the movement of the cracks towards the surface. The kinetics of destruction of thermally treated and ion nitrided samples is characterized by the fact that, under the action of the load and mostly of the arisen tangential stresses, dislocations originate. They move to the surface, reaching the border between the diffusion zone and the core, and stay there. A lot of dislocations accumulate at the border and local tensile stresses arise, what leads to creation of a source of rupture under the nitrided layer. The diffusion zone here plays an essential role, hindering the flow of the plastic deformation.

### *Fracture toughness*

The results in Table 2 show that fracture toughness  $K_{IC}$  increases along with the increase in the temperature of tempering.

For steel 4Cr5MoVSi the positive influence of ion nitriding on  $K_{IC}$  is very strongly felt. From Table 2 it can be seen that after ion nitriding, all samples from steel 4Cr5MoVSi, tempered at the three different temperatures (600°, 650°, 700°C) increase their  $K_{IC}$ . While for steel 3Cr2W8V the same three temperatures of tempering (600°, 650°, 700°C) and the chosen mode of ion nitriding, have a negative influence on  $K_{IC}$ .

The phase composition of the combined zone for both steels does not play a significant role for  $K_{IC}$  – Table 1. This fact shows that only the thickness and the structural peculiarities of the diffusion zone considerably influence the fracture toughness  $K_{IC}$ . The availability of nitride (carbonitride) deposits in the diffusion zone favour the movement of the crack, since tensile forces develop, which are perpendicular to the direction of movement. An essential role for steel destruction plays the structure of its core.

After thermal treatment in a vacuum furnace, big amount of undissolved secondary carbides of the type  $\text{Fe}_3\text{W}_3\text{C}$  ( $\text{M}_6\text{C}$ ) and a considerable amount of carbides at the borders of the grains remain in the structure of steel 3Cr2W8V. Due to its high density, irregular shape and bigger dimensions, the carbide particle  $\text{Fe}_3\text{W}_3\text{C}$  is a source of microscopic cracks, developing into macroscopic cracks, thus leading to sample destruction at lower load values.

When vacuum-thermally treated and ion nitrided samples from steel 3Cr2W8V are tested to three-point bending, processes of reduction of the residual compressive stresses occur. This is accompanied by plastic deformation of the layer and its premature micro-cracking at small loads. A plastic zone is formed in front of the crack tip, which is the smallest for steel 3Cr2W8V. The course of plastic deformation in front of the crack tip under loading most probably causes micro-cracking of the carbide particle ( $\text{M}_6\text{C}$ ), located in the plastic zone or in closest proximity to it. Microscopic cracks are formed both in the matrix and the layer, and their propagation in the latter is impeded by the residual compressive stresses. At a certain load the residual stresses considerably decrease, thus creating conditions for propagation of microscopic cracks in the layer and in the core material. Under these conditions the united microscopic cracks in the matrix and the layer merge and form a bigger crack, what results in the fact that the samples, which are both thermally treated and ion nitrided, are destroyed at lower loads than those, which are only thermally treated.

The positive influence of the process of ion nitriding on fracture toughness for steel 4Cr5MoVSi

is based on the arisen residual compressive stresses on the surface, which prevent the growth of the microscopic cracks. The structure of the matrix does not play a significant role. The structure contains a lower amount and, at the same time, higher dispersion of carbide particles, than they are in steel 3Cr2W8V.

It can be noted that for steel 4Cr5MoVSi the chosen mode of ion nitriding favorably influences the surface hardness ( $HV_{0.1}$ ), the tensile stress ( $R_m$ ), the arbitrary yield strength ( $R_{p0.2}$ ), fatigue limit ( $\sigma_{-1}$ ), and fracture toughness ( $K_{IC}$ ). For steel 3Cr2W8V, the chosen mode of nitriding influences negatively only the fracture toughness ( $K_{IC}$ ).

#### IV. Conclusions

1. After the vacuum-thermal treatment of the studied steels, the tensile strength, the arbitrary yield strength and the modulus of elasticity, as well as the fatigue limit and the fracture toughness have been defined.

2. It has been proved that after ion nitriding of details with a diameter 7,5 mm, their tensile strength ( $R_m$ ), arbitrary yield strength ( $R_{p0.2}$ ), and Young's modulus ( $E$ ) increase by 8 ÷ 12 %.

3. It has been established that the process of ion nitriding at temperature  $t_{nitr.} = 530^\circ\text{C}$ , ammonia pressure  $P = 300$  Pa and time of treatment  $\tau = 7$ h for steel 4Cr5MoVSi has a favorable influence on the surface hardness, tensile strength, arbitrary yield strength, fatigue limit, and fracture toughness. For steel 3Cr2W8V this mode of treatment has a negative influence only on its fracture toughness.

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## ABOUT THE INFLUENCE OF ION CARBONITRIDING ON THE CHEMICAL COMPOSITION OF THE CARBONITRIDE ZONE

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**Abstract:** The aim of the present paper is by means of GDOES-analysis to study the distribution of nitrogen, carbon and oxygen in the carbonitride zone after ion carbonitriding of Armco-iron in a medium of ammonia and corgon (82% Ar + 18% CO<sub>2</sub>).

The obtained results show that increased amount of carbon is observed both in the combined zone and in the diffusion zone of the carbonitrided layer. Oxygen is registered by the GDOES-analysis only in the combined zone of the layer. It has been established that after carbonitriding of Armco-iron at  $t=550^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 280 \text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 120 \text{ Pa}$ ,  $\tau = 4 \text{ h}$ , the most gradual change of the content of carbon, nitrogen and oxygen in the carbonitride zone occurs.

**Key words:** carbonitrided layers, low-temperature plasma, GDOES-analysis

### I. Introduction

The Glow Discharge Optical Emission Spectroscopy analysis (GDOES- analysis) is an atomic emissive process for making a deep profile analysis. It combines sputtering and atomic emissions in order to enable an extremely fast and sensitive analysis. Plasma is generated in an analytical chamber by means of the applied voltage between the anode and the cathode, and also due to the availability of argon under low pressure. The ionized argon atoms cause sputtering of the area of the sample. The deposited atoms are excited in the plasma and emit photons with characteristic wave lengths [1, 2, 3, 4]. GDOES-studies are carried out by means of a glow discharge source and an optical spectroscope. They allow for preparing a deep profile of the chemical composition of a hard material layer. For the analysis, argon ions are forced in the glow discharge plasma on the surface of the sample, connected to the cathode. As a consequence of the impulse exchange of argon ions, mostly atomic particles of the layer are detached from the surface of the sample. The positive argon ions are

dragged out of the plasma, focused and directed towards the sample. The atoms, freed from the sample, are excited in the plasma, chiefly by electron collisions, and they become a source of a characteristic radiation, which is detected and analyzed by the spectroscope.

GDOES-analysis is normally used for defining surface coatings, hidden connections, layer profiles and deep profiles. The technique offers quick, reliable and economically efficient decisions. It offers additional information for the rest of the methods for surface analysis [3,5]. The aim of the present work is to study the possibility to define the distribution of carbon, nitrogen and oxygen in the depth of the carbonitrided layer, formed in low-temperature plasma in a medium of ammonia and corgon.

### II. Methodology of study

#### 2.1. Thermal treatment

For carrying out the analysis armco-iron was chosen, with chemical composition, checked by the equipment for automatic analysis "Spectrotest" and given in Table 1.

**Table 1.** Chemical composition of Armco-iron

Materials	Chemical elements, weight percentage							
	C	Si	Mn	Cr	Ni	S	P	Mo
Armco-iron	0.02	0.01	0.07	0.02	0.03	0.002	0.002	0.02

Testing samples were made from the material, with dimensions 15 x 15 x 10 mm and hardness 75HV. Treated this way, the samples were then grinded to surface roughness  $R_a = 0.63 \mu\text{m}$ . After that they were ion carbonitrided in the installation "Ion – 20" under a

few modes, given in Table 2. Ammonia (NH<sub>3</sub>) and corgon (82% Ar и 18%CO<sub>2</sub>) in different percentage ratio were used as saturating gases. The temperature of treatment was 550°C.

**Table 2.** Modes and results from the ion carbonitriding of Armco-iron

№ of the mode	$\tau$ h	$P_1$ NH <sub>3</sub> Pa	$P_2$ corgon Pa	P total Pa	Armco-iron			
					HV <sub>0,1</sub>	$\delta_{tot}$ $\mu$ m	$\delta_{c.z}$ $\mu$ m	U V
1	4	360	40	400	420	280	7	470
2	4	200	200	400	390	265	6,5	415
3	4	280	120	400	480	290	8	435

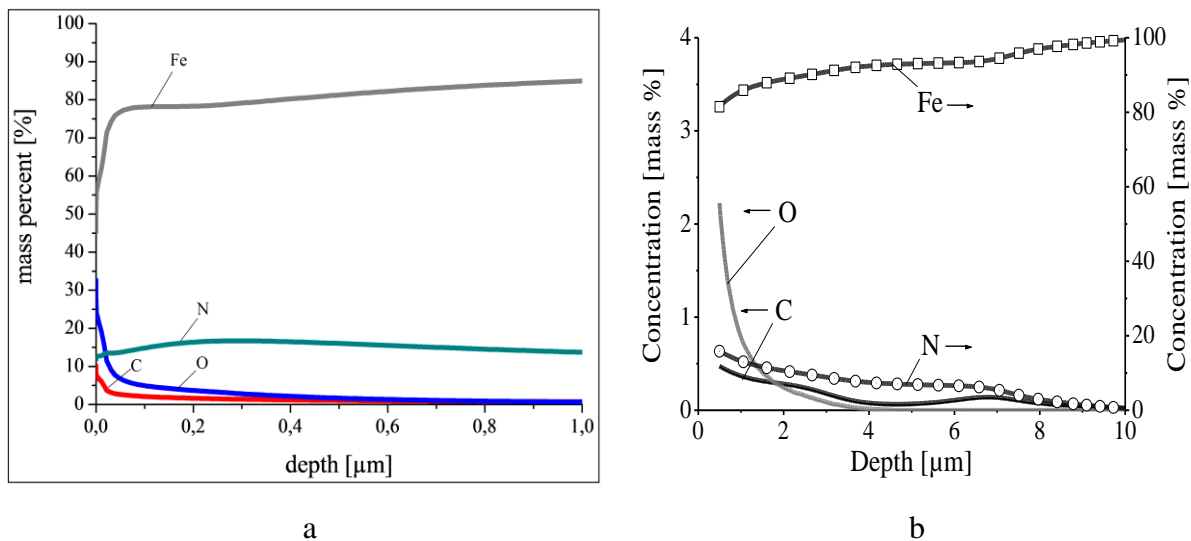
**2.2. Glow discharge optical spectral analysis**

The distribution of nitrogen, carbon and oxygen in the carbonitrided testing samples was determined by the device GDOES – GDA – 750, vom Spectruma-Analytik GmbH. The parameters of the glow discharge plasma were: current 20 mA, voltage 800 V, plasma density  $10^{10}$ - $10^{11}$  cm<sup>-3</sup>, temperature of the electron 0.1 - 0.5 eV and plasma volume 15 cm<sup>3</sup>. The turbomolecular pump (56  $\ell \cdot s^{-1}$ ) operated continuously. The basic pressure was  $10^{-6}$  Pa. The surfaces were polished in advance to achieve

packing of the plasma section of the device GDOES. The device calibration was done by means of a testing sample, containing 7 weight percents of nitrogen and 1 weight percent of carbon.

**III. Results from the study and analysis**

Fig. 1 gives the distribution of carbon, nitrogen, and oxygen in Armco-iron after carbonitriding at :  $t = 550$  °C,  $P_{NH_3} = 360$  Pa,  $\tau = 4$  h,  $P_{82\% Ar + 18\% CO_2} = 40$  Pa, mode 1 - Table 2.



**Figure 1.** Distribution of carbon (C), nitrogen (N) and oxygen (O) in Armco-iron after carbonitriding at  $t = 550$  °C,  $P_{NH_3} = 360$  Pa,  $P_{82\% Ar + 18\% CO_2} = 40$  Pa,  $\tau = 4$  h

Under this mode of treatment a layer with surface micro-hardness 420HV<sub>0,1</sub>, total thickness 280 $\mu$ m and combined zone thickness 7 $\mu$ m is obtained. The concentration of carbon in the depth of the carbonitride zone is comparatively low, on the surface it reaches 0,45 % and at 4,7  $\mu$ m it is the lowest (0,14 %). Small increase in the amount of carbon up to 0,25 % is observed at the end of the combined zone (7 $\mu$ m). The distribution of the nitrogen in the depth of the carbonitride zone is smooth, reaching at its end up to 4.9 %.

The distribution of oxygen in the combined zone is steep to 1,2 $\mu$ m, and then it starts changing smoothly, reaching depth of up to 4 $\mu$ m. For this

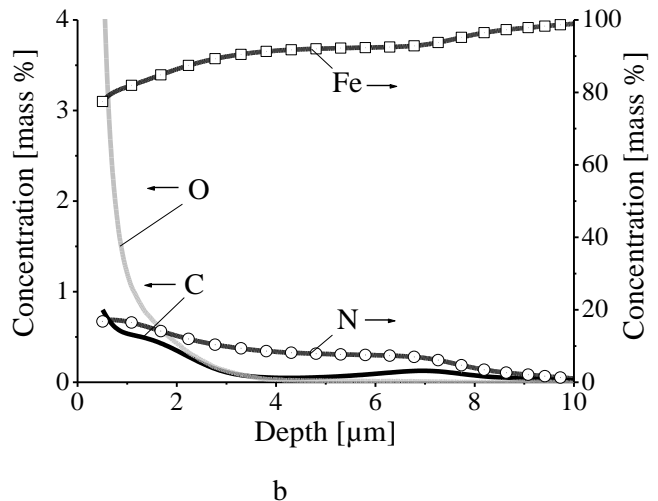
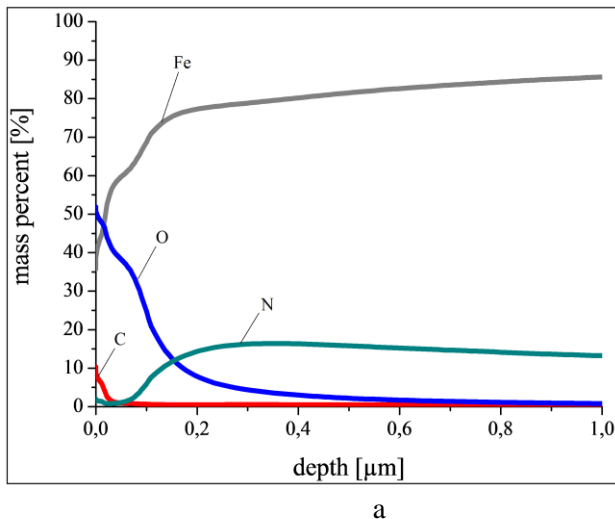
mode of carbonitriding the amounts of carbon and nitrogen change smoothly and gradually but they are with lower concentration in the depth the combined zone than under mode 3 – Table 2.

After carbonitriding of Armco-iron under mode 2 a layer is obtained, having surface micro-hardness 390HV<sub>0,1</sub>, total thickness 265  $\mu$ m and combined zone thickness 6,5  $\mu$ m. The distribution of carbon, nitrogen and oxygen in the depth of the carbonitride zone is given in Fig. 2.

From Fig. 2 it can be seen that at the end of the combined zone in the carbonitrided layer, at 6,5 $\mu$ m, small increase in the content of carbon to 0,25 % is observed, wherein the distribution of carbon in the

depth of the combined zone is smooth to the moment of reaching a depth of 4 $\mu\text{m}$  with concentration of 0,10 %. At the end of the carbonitride zone the concentration of carbon increases to 0,25 %. The distribution of nitrogen in the carbonitrided zone is smooth and at the end of the combined zone (6,5 $\mu\text{m}$ )

it reaches 3.5 %. Another type of distribution is observed with oxygen. In the combined zone the distribution of oxygen is steep to 1.5 $\mu\text{m}$  and then it changes smoothly and gradually, reaching a depth of up to 4 $\mu\text{m}$ .



**Figure 2.** Distribution of carbon (C), nitrogen (N) and oxygen (O) in Armco-iron after carbonitriding at  $t = 550^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 200 \text{ Pa}$ ,  $P_{82\% \text{Ar} + 18\% \text{CO}_2} = 200 \text{ Pa}$ ,  $\tau = 4$

After ion carbonitriding of Armco-iron under mode 3 from Table 2, a layer is formed with the highest micro-hardness 480HV<sub>0,1</sub> of all considered modes of treatment, what can be explained by the distribution of carbon, nitrogen and oxygen in the carbonitrided zone – Fig. 3.

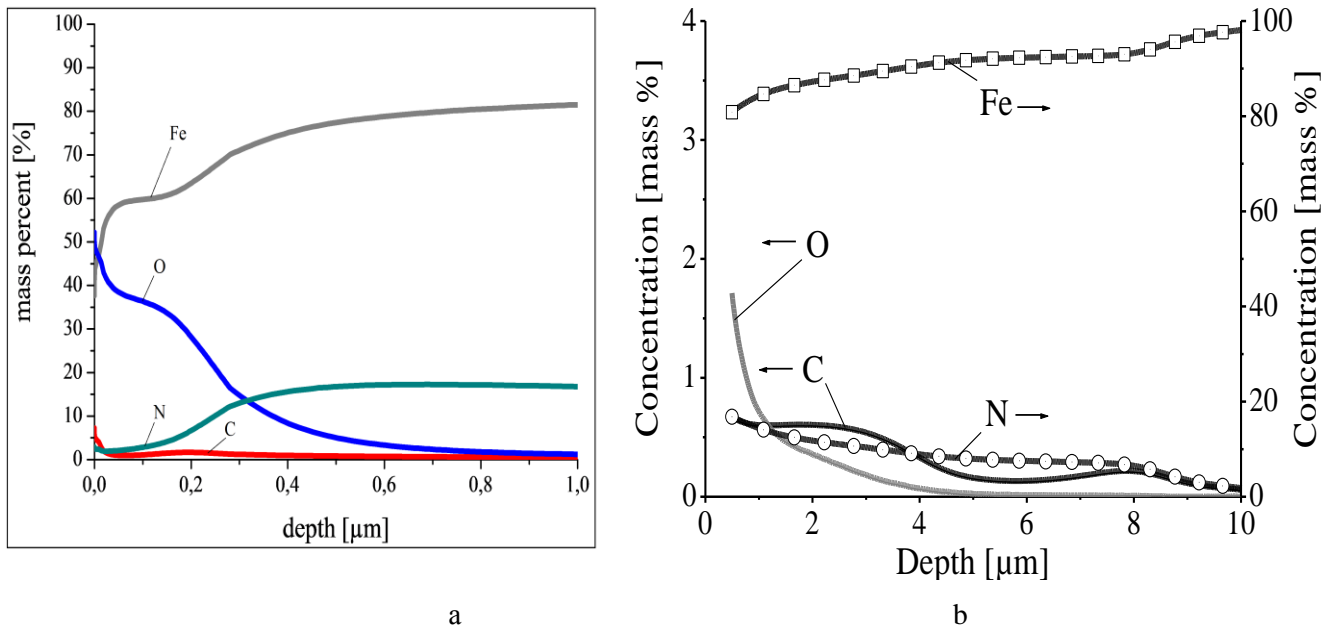
From the figure it can be seen that there is increased concentration of carbon in the depth of the combined zone to the point of 3 $\mu\text{m}$ , it reaches 0,65 % and stays almost constant. After that, to a depth of 6 $\mu\text{m}$ , it decreases and then increases (0,45%) at the end of the carbonitride zone of the layer (8 $\mu\text{m}$ ). The distribution of nitrogen in the carbonitride zone is smooth with increased concentration. It can be noted that under this mode of carbonitriding we have a smoother variation of the content of carbon and nitrogen, which are with higher concentration in the depth of the carbonitride zone of the layer. Different type of distribution is observed with oxygen. In the combined zone the distribution of oxygen is steep to a depth of 1.2 $\mu\text{m}$  and then it changes smoothly and gradually, reaching a depth of up to 6 $\mu\text{m}$ . It is obvious that this amount of oxygen influences positively the process of combined zone forming. Oxygen in the vacuum chamber probably combines with hydrogen and decreases the partial pressure of hydrogen, what, in turn, leads to increasing the potential of nitriding. This concentration of oxygen

speeds up the process of surface saturation with nitrogen.

It can be noted that when in the process of carbonitriding a saturating medium, containing bigger amount of CO<sub>2</sub> (P=200Pa,) is used, then on the surface of Armco-iron a combined zone with highest concentration of carbon 0,78% is formed (Fig.2, mode 2, Table 2), while, in case of a smaller amount of CO<sub>2</sub> (P=40Pa), the concentration is the lowest - 0.48%. From the considered modes of ion carbonitriding of Armco-iron the most uniform distribution of nitrogen, carbon and oxygen in-depth the layer is observed under mode 3 from Table 2. The active role of argon in bringing carbon, nitrogen and oxygen on the surface of the treated material is worth underlining. Due to its bigger atomic mass and higher discharge voltage 470 V (mode 1, Table 2), argon has a strong sputtering action. With the high coefficient of sputtering the length of the free run of the sputtered atoms is bigger, so the chance for backward diffusion of carbon, nitrogen and oxygen is smaller. Together with the variation of both the pressure and the content of argon in the saturating medium (ammonia and argon), the backward diffusion of nitrogen, carbon and oxygen can be regulated, thus obtaining layers with various parameters and properties. The increase of CO<sub>2</sub> pressure from 40Pa to 200Pa leads to decrease in the discharge voltage from 470 V to 415V (Table 2),

what considerably influences the coefficient of sputtering. This leads to a different concentration profile of the distribution of carbon, nitrogen and

oxygen in the combined zone of the carbonitrided layer.



**Figure 3 .** Distribution of carbon (C), nitrogen (N) and oxygen (O) in Armco-iron after carbonitriding at  $t = 550\text{ }^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 280\text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 120\text{ Pa}$ ,  $\tau = 4$

From the conducted GDOES-analysis of the carbonitrided samples it is necessary to note that at a distance of  $0.2\mu\text{m}$  from the surface of the combined zone an anomaly of the concentration of carbon, nitrogen and oxygen is observed. This is probably due to the complex chemical processes going on the cathode surface because of the glow discharge.

#### IV. Conclusions

1. It has been proved that after carbonitriding of Armco-iron at  $t=550\text{ }^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 280\text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 120\text{ Pa}$ ,  $\tau = 4\text{ h}$ , the smoothest change of the content of carbon, nitrogen and hydrogen occurs in the carbonitrided zone of the layer.

2. Increased amount of carbon has been established both in the combined zone and in the diffusion zone of the carbonitrided layer.

3. It has been proved that oxygen is only observed in the carbonitrided zone of the layer.

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## THE INFLUENCE OF THE PLANTS' PACKAGING ON THE QUALITY OF *MENTHA SPICATA* AND *TILIA EUROPEA* TEAS

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**Abstract.** The influence of the plant packing on the tea quality is less studied. Furthermore, plant classification into quality classes is made especially for the dry leaf of the tea tree, *Camellia sinensis* species, and rarely for medicinal plants of other species. Considering these aspects, the aim of this paper was to study the packaging influence on the plants' quality and on the quality of the teas prepared from these plants, as well.

In order to obtain qualitative and safe for consumer use products there are presented the results of an experimental research whose objective was to study the after dry packing influence on the plants' physico-chemical parameters and on the obtained teas' sensory properties, as well. For this analysis, there were selected eight samples from two plant species (mint - *Mentha spicata* and linden – *Tilia europea*) which were bulk, bag, paper and filter paper sachets packed. The evaluated physico-chemical indicators were moisture, tanning substances and ash content. The studied sensory parameters were the plants' aspect after the infusion preparation and the tea color, limpidity, aroma and smell. Based on the obtained results following these analyzes it was determined which is the plants' packaging that ensures the achievement of a high quality tea.

### I. Introduction

The large variety of medicinal plants used for tea preparing causes a complex composition of these beverages, which directly depends on the utilized plant and on the environment, climate, annual variations and other endogenous and exogenous factors. Likewise, the tea composition is influenced by both the plants' quality and the preparation mode, concentration, temperature and infusion time (Kabelitz, 2003). The plant as a whole is considered the active principle of tea, whether all components with therapeutic activity or which contribute to it are known or not. Currently, the research into herbal teas domain have regard to production, consumption and therapeutic use in terms of region, the plants' quality and composition. In the matter of teas' composition, the latest issues of interest are the phenolic compounds content and the antioxidant activity. The quality of tea plants depends on composition and contaminants, especially the chemical (pesticides) and microbiological ones. In order to assess the quality of plants there currently exist modern methods with high accuracy which provide a full analysis in a short time.

Other points of interest in tea preparing are the storage period and additives (sweeteners, ascorbic acid) influence on the beverages' composition. Materska (2010) observed a reduction in the phenolic compounds content of the plants' ethanolic extracts, including mint and sage, after a storage period of 3 and 6 months. While in case of the sage extract the largest decrease is recorded in the first 3 months of storage, for the mint leaves extract a shelf life over 3 months has a significant influence on the phenolic compounds content, which is reduced at the

less than 50% of the initially determined value in the extract.

Regarding the influence of certain additions on the herbal teas composition, Piljac-Zegarac, Samec & Piljac (2013) observed that the ascorbic acid addition increases the antioxidant activity. As concerns the addition of honey in floral teas, it was observed that it remotely affects the beverage antioxidant content (Belščak, Bukovac & Piljac-Žegarac, 2011).

Important components in medicinal plants are organic acids that contribute to their aroma and have an essential role in their microbiological stability. Truică, Teodor & Radu (2013) have studied the organic acids content (succinic, malic, tartaric, citric and lactic) of three sorts of tea: chamomile, mint and linden. The teas' obtaining conditions were a temperature of 100°C and a 5-minute infusion. In the first case, the water was added over the plants' sachets which were then left to infuse, while in the second case the plants were boiled in water for 5 minutes. The used method of analysis was the capillary electrophoresis.

In the matter of the packaging influence the on the tea quality, Komes *et al.* (2010) have showed that the antioxidant activity and the catechin content of the green tea varies when the leaves are integer, shredded or packed in sachets. The latter two types have provided a higher phenolic compounds content in tea regardless of the extraction temperature. The total content of flavonoids was in this case 1 g/l, while that of the integer leaf tea made by infusing varied between 0.35 and 0.9 g/l. The highest concentrations were obtained at a 80°C temperature, with a 5-minutes infusion time for the shredded



leaves, 15 minutes for those packed in sachets and 30 minutes for the integer leaves (Komes *et al.*, 2010). The increase of both the temperature and the infusion time had a positive influence on the antioxidants extraction. However, there are studies that have shown that the efficiency of phenolic compounds extraction from the white tea (Rusak *et al.*, 2008) and from the green tea (Samaniego-Sanchez *et al.*, 2011) is not influenced by the plants' packaging mode.

## II. Materials and methods

The aim of the present research was to study the combined influence of the plants' packaging mode after their drying and of the plants' shredding degree on the physico-chemical parameters of the plants and on the sensory properties of the obtained teas, as well. The evaluated physico-chemical indicators were moisture, tanning substances and ash content.

For the analysis, there were selected eight samples from two plant species: mint (*Mentha spicata*) and linden (*Tilia europea*). These were purchased from the commercial network in Suceava county. The packing mode and coded notation used to identify each sample are shown in Table 1.

**Table 1.** The samples' packaging and identification mode

Type of plant (species)	Packaging mode	Assigned code
Mint ( <i>Mentha spicata</i> )	bulk packaging	P1
Mint ( <i>Mentha spicata</i> )	bag packaging	P2
Mint ( <i>Mentha spicata</i> )	paper packaging	P3
Mint ( <i>Mentha spicata</i> )	sachet packaging	P4
Linden ( <i>Tilia europea</i> )	bulk packaging	P5
Linden ( <i>Tilia europea</i> )	bag packaging	P6
Linden ( <i>Tilia europea</i> )	paper packaging	P7
Linden ( <i>Tilia europea</i> )	sachet packaging	P8

Regardless of the plant' packaging mode when purchasing it, it was considered for all the samples to have the same grind degree when carrying out the analyzes. Therefore, the integer leaves or flowers were shredded.

In order to assess the teas' sensory properties there were conducted tastings. The analyzed infusion was prepared by adding 3 g of tea plants in a porcelain kettle, in which there were poured 125 ml of hot water, followed by a 5-minutes infusion time. For examining the tea plants, they were topped on the cover and their color and appearance were appreciated. The tasting was conducted by 10 panelists for each sample.

The evaluated organoleptic properties were:

- the plants' aspect: it must be uniform, in the form of thin fibres, gnarled, integer or fragmented, clean, with no conglomerations and no mineral or vegetal impurities. Plants in small packs (sachets which are used as such) should be in powder form with uniform appearance, clean and with no foreign bodies. The color must be specific to the plant species, uniform;
- the colour: this varies from yellow to reddish-brown;
- the limpidity: the infusion should be clear, with no sediment;
- the aroma: it must be characteristic to the plant, well defined;
- the smell: distinctive, without foreign smells (mold).

In order to assess the each sensory attribute it was used the scoring scale method, from 0 to 5 points. The systems with a small number of points are characterized by simplicity, clarity and the convenience in appreciation as they contain net delimitative notions. The 5-points system consists in the fact that for each feature there are set 6 ranges (from 0 to 5), thus achieving a differentiated assessment of the product. If the product has completely changed features and it is not proper for consumption, 0 points are assigned. The assessment ranges in the 5-points system are shown in table 2.

The score assigned by the tasters to each organoleptic property has been included in the individual form of sensory analysis.

**Table 2.** The score scale for the sensory analysis by the 0-5 points scale method

5	Very good	Ideal exceptional qualities
4	Good	Qualities corresponding to standards
3	Satisfactory	With slight defects
2	Unsatisfactory	With obvious defects
1	Bad	With strongly pronounced defects
0	Adulterated	Adulterated, with major changes in the characteristics

### III. Results and discussion

The difference in the plants' moisture content according to the type of packaging is graphically shown in figure 1. As it can be seen, the mint leaves which were bag packaged presented the highest moisture content, followed by those which were bulk packaged. As in these two cases the plastic material from which the packaging is made is usually the same, the higher moisture content for the plants packed in bags can be explained by the fact that their grammage is lower than the typical grammage of the bulk packaging. Thereby, after the packaging is opened, the plants absorb more easily the humidity

from the atmosphere. The mint packed in filter paper sachets presented the lowest moisture content, of 7.21%. Similarly, for the linden flowers packed in sachets it was determined the lowest moisture content value (7.02%). Also, the linden plants packed in bags had the highest moisture content value. In the case of the linden flowers it can be easily observed that keeping plants in paper containers fosters the moisture content increase.

Except for the moisture content value of the mint leaves packaged in bags, the rest of the determined values do not exceed the maximum limit specified by ISO 3720: 2011, i.e. 9%.

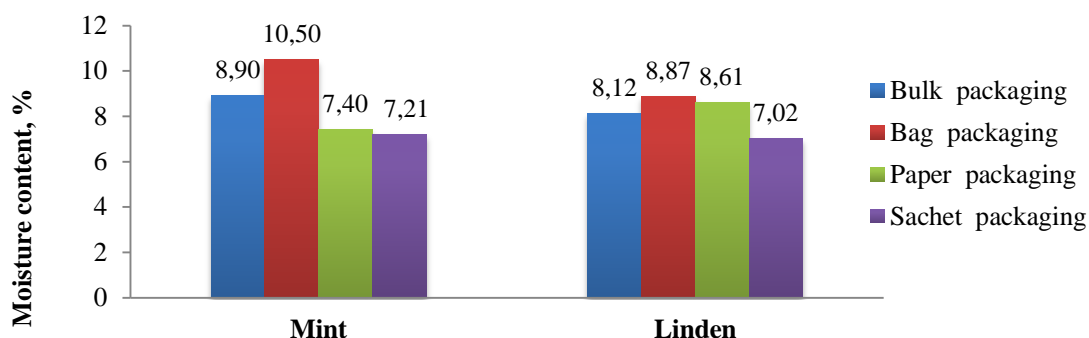


Figure 1. The variation in plants' moisture content according to the packaging mode

The ash content of the plants should not exceed 6.5%. As the figure 2 shows, this level is exceeded in the case of the bulk and bag packaged mint and for

the bag and paper packaged linden, too. The lowest ash content was determined for the bulk packaged linden flowers (5.98%).

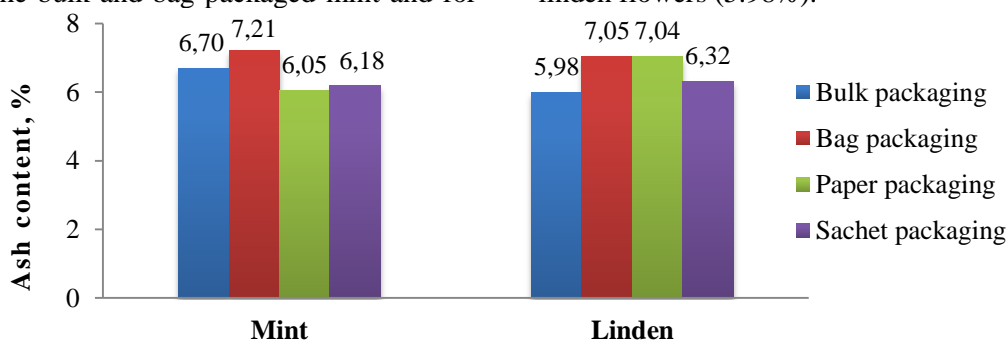


Figure 2. The variation in plants' ash content according to the packaging mode

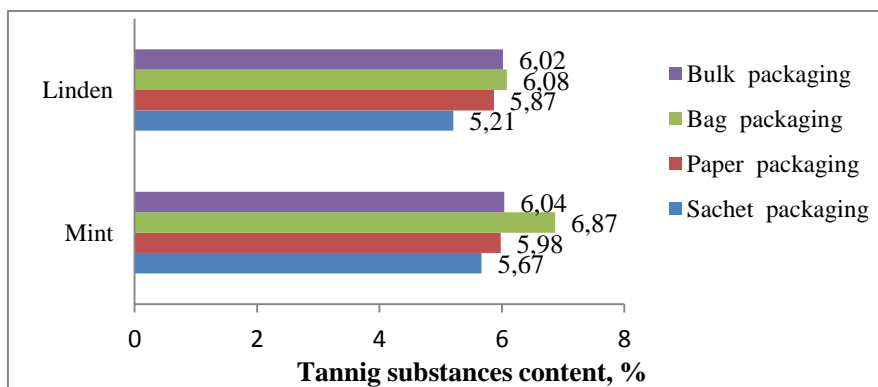


Figure 3. The variation in plants' tanning substances content according to the packaging mode

As it is shown in the figure 3, the mint leaves generally have a higher content of tanning substances than the linden flowers. The bag packaging maintains high concentrations in these compounds, the determined content being 6.87%. For the bulk packaged mint leaves it was determined a tanning substances content of 6.04%. The lowest tanning substances content is characteristic to the plants packaged in filter paper sachets, the determined value for the mint being 5.67%, while for the linden it was determined a lower value of 5.21%. The difference between the tanning substances content of the bulk packaged linden flowers (6.02%) and that of the bag packaged linden flowers (6.08%)

is very small compared to that obtained for the mint leaves. The ISO 3720:2011 standard establishes a maximum content of tanning substances in the extract of 7%, and thus it can be concluded that the values determined for the analyzed samples in the present case fall within the limits established by law.

*The sensory analysis of linden and mint teas*

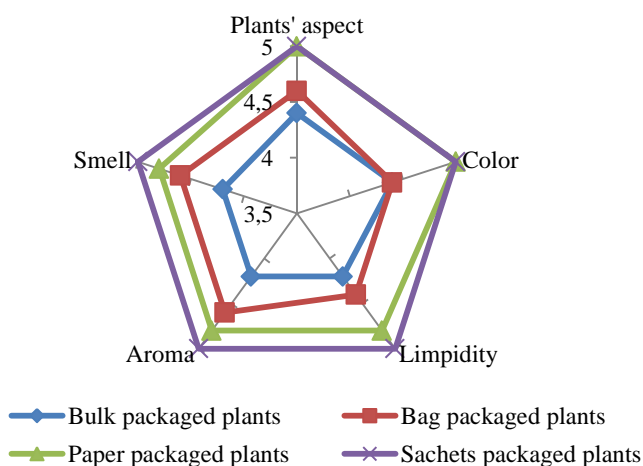
The sensory analysis for the tea samples was carried out by 10 tasters, the studied parameters being the plants' aspect after the infusions preparation and the tea color, limpidity, aroma and smell. The average scores obtained for each of these sensory characteristics of the analyzed samples are noted in table 3.

**Table 3.** The average values obtained for the sensory parameters of mint tea

The sensory characteristic	Plants' packaging mode			
	Bulk	Bag	Paper	Sachets
Plants' aspect	4,4	4,6	5	5
Color	4,4	4,4	5	5
Limpidity	4,2	4,4	4,8	5
Aroma	4,2	4,6	4,8	5
Smell	4,2	4,6	4,8	5

The average values obtained for the mint tea samples' sensory properties are graphically represented in figure 4. The most appreciated sensory characteristic was the plants' aspect after the infusion process, for which the average was 4.75 points. The sensory analysis for the mint tea showed that the most appreciated tea samples are the ones obtained by infusing the plants packaged in filter paper sachets and the paper packaged mint leaves. For the first ones, it was achieved a maximum score

for the plants' aspect and the tea color, limpidity, aroma and smell, too. In comparison with the teas obtained by infusing the mint leaves sachets, those prepared from paper packaged leaves received the same score (5 points) for the plants' aspect after the infusion process and the infusion color and lower scores for the remaining sensory characteristics, those being noted by 4.8 points for the tea limpidity, aroma and smell.



**Figure 4.** The graphical representation of the obtained scores for the sensory characteristics of the mint tea studied samples

Less appreciated by the tasters were the bag and bulk packaged mint leaf teas. The latter tea sample obtained the lowest score (4.2 points) for the infusion's limpidity, aroma and smell. This score can be justified by the fact that bulk packaged plants generally have a high grammage, and an improper handling leads to losses of package integrity and thereby reduces the plants' quality. Moreover, after the package opening it no longer effectively protects the product from the water vapor permeation, which favors the moisture content growth and consequently the degradation of certain flavor compounds and tanning substances. For this reason, this type of packaging should be avoided

when there are not required high amounts of plants for the tea preparation.

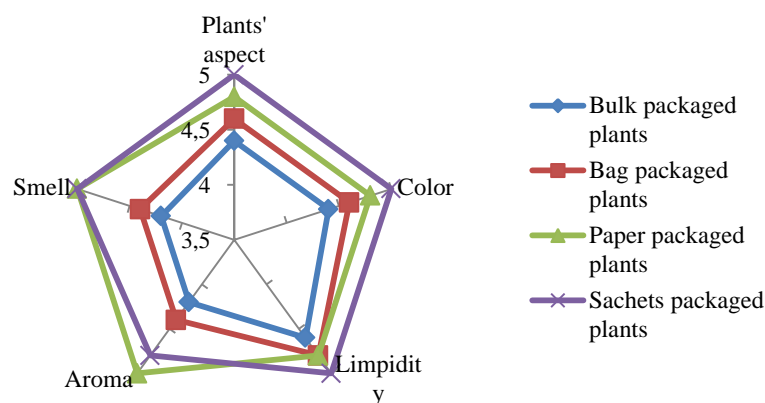
The tea made from bag packaged mint leaves was noted by 4.6 points for the plants' aspect and the infusion's aroma and smell. The color and the limpidity were less appreciated by the tasters, the average score obtained for these sensory features being 4.4 points.

The average scores obtained for the linden plants' aspect after the infusions preparation and the linden tea color, limpidity, aroma and smell are noted in table 4.

These values are graphically illustrated in figure 5.

**Table 4.** The average values obtained for the sensory parameters of linden tea

The sensory characteristic	Plants' packaging mode			
	Bulk	Bag	Paper	Sachets
Plants' aspect	4,4	4,6	4,8	5
Color	4,4	4,6	4,8	5
Limpidity	4,6	4,8	4,8	5
Aroma	4,2	4,4	5	4.8
Smell	4,2	4,4	5	5



**Figure 5.** The graphical representation of the obtained scores for the sensory characteristics of the linden tea studied samples

As it can be observed from figure 5, the most appreciated sensory attribute was the limpidity of the linden tea. In the case of the tea prepared from sachet packaged plants it was obtained a maximum score for the plants' aspect and the infusion's limpidity, color and smell. The tea aroma was less appreciated, being noted with 4.8 points. The aroma and the smell of the tea made of paper packaged linden flowers were given the maximum score, while the tea's color and limpidity and the plants' aspect were noted by

4.8 points each. These two tea samples were the most appreciated by the tasters.

As in the case of the mint tea sensory analysis, the linden tea samples prepared from bag and bulk packaged plants were less preferred by the tasters. Although the limpidity was more appreciated (4.8 and 4.6 points), the other sensory attributes had lower average scores, of 4.4 and 4.2 points. Based on these observations and on those anteriorly made, it may be concluded that in terms of sensory

parameters, the sachets and paper packaged plants are preferable.

#### IV. Conclusions

In the present paper it has been studied the influence of the medicinal plants packaging on teas' quality.

This theme is less studied in the case of the plants belonging to other species than *Camellia sinensis* (tea tree). The recent researches usually look at the beneficial effects of tea consumption and its composition, being particularly studied the profile of the phenolic compounds and the antioxidant content.

For the experimental analysis, there were selected two plant species, namely mint (*Mentha spicata*) and linden (*Tilia europea*). The quality of the tea produced from each specie was studied in following packaging conditions of the plants: bulk, plastic material bag, paper bag and filter paper sachets. The plants' grind degree was the same and the sample preparation was carried out according to each method of analysis.

The quality of the packaged plants was assessed by analyzing the following physico-chemical indicators: moisture, ash and tanning substances content. Based on the obtained values it was determined that the moisture and the ash content of plants is within the limits set by standards, except for the bag packaged mint leaves, whose moisture content exceeds the maximum value of 9%. However, for the bag packaged plants there were determined the highest concentrations of tanning substances.

The quality of the linden and mint tea was evaluated based on sensory analysis. For the infusion obtaining there were used 3 g of shredded plants and 125 ml of boiling water. The infusion time was 5 minutes. The sensory parameters studied within the sensory analysis were: the plants' aspect after the infusion process and the tea's color, limpidity, aroma and smell. The most appreciated samples, both for the mint tea and for the linden tea, were those

prepared from plants packaged in sachets and paper bags.

Considering the physico-chemical determinations and the sensory analysis results, the most efficient packaging mode for plants is represented by the filter paper sachets. These packages ensure maintaining the physico-chemical parameters of plants and protect the product against the water vapor permeation. Not the least, the teas obtained from sachet packaged plants present superior sensory attributes.

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## USE OF ESSENTIAL OILS IN DAIRY PRODUCTS 2. ESSENTIAL OIL OF CARAWAY (*CARUM CARVI* L.)

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**Abstract.** Lactic acid products with enriched composition are developed by adding linseed and sesame seeds, oat flakes, honey and essential oil of caraway (*Carum carvi* L.). The effect of the additives on the process of acid formation, syneresis, and the development of lactic acid bacteria has been studied. It was found that they have a good effect on the lactic acid process. The received products have got good organoleptic parameters with the specific for the caraway fruits taste and smell.

**Key words:** dairy products, titratable acidity, syneresis, lactic acid bacteria.

### I. Introduction

Food is important to maintain and protect human health. A lot of traditional products (milk, fruits, vegetables, etc.) contain components with potential health benefits. New ones based on these food are being developed and they increase or join their useful components because of their benefits or desirable physiological effects. Today functional food based on milk takes up two- thirds of the total volume of the functional foods on the market as dairy foods are foods with naturally balanced composition of the essential nutrients such as protein, fats, carbohydrates, minerals, and enzymes. In the lactic acid products might be used: probiotics, dietary fibres (soluble and insoluble), vitamins, mineral elements, polyunsaturated fatty acids, essential oils, antioxidants, inulin, lactulose, etc. [2, 4, 15, 18, 21].

In our previous work [7] were prepared and examined dairy products containing linseed and sesame seeds, oat flakes, and honey. It was found that the products have the properties of functional food and the additives have positive effect on the development of lactic acid process.

Interest in recent years is the use of essential oils in food products in order to increase their absorption by the human body, to enrich the composition, to improve the aroma, to prolong the durability, etc.[1, 5, 9, 10, 11, 12, 17, 23].

The results from our previous studies [16] show that the essential oil of caraway has got antimicrobial activity but it does not inhibit the development of the lactic acid bacteria in dairy starter cultures.

The purpose of this work is to develop and examine dairy products with enriched composition by adding linseed, sesame seeds, oat flakes, honey and caraway oil.

### II. Materials and methods

The studies were conducted in laboratory conditions with cow milk which was obtained from Razgrad region, northeastern Bulgaria.

The physicochemical parameters of raw milk (fat, solids-nonfat (SNF), density, added water, protein) were determined by the milk analyzer EKOMILK Company BULTEH 2000.

The microbiological parameters of the raw and pasteurized milk were tested by conventional methods [22].

The fermented milk product with set coagulum (control) was prepared by a classical technology with the symbiotic starter culture of the strains *Lactobacillus delbrueckii subsp. bulgaricus* and *Streptococcus thermophilus* purchased by the company Selur Pharma Ltd.

The control sample was obtained by traditional technology for yogurt [8].

The studied samples (№ 1 to 3) were prepared by traditional technology by adding: oat flakes (6%), linseed (4%), sesame seed (2%) and honey (4%) (№ 1); essential oil (№ 2); the combination of the ingredients of the first and second examined samples (№ 3).

The additives used were purchased from the market, the essential oil of caraway was obtained in laboratory conditions [16]. The amount of the oil is 0.8 mg/kg of final product, which was consistent with the known literal data and our previous studies [10, 16].

The prepared dairy products were analyzed on chemical, microbiological and organoleptic characteristics:

- The dynamics of the lactic acid process was monitored by the determination of the titratable acidity (°T) [8, 22].

- Microbiological research - total number of viable lactic acid bacteria - *Lactobacillus delbrueckii subsp. bulgaricus* and *Streptococcus thermophilus* were carried out by growing on the synthetic medium M17 and MRS (Merck) methodology of IDF [13, 14].

- The organoleptic assessment of the lactic acid products was carried out according to BNS 15612-83 [3].

### III. Results and discussion

The milk used for the experimental work meets the requirements of raw cow milk [6, 20].

Figure 1 presents the dynamics of the lactic acid process.

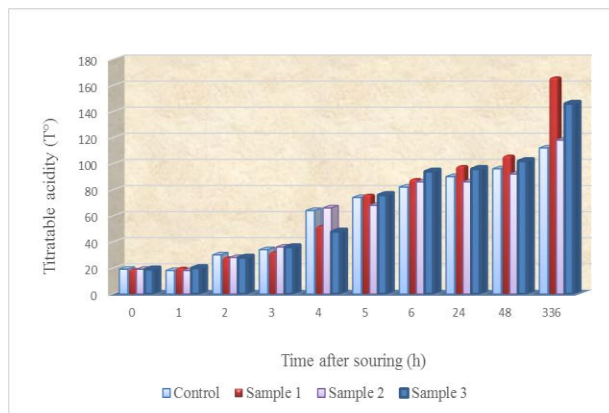


Figure 1. Dynamics of the lactic acid formation

The results show raising in the titratable acidity in all four samples as a result of the metabolism of lactic acid bacteria. More active lactic process was found in the samples with additives and when they were combined with caraway oil. For these samples the tendency to increase the acidity was maintained until the end of the study period as the 336<sup>th</sup> hour (14 days of the storage) the titratable acidity was higher than the control. The acid formation in these samples with added essential oil is the same like the control sample.

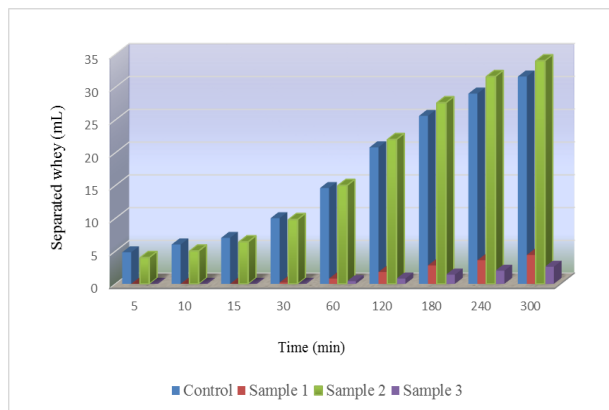


Figure 2. Syneresis of the fermented milk products

Figure 2 presents the results for the values of the syneresis of the prepared dairy products. The amount of the separated whey for 5 hours is highest in the control sample (31.6 mL) and in the milk with caraway oil (34 mL). Significantly less whey was separated in sample №1 (4.4 mL) and in sample №3 (2.6 mL), because of the ability of oat flakes and seeds to connect the water that leads to reduction of the aqueous phase of the milk.

The effect of the additives on the development of the lactic acid bacteria *Lactobacillus delbrueckii subsp. bulgaricus* and *Streptococcus thermophilus* in the tested products are shown in Figures 3 and 4.

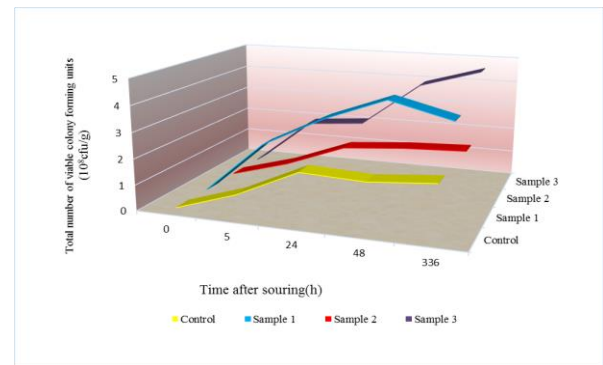
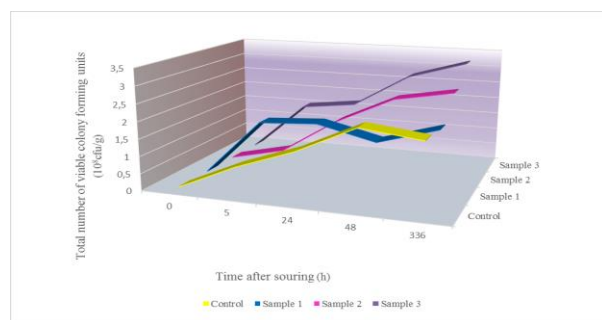


Figure 3. The dynamics of the growth of *Lactobacillus delbrueckii subsp. Bulgaricus*

It is obvious from the data obtained that with the exception of the dairy product with caraway oil, all the rest samples during the first 24 hours cells of *Lactobacillus delbrueckii subsp. bulgaricus* growth actively. After that to the end of the study period (14<sup>th</sup> day) the number of the viable cells was kept relatively invariable as in the dairy products with additives in combination with caraway oil (№1 and №3) it was higher content of the nutrients needed for the development of the lactic acid bacteria. The obtained results correspond to the prescribed values for the titratable acidity (Fig. 1).

In the examined samples the number of the viable cells of *S. thermophilus* was increased to 24<sup>th</sup> hour. Then the speed of the growth was kept relatively unchanged as at the end of the study period the number of cells increases faintly (Fig. 4). The lactic acid bacteria *S. thermophilus* develop more speed in the samples with the additives and they reach the largest number in combination of all additives and the essential oil (sample №3).

The caraway oil to a certain extent inhibits the development of the lactic acid bacteria *L. delbrueckii subsp. bulgaricus* and *S. thermophilus*, that is related to its antimicrobial activity [10, 12].



**Figure 4.** The dynamics of cell growth of *Streptococcus thermophilus*

The data from the qualification of the obtained dairy products according to organoleptic parameters are presented in Table 1. The obtained products were characterized with very good and balanced lactic acid taste, thick and smooth coagulum, homogeneous consistence and structure.

**Table 1.** Organoleptic indicators

Parameters	Control Sample	№ 1	№ 2	№ 3
Surface	smooth	smooth	smooth	smooth
Colour	white with cream-coloured shade	white with cream-coloured shade	white with cream-coloured shade	white with cream-coloured shade
Type of coagulum	thick, smooth	thick, smooth	thick, smooth	thick, smooth
Structure after cutting	smooth surface with slight serum separation	smooth surface without serum separation	smooth surface with slight serum separation	smooth surface without serum separation
Consistency after whipping the coagulum	homogeneous, like cream	homogeneous, like cream	homogeneous, like cream	homogeneous, like cream
Taste and flavor	tasty specific lactic acid	tasty specific lactic acid with a hint of the used nuts and honey	tasty specific lactic acid with a hint of caraway	tasty specific lactic acid with a hint of the used nuts and honey, and caraway

#### IV. Conclusion

Dairy products with added oat flakes, sesame seeds, linseeds, honey and essential oil of caraway (*Carum carvi* L.) were prepared. The combination of these additives affects adversely on the speed of lactic acid process, syneresis, and their organoleptic parameters. The products have got the specific for the fruits of caraway taste and aroma.

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## **STUDYING CRACK FORMATION IN THERMALLY TREATED STEELS BY ACOUSTIC EMISSION**

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**Abstract:** *The aim of the present paper is to study the possibility to use acoustic emission for studying the processes of microcracking and fracture of thermally treated materials.*

*The obtained results show that the acoustic emission can be used as an indicator of pre-destructive processes for thermally treated materials. It has been established that the values of  $K_Q$  (AE), defined for a material in a non-destructive way in laboratory conditions, can well serve in production as a criterion of forthcoming brittle fracture.*

**Key Words:** acoustic emission, fracture, thermally treated steels

### **I. Introduction.**

Reliability and exploitation life of tools and details depends mainly on origination and propagation of cracks, expressed by the following characteristics – fracture toughness  $K_{Ic}$  and critical opening of the crack banks  $\delta_{Ic}$  [4, 5, 6, 9].

In addition to wear at high contact loads and high temperatures, resistance against formation of cracks on the surface is essential for tools for hot working.

Tool steels for hot working, being not very plastic, are very sensitive to brittle fracture. About 70% of the reasons for failure of the molds for casting nonferrous alloys under pressure are due to magistral and thermal cracks [4, 5].

A number of methods for studying the processes of formation and development of cracks in multi-layer systems have been described in [1, 2, 10, 11, 12, 13]. Common disadvantage of most of these methods is that they are applied after completion of the fracture. One of the most modern methods for studying the processes of microcracking and fracture in the matrix and its adjacent thin layers is acoustic emission.

The acoustic emission (AE) is based on physical phenomena, related to radiation of acoustic impulses in the material. The sources of AE can be divided into two groups. The first one characterizes the phenomena, related to plastic deformation: twinning of the crystals, slipping along the grain boundaries and, most of all, own motion of the dislocations [1, 2, 11]. The phenomena, related to the motion of the dislocations are less energetic. They are registered by a continuous AE. The second group consists of the more pronounced energetic phenomena, accompanying the mechanisms of fracture: formation and propagation of the micro-crack, intercrystalline and

transcrystalline fracture, phase transformations etc. These phenomena are registered by an impulse AE.

The impulse type acoustic emission is observed in materials when suddenly mechanical energy of elastic deformation is released, at the moment of microcracking or propagation of cracks. Energy release in the deformed material goes discreetly as a series of individual acts, registered as AE-impulse and AE-phenomena (events) in a minor volume of the material. Then they propagate in the form of waves of elastic deformation (stress waves, AE-waves) throughout the volume. Registration of the spectrum and the parameters of AE, radiated by a material, subjected to deformation, gives significant information about the mechanisms of the process of crack formation and fracture.

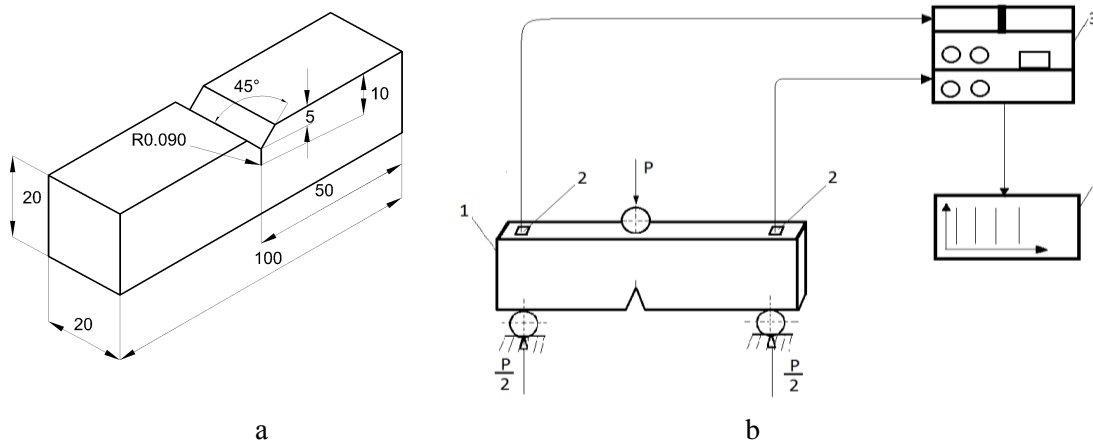
The aim of the present paper is to study the possibility to use acoustic emission for studying the processes of microcracking and fracture in thermally treated materials.

### **II. Methodology of study**

Experiments were conducted with steel BH11 BS4659 (4X5MΦC - ΓOCT), from which standard samples with a notch for three-point bending were produced [7, 8] – Fig. 1.

The spherical waves, emitted by the source, were transformed into surface AE-waves (stress waves), and registered by the sensor (2), attached to the sample (1). The mechanical energy of the acoustic-emission impulse was converted into an equivalent electrical signal. After filtration it was fed into the pre-amplifier and from there – into the analogue part for additional amplification and processing by the computer block of the AE-equipment PAC 3000/3104 (3). The processing of the characteristics of the AE-signal (duration, rise time, impulses, amplitude, energy etc.) was carried out by the

microcomputer of the AE-system and could be printed by a printing machine (4). The experiments were conducted at room temperature.



**Figure 1.** a - sample, b – block-scheme of the experiment  
1- sample, 2- sensors, 3- AE systems, PAC 3000/3104, 4-printer

Two samples were studied, quenched in a vacuum furnace VKUQ–Degussa of 1313K (1040°C) with gas argon at 6 barr pressure, and hardness of 54 HRC was reached. After that the samples were tempered at 873K (600°C, sample 253, hardness 51HRC) and 923K (650°C, sample 255, hardness 46 HRC). The tip of the notch was made on a thread electrical erosive machine with a radius of curvature of 0,09 mm and a length of 5 mm. After the thermal treatment the samples were grinded to  $R_a = 0,32 \mu\text{m}$ .

The resistance against crack propagation was defined for three-point bending of the samples by means of a universal testing machine INSTRON 1343 at velocity of loading 0,5mm/min. The motion of the crack banks ( $V_9$ ) was registered at room temperature by a console tenso-resistive perceiver with sensitivity 2,5  $\mu\text{V}/\text{mm}$ , base 10 mm and step 2 mm, having the diagram force (P) – crack banks motion recorded at the same time ( $V_9$ ). For studying the AE-activity in three-point bending and fracture of the samples a four-channel AE-system PAC 3000/3104 with wide-band sensors Wd was used – Fig. 1. The sensors were placed on a sample, locally doped with silicon paste, and fastened by special springs, providing constant pressure. The sensitivity of the sensors was controlled by the imitator of Xcy. At total amplification of 80 dB (40 dB pre-amplification) and constant threshold of 1V, a registered signal of 98 dB from the imitator was taken as good sensitivity.

For clearing out and correct interpretation of the results from the acoustic-emission (AE) tests,

calibration curves were obtained based on metallographic and fractographic analyses, concerning the different structural states.

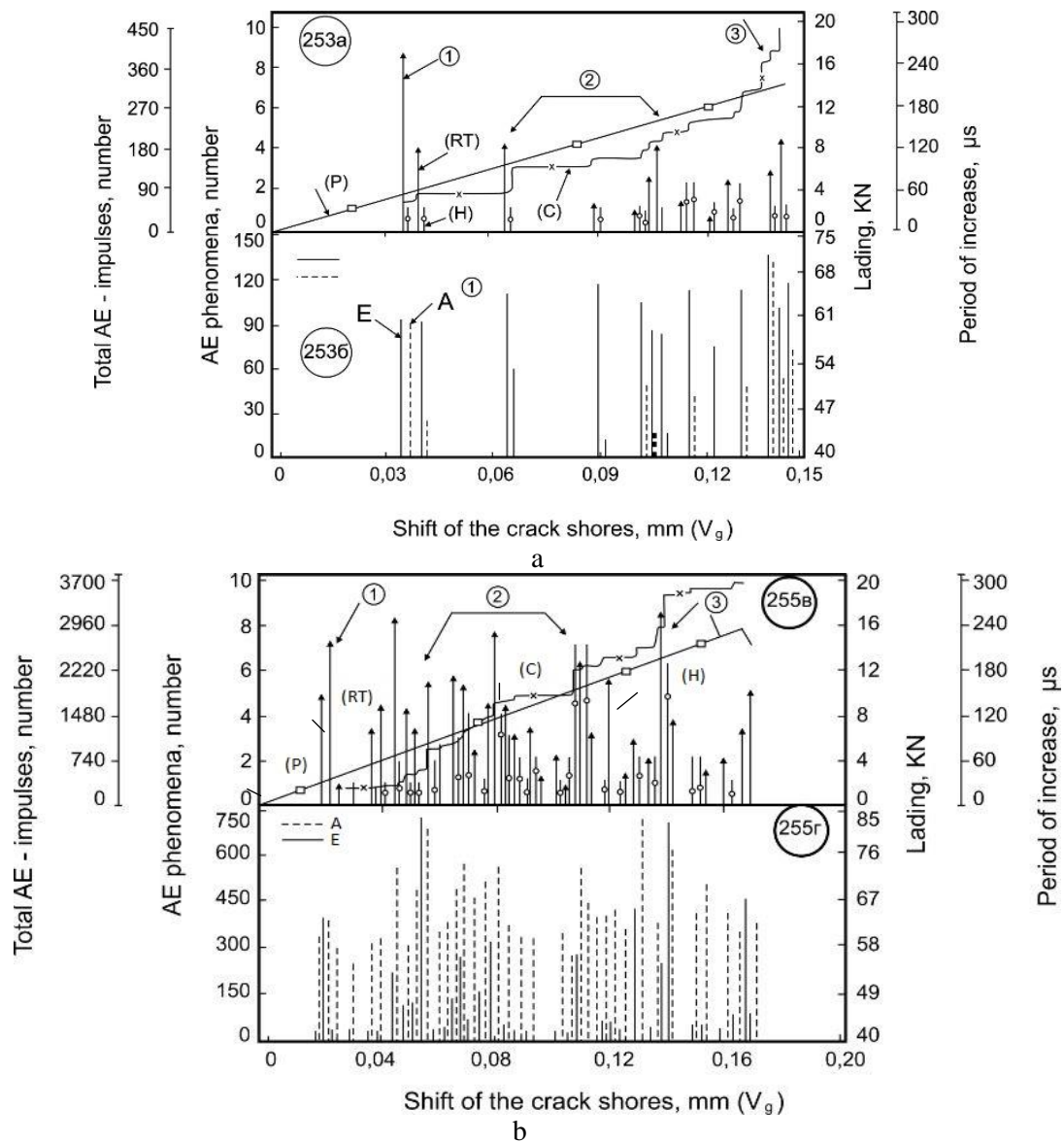
The obtained graphical and tabular AE-information was cleared at the maximum from the influence of noises by appropriate conduction of the experiments and consequent analysis of the data.

### III. Experimental results and analysis

The acoustic-emission parameters: number of AE-events (H), AE-impulses (C), rise time (RT), AE-energy (E), AE-amplitude (A) and pressure (P) are shown in dependence on the displacement of the crack banks ( $V_9$ ) – Fig.2.

The experimental results from the acoustic-emission activity of the vacuum-thermally treated samples (№ 253 и № 255) speak of brittle fracture with clearly expressed character.

The fracture is in the linear (elastic) zone of the curve “pressure – displacement (opening) of the crack banks” without any signs of stable growth of the crack in microscopic aspect. The differences in the slopes P –  $V_9$  for the two samples (Fig. 2) are due to structural distinctions – grain structure, distribution, size and shape of the carbides.

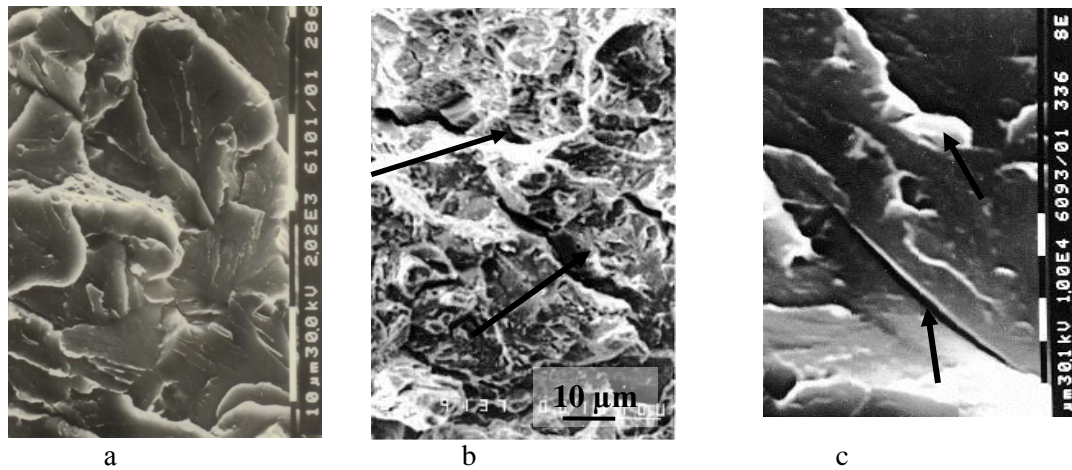


**Figure 2.** Change of the AE-parameters and the load in dependence on the displacement of the crack banks for the thermally treated samples

AE-phenomena with low energy, amplitude and impulses but with sufficient rise time were observed even at the lowest values of the load. They are denoted in Fig. 2, zone ① and indicate the beginning of formation of a new zone of plastic deformation in front of the crack tip. In this zone from 20 to 60% of the load AE-phenomena with increased number of AE-impulses, energy and amplitude are observed but with shorter rise time, what is an evidence of the beginning of a brittle micro-cracking. Such AE-signals of brittle materials are related to fracture or to de-cohesion of the carbides and the intergranular brittle fracture at micro-level. Most probably fracture of the carbides begins, together with microcracking in local areas, near the crack tip [3, 4]. Low-

energetic AE-signals are also observed, which are due to the fracture of most of the disperse carbides (Fig.2a, zone ②). A common feature of the samples in this series is the appearance of signals with high amplitudes and energy, with very short rise time and duration under a load, close to the fracture load. These AE-signals can be taken as a harbinger of the end of the unstable brittle fracture. In fig. 2 they are separated in zone ③ of the AE-tests.

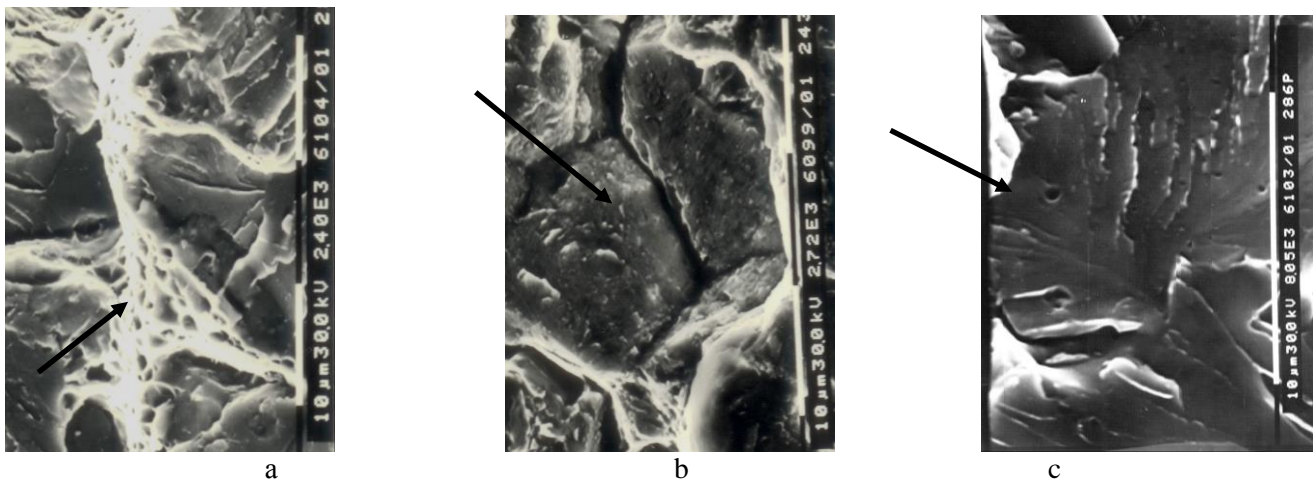
These signals are due to the growth of microcracks and the formation of the facets, observed at the fractures of the samples by means of a scanning electronic microscope (SEM) – Fig. 3.



**Figure 3.** Fractographs of thermally treated samples after tempering at: a,c - 600 °C; b- 650 °C

Isolated carbides were observed by means of SEM in the vicinity of the crack tip at the possible boundary of the zone of micro-plastic deformation, and they are sources of AE-signals. Zones of blunting the crack tip and its successive unstable growth after reaching the critical micro-stresses for

initiating the unstable brittle fracture were also observed. Facets with big areas, free of micro-pores, prevail in these zones. Together with the increase of the temperature of tempering, sections of micro ductile fracture are observed around the facets – Fig. 4.



**Figure 4.** Fractographs of thermally treated samples after annealing at: a,c - 600 °C; b- 650 °C

These sections, in addition to the increased content of carbides, are the reason for the increased AE-activity in the sample, tempered at 923K (650°C). The inter-crystalline cracks prevail in this sample and contribute to emitting high-energy AE-signals both in zone ② and ③ - Fig. 4b. It can be confidently asserted that all processes of internal and

inter-crystalline brittle structure emit AE-signals, which can be registered.

Together with the increase in the temperature of tempering, overall increase of AE-activity is observed, which is best expressed in graphical representation of the total (cumulative) AE-energy depending on the load – Fig. 5.

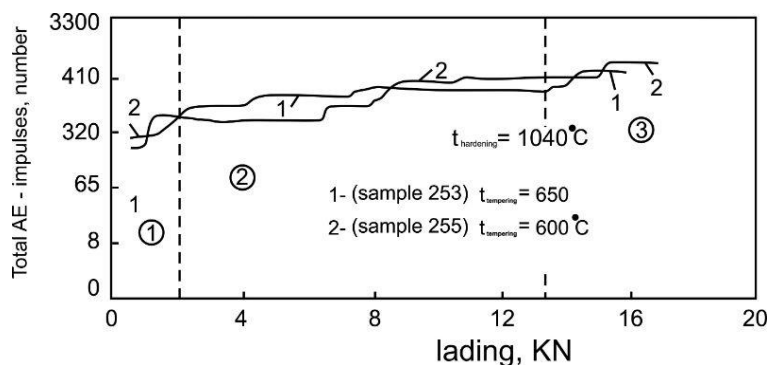


Figure 5. Change of the total energy with respect to the load of the studied samples

The increase in plasticity of the material leads to an increase in the AE-activity at the low values of loading, due to the larger zone of micro-plastic deformation in front of the crack tip – zone ①. Zone ② is characterized for all samples by comparatively uneven frequency of appearance of high energy AE-phenomena. In zone ③ the AE-phenomena with high energy for samples, tempered at 873 K and 923 K, are an excellent indicator of the end of the brittle fracture. The quantitative characteristics of the fracture of the thermally treated samples is made by means of the parameter “total (cumulative) energy” and expressed in Fig. 6.

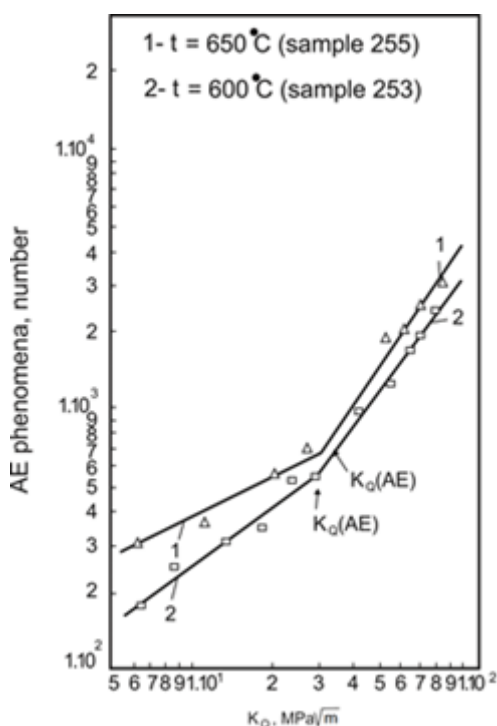


Figure 6. Change of the total energy with respect to  $K_0$

From Fig. 6 it can be seen that at temperature of tempering the steel 923 K (650°C), the value of  $K_0$  (AE) is the highest, what shows that the number of sources of AE is bigger.

The points of breakage on the graphs, denoted by  $K_0$  (AE), are the beginning of unstable fracture. Reaching this moment of loading, value of  $K_0$  and total AE, unsteadily growing “quasibrittle” crack starts developing in the material.

The values of  $K_0$  (AE), defined in a non-destructive way in laboratory conditions for the material, can serve well in production as a criterion of its forthcoming brittle fracture.

#### IV. Conclusions

Acoustic emission can be used for studying pre-fracture processes, going on in thermally treated materials.

The values of  $K_0$  (AE), defined in a non-destructive way in laboratory conditions for the material, can serve well in production as a criterion of forthcoming brittle fracture.

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## SPECIFIC MEASURES FOR QUALITY MANAGEMENT IN WILD BERRY PROCESSING

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**Abstract:** *The present paper focuses on the development of specific measures for quality management and product safety in polyphenols-enriched wild berries juice production. In order to produce a safe product, of high quality, that meets the consumer expectations, one should insure the food safety in addition to the health beneficial properties, along with its organoleptic and nutrition values.*

**Key words:** quality management, food safety, wild berries, polyphenols

### I. Introduction

Like other kinds of fruits and vegetables, wild berries are an important dietary source of vitamins, minerals and fiber. Furthermore, they contain a broad spectrum of substances with potential health related to their antioxidant, anti-inflammatory, antibacterial and antiviral activity. Compared to most fruits, wild berries are rich in anthocyanins, which is due to their red, violet, purple or blue color. Berries can be consumed fresh, but also are widely used in the production of jams, juices, purees, fruit fermented milks and ice creams.

Of the various bioactive substances in wild berries, most attention is paid to the polyphenols, including anthocyanins, flavonols and phenolic acids. Numerous *in vitro* studies have shown that polyphenols of wild berries possess high antioxidant activity. Furthermore, the antioxidant potential of food and beverages from berries depends on the conditions of processing and storage.

Processing of wild berries, currently, along with ensuring food safety is crucial satisfying consumer demand for natural products with increased health potential. This requires the development of specific measures for quality management and product safety.

### II. Specific aspects of safety

The technology for the production of juice of wild blueberries with high antioxidant activity must comply with the regulatory framework set in the Regulation on the requirements for fruit juices and certain similar products intended for human consumption (2003).

While Regulation (EC) №178 / 2002 comment and discuss the concept of "risk" associated with food safety, the Codex Alimentarius (2003) defines

"threat". To determine the specific aspects of safety and quality biological, chemical and physical criteria of safety must be addressed.

Microbiological safety criteria are those microorganisms that are pathogenic and can cause foodborne illness (Mollov al., 2007). According the recommend microbiological standards for raw vegetables, fruits and their products in EU Regulation 2073/2005 *Salmonella* is a microbiological indicator of safety criteria, while *E. coli* is an indicator of hygiene of processes.

The Food and Drug Administration (FDA), bringing together in one place information from the Centers for Disease Control and Prevention (CDC), USDA Office of Food Safety Inspection and the National Institutes of Health, reissued in 2012 "Bad Bug Book" (US Food and Drug Administration, MD, USA). This handbook provides basic facts on food pathogens and natural toxins.

Of interest recently are diseases carried by animals - zoonoses. Ackerman (2006) analyzed a number of trends that may have an impact on threats and vulnerabilities to the food chain, in particular on the development and spread of diseases, zoonotic more precisely - diseases that can be transmitted from animals to humans.

EFSA publishes regular reviews of the development of zoonoses in the EU as one of the regulatory tasks of the European Community, as defined under Directive 2003/99 / EC. The specific zoonoses and disease-causing pathogens, whose data should be provided for, are listed in the Annex to Directive 2003/99 / EC. These include brucellosis (caused by *Brucella*), campylobacteriosis (*Campylobacter*), listeriosis (*Listeria*), salmonellosis (*Salmonella*), tuberculosis due to *Mycobacterium bovis* and verotoxigenic *E. coli*. In addition, parasitic diseases that must be reported include



echinococcosis (*Echinococcus*) and trichinellosis (*Trichinella*). (Kleter and Marvin, 2009).

Human alveolar echinococcosis caused by *Echinococcus multilocularis* called also fox tapeworm is considered the most pathogenic zoonosis in temperate and arctic regions of the Northern hemisphere. In earlier years, the mortality rate exceeded 90 percent within 10 years (Ammann and Eckert, 1996). In Europe, the red fox (*Vulpes vulpes*) is the main end host for *E. multilocularis*. Collected last decade data show that the natural range of the parasite spreads further in east and north Europe (Romig et al., 1999; Eckert et al., 2000).

In their research Todorov and Boeva (1999) indicate that human cystic echinococcosis is still a major problem in Bulgaria, and although there is a reduction of the incidence over the past 20 years, the disease is still widespread in all parts of the country. From 1991 to 2000 the incidence of disease occurrence was 2,4–8,5 per 100 000. As a result from the national program for control of echinococcosis, cases of morbidity have fallen to 6,28 per 100 000 in 2006, 6,24 in 2007 and 5,61 in 2008 (Golemanov et al., 2011).

Chemical hazards are associated with foodborne diseases and injuries (Mollov et al., 2007). Regulatory requirements in terms of maximum levels for contaminants in food are presented in Regulation № 5/ 2015 of the Ministry of Health and Regulation (EC) 1881/2006.

Under Regulation №31/2003 of the Ministry of Health in determining the amount of toxic elements in food recovery must be up to 120% from the values of the standards in the ordinance. Bekiarov and others (2006) use different instrumental techniques for the determination of Pb, Cd, As, Cu and Zn in natural fruit juices, and the results obtained meets the requirements for the control of heavy metals in foods. In developed by Velchev and Nikolov (2004) model a HACCP plan for clear fruit juices, as chemical hazards are indicated residues of plant protection products, which in the case of wild berries are not relevant.

In terms of packaging materials and possible migration, attention should be paid to Regulation (EC) № 1935/2004 on materials and articles intended to come into contact with food, according to which, all materials and articles intended for contact with food must be inert enough to prevent the transfer of substances in food in quantities large enough and threaten human health or cause an unacceptable change in the composition of the food or a deterioration of its organoleptic qualities. Regulation

(EU) № 10/2011 examines materials and articles of plastics intended for food contact.

Physical hazards are associated with foreign bodies or foreign matters that are not normally found in food (Mollov et al., 2007). They can occur at any stage of the food chain and actions should be undertaken to minimize the chance of occurrence of foreign objects in food. However, 25% of the complaints of consumers are connected to the physical contaminants (Aladjadjyan, 2006), and about 1-5% of the small or serious injury are caused by foreign objects ingested (Olsen, 1998).

After physical contamination can occur at any stage and often cannot be removed during production processes (such as heating), these hazards should be controlled by preventive measures (Luning and Marcelis, 2009).

### **III. Specific aspects of quality**

An important aspect of product quality is the determination of total polyphenols. There are values for Dietary Reference Intake (DRI) of vitamins and minerals, as well as guidelines for optimal range of intake to avoid deficiency and prevent toxicity. Polyphenols are widely distributed in plant foods, and are related to improving human health by reducing the risk of chronic diseases, especially cardiovascular. A new approach and a new way of thinking that can be applied not only polyphenols, but also for other phytochemicals. Today, it is necessary to establish a target value for intake of polyphenols as "essential" substances and which is based on the amount of polyphenols in the "5-a-day" (Williamson and Holst, 2008). Unlike vitamins, polyphenols are not necessary for the growth and development and for the maintenance of vital functions of the organism. However, for selected polyphenols and plant sources of polyphenols, there are clinical and epidemiological evidences showing reduced risk of chronic diseases. this means that they are and other nutrients essential for reaching a full life (Holst and Williamson, 2008). The estimated intake of polyphenols from "5-a-day", using data obtained from the database USDA (<http://www.nal.usda.gov/fnic/foodcomp/Data/>), show that a person who consumes "5-a-day" can provide more than 500 mg of polyphenols a day. Consumption of cocoa, tea or coffee and related hydroxycinnamic acids, could easily increase that intake to 500-1000 mg (Williamson and Holst, 2008).

**Table 1** Nutrient Database for some berries adapted from United States Department of Agriculture Agricultural Research Service

Nutrient	Unit	Value per 100 g			
		Blueberries	Cranberries	Black currents	Elderberry
Water	g	84,21	87,32	1,96	79,80
Energy	kcal	57	46	63	73
Protein	g	0,74	0,46	1,40	0,66
Total lipid (fat)	g	0,33	0,13	0,41	0,50
Carbohydrate, by difference	g	14,49	11,97	15,38	18,40
Fiber, total dietary	g	2,4	3,6		7,0
Sugars, total	g	9,96	4,27		
<b>Minerals</b>					
Calcium, Ca	mg	6	8	55	38
Iron, Fe	mg	0,28	0,23	1,54	1,60
Magnesium, Mg	mg	6	6	24	5
Phosphorus, P	mg	12	11	59	39
Potassium, K	mg	77	80	322	280
Sodium, Na	mg	1	2	2	6
Zinc, Zn	mg	0,16	0,09	0,27	0,11
<b>Vitamins</b>					
Vitamin C, total ascorbic acid	mg	9,7	14,0	181,0	36,0
Thiamin	mg	0,037	0,012	0,050	0,070
Riboflavin	mg	0,041	0,020	0,050	0,060
Niacin	mg	0,418	0,101	0,300	0,500
Vitamin B-6	mg	0,052	0,057	0,066	0,230
Folate, DFE	µg	6	1	0,00	6
Vitamin B-12	µg	0,00	0,00	12	0,00
Vitamin A, RAE	µg	3	3	230	30
Vitamin A, IU	IU	54	63	1,00	600
Vitamin E (alpha-tocopherol)	mg	0,57	1,32		
Vitamin K (phylloquinone)	µg	19,3	5,0		
<b>Lipids</b>					
Fatty acids, total saturated	g	0,028	0,008	0,034	0,023
Fatty acids, total monounsaturated	g	0,047	0,018	0,058	0,080
Fatty acids, total polyunsaturated	g	0,146	0,055	0,179	0,247
Fatty acids, total trans	g	0,000	0,000	0,000	0,000
Cholesterol	mg	0	0	0	0

However, processed foods may contain varying amounts. This is a challenge for the food industry. There are approved and certified methods for determining polyphenols in food.

According to Aprifel (Agence fruits et légumes frais) intake of polyphenols may reach one gram a day and desirable intake to approach the 2 to 3 g per day.

According to Regulation (EC) №1169 of EP and the Council on the provision of food information to consumers, to state that the content of vitamins and minerals is significant it should be 7,5% of the nutrient reference values obtained from 100 ml in drinks or 15% of food reference values obtained from 100 g or 100 ml for non-beverage products. Based on these benchmarks Katsarova and others (2012) developed apricot drinks with and without herbal extract with vitamin C content exceeding the recommended daily intake up to 41 mg. The review of Penov and others (2012) gives grounds to state that fruits and vegetables are healthy foods and selection of appropriate formulas and technologies that preserve the antioxidant capacity, can create a variety of products for healthy diet.

Nowadays, there is growing interest in the commercialization of red fruit or vegetable juices rich in soluble red pigments and polyphenols. Apart from the typical red fruit juices, some red fruit juices are commercialized and labeled as Antiox juices, suggesting a beneficial effect on the health of consumers (Bub et al., 2003). Red pigments found in these fruit and vegetable juices are anthocyanins and betacyanins (Obon et al., 2011).

For information and consumer protection it is important to ensure both the quality and authenticity and red fruits or drinks from them (Fugel et al., 2005). The Codex Alimentarius Commission was established by FAO and WHO to develop food standards, guidelines and related texts such as codes of practice, with the primary aim of protecting the health of consumers and ensuring fair trade practices in the food trade. Codex-Standard 247-2005 common code that includes methods of analysis for checking the composition, quality and authenticity of fruit juices and nectars.

In the case of red fruit juices selected authentication method of quality is the International Federation of fruit juices (IFU) Method No. 71 (1998), which determines the profile of anthocyanins by HPLC. This method has been validated as " Type I " by screening committee IFU. The anthocyanin "fingerprint" for each red fruit juice is pretty well established by this method (Goiffon et al., 1999). Although the principle of this method is simple and can be found counterfeiting, the correct interpretation of the chromatograms was not so easy. The model can be changed depending on the variety of fruit ripening stage, conditions for processing or

storage conditions. For this reason, developing a unique method for assessing the polyphenol content of the food is an important tool to build a global database of polyphenols in food (Neveu et al., 2010). Complete database is of great importance to assess the polyphenols related health claims fruits or vegetables and products thereof, and to assess the authenticity and quality of fruit and vegetable juices.

#### IV. Conclusion

Today, food safety and quality management is becoming increasingly important in processing plants for food. After the first step to ensure food safety, it is necessary to prepare food with quality that meet the requirements and needs of customers, organoleptic qualities and nutritional value.

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## **ABOUT THE INFLUENCE OF ION CARBONITRIDING ON CORROSION RESISTANCE OF STEELS**

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**Abstract.** *This paper studies the influence of carbonitriding in low-temperature plasma with gas Corgon<sup>®</sup> 18 on the electrochemical behavior of alloyed steel 25CrMnSiNiMo. The obtained results give evidence of the fact that the process of ion carbonitriding of this steel in a medium of ammonia and corgon, shows a better corrosion resistance in a medium of 3% NaCl and 0.1 MNa<sub>2</sub>SO<sub>4</sub>, than the same process, going on in the saturating medium of ammonia and propane-butane.*

**Key words:** Ion carbonitriding, Corgon<sup>®</sup> 18, propane-butane, electrochemical corrosion

### **I. Introduction**

Protection of metals against corrosion by coating is based on reducing the degree of thermodynamic instability by avoiding a direct contact of the metal surface with the aggressive medium.

The use of direct methods for defining the speed of corrosion is hindered or impossible due to the thickness of the layers, obtained in the process of ion carbonitriding. On the other hand, the corrosive destruction of the metals has in most cases electrochemical nature and therefore when assessing the corrosion behavior of carbonitrided layers it is reasonable to use electrochemical methods: measuring the stationary potential of the studied system “layer – basic material” in a certain electrolyte; capturing the curves of cathodic and anodic polarization. One of the characteristics of the process of corrosion is the difference between the potentials of the metal and the electrolyte solution. The absolute value of this characteristic cannot be defined, and, instead, the relative potential is measured with respect to a certain comparative electrode – hydrogen, calomel, chlorine-silver etc. Most often in practice the calomel electrode is used as a comparative electrode, since its potential is with the highest stability.

By the value of the measured electrode potentials, the nature (reversible or irreversible) of the process of interaction between the metal and the electrolyte can be defined, as well as the controlling factor of corrosion. Tracking the potential change during the retention time of the sample in the electrolyte gives useful information about the protective properties of the cathode coatings. Cathode coatings are the ones with a more positive potential than the basic material – the basic material plays the role of a dissolving anode. The lower the thickness of the layer and the higher the level of porosity, the closer the values of

the stationary potential of the coated sample are to the value of the potential of the core.

In thin coatings, for which tensile stresses are typical, the nature of the corrosion processes is mainly electrochemical. In coatings (layers) with an average thickness or greater (over 10µm – carbonitrided and nitride layers), compressive stresses prevail. The occurrence of corrosion processes under the coating also depends on its thickness. When the coatings are thin, large foci of corrosion are most frequently formed in the surface layer of the substrate; when they are thick, corrosion destruction extends in depth and can lead to a breakthrough in the thin-sheet substrates– the reason is in the realization of a mechano-chemical mechanism of corrosion.

Nitriding and carbonitriding are increasingly used in practice as a surface treatment, ensuring increased corrosion resistance of details and tools. In some cases this treatment can successfully replace oxidation and certain galvanic types of treatment such as galvanizing, cadmium plating etc. However, the studies in this direction have not been systematized and are quite incomplete [1, 2, 3, 4, 6, 11]. Unlike non-alloyed or low-alloyed steels, stainless steels after nitriding and carbonitriding under certain modes worsen their corrosion resistance. This is due to the formation of CrN and depletion of the chromium matrix in the layer, what leads to reduction of the electrochemical potential [6]. By using a suitable process of oxidation, properties of the carbonitriding layer under the influence of tribological and dynamic loads, can be combined with improving the resistance against corrosion.

The following processes, comprising nitriding or carbonitriding, combined with oxidation, are known worldwide: NITROTEC, TENIFER-QRQ,

SURSULF-OXYNIT, NIOX, IONIT-OX, carbonitrided layer improves the exploitation duration of the materials. This can be associated with a decreased tendency of the oxides (Fe<sub>3</sub>O<sub>4</sub>) to adhesion, which results in a reduction of the coefficient of friction. In the reviewed literature there are no data on the influence of ion carbonitriding on the corrosion resistance of the layers formed in a gas medium, comprising ammonia and Corgon®18 (82% Ar and 18% CO<sub>2</sub>). The aim of the present paper is to study the influence of ion carbonitriding in active media, comprising either of ammonia and Corgon®18 or of ammonia

NITROBLACK [8, 9, 10]. The oxidation of the and propane-butane, on the corrosion resistance of steel 25CrMnSiNiMo.

## II. Methodology of study

### 2.1. Materials for studying and modes of thermal treatment

The object of study was alloyed steel 25XГЧМА, whose chemical composition was tested by means of the equipment for automatic analysis “Spectrotest” and given in Table 1. Samples with dimensions 15 x15x10 mm and surface roughness R<sub>a</sub>=0.63 μm were made of the considered steel.

Table 1. Chemical composition of the studied steel

Steel	Chemical elements, weight percentages							
	C	Si	Mn	Cr	Ni	S	P	Mo
25CrMnSiNiMo	0.24	1.45	1.28	0.87	1.36	0.002	0.002	0.12

The samples were treated thermally in a chamber furnace in an oxidative medium according to the modes, given in Table 2.

Table 2. Modes of preliminary thermal treatment

Steels	Quenching t <sub>quench.</sub> , °C	Cooling medium	Tempering t <sub>temp.</sub> , °C	Cooling medium
25CrMnSiNiMo	880	Oil	600	Air

Treated this way, the samples were then ion carbonitrided in the installation “Ion 20” under the modes, given in Table 3. As saturating gases ammonia and propane-butane were used on the one

hand (C<sub>3</sub>H<sub>8</sub> - C<sub>4</sub>H<sub>10</sub>), and, on the other hand, ammonia and Corgon®18 in different percentage ratio. The temperature of treatment was 550 °C.

Table 3. Modes of ion carbonitriding of steels for studying their corrosion resistance

№ of the mode	Material	τ	P <sub>1</sub>	P <sub>2</sub>	P <sub>2</sub>	P
			ammonia	Corgon®18	Propane-butane	total
		h	Pa	Pa	Pa	Pa
1	25CrMnSiNiMo	4	200	200	-	400
2	25CrMnSiNiMo	4	360	-	40	400

### 2.2 Methodology of testing the corrosion resistance of the studied steel

Capturing the anodic and cathodic polarization curves can be done by one of the following methods: galvanostatic, potentiostatic and potentiodynamic. When the galvanostatic method is used, current with certain density runs through the metal and the stationary potential is measured. According to the potentiostatic method, constant potential is maintained on the surface of the metal by means of a potentiostat, while the change of the current over time is fixed. The potentiodynamic method is used in

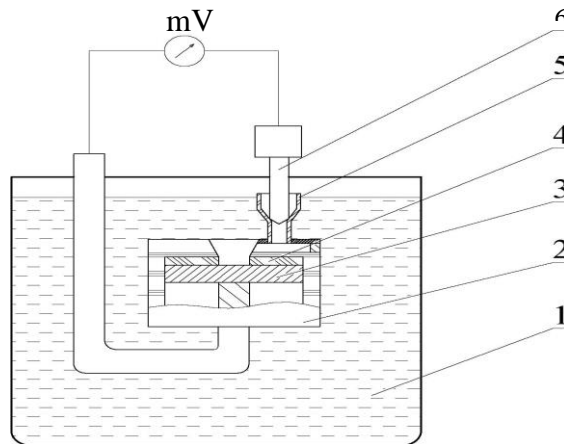
this paper for studying the corrosion resistance of the carbonitrided samples – fig. 1.

A three-electrode scheme is used. The studied carbonitrided sample and a platinum counter-electrode are placed in a glass cell with electrolyte solution, and a calomel or chlorine-silver electrode is used for comparison. The potentiodynamic polarization curves are captured by predefining a certain speed of potential change (normally 20–100 mV/min). Standard 3% water solution of NaCl and 0.1% Na<sub>2</sub>SO<sub>4</sub> is used as aggressive medium.

The defatted samples are mounted in a Teflon holder, whose opening ensures a constant contact

surface with the electrolyte 0.4cm<sup>2</sup>. At a distance of 2 mm from this surface, Luzhin capillary, ending

with a glass at the opening, has been punctured through the Teflon body.



**Figure 1.** Scheme of measuring the change of the free potential [6]

1- electrolyte (in this case 3% NaCl); 2 – Teflon holder, where the sample is placed (it has an opening in the upper part, through which the sample gets into contact with the electrolyte); 3 – carbonitrided sample – working electrode; 4 – rubber gasket; 5- Luzhin glass capillary (we place there the saturated calomel electrode; Luzhin capillary is a small opening, ensuring access for an electrolyte, directly contacting the tested surface, to the calomel electrode; part of it is in the Teflon holder); 6- saturated calomel electrode (SCE) – a comparative electrode.

The corrosion behavior of the carbonitrided samples is defined by capturing potentiodynamic curves of external polarization. The test is conducted in 3% water solution of NaCl and 0.1% Na<sub>2</sub>SO<sub>4</sub>. For comparison a saturated calomel electrode is used, having a potential of +245 mV with respect to the hydrogen electrode at room temperature. The area, subjected to studying, is 0,4 cm<sup>2</sup>. The potentiodynamic curves (PDC) are captured using a three-electrode cell, composed of: a working electrode - tested sample; a comparative electrode – a saturated calomel electrode; and a platinum counter-electrode. The external potential is changed within -600 mV to +1200 mV with a speed of 1 mV/s. A special Teflon holder is used for insulating the uncovered portions of the sample and for defining a constant contact surface with the electrolyte. The external potential is given by the potentiostat Radelkis-oh-405. The following parameters are defined by the potentiodynamic curves: E<sub>cor.</sub> – potential at which a transition from

cathodic to anodic zone is realized; i<sub>A</sub> – density of the anodic current.

### III. Experimental Results and Analysis

#### 3.1. Medium, composed of 3% water solution of NaCl.

Potentiodynamic curves were captured for all studied samples and the core (basic material). From the PDC it can be noted that the left part is the cathodic curve, the right one is the anodic curve. The boundary between them (min) defines the potential of corrosion E<sub>cor.</sub>. The beginning of the cathodic curve follows the process of hydrogen release, while the end of the curve – the area of oxygen ionization. The anodic curve characterizes the dynamics of the dissolution of the carbonitrided layer, of which in our case we are interested more. The results from the study of the corrosion resistance of steel 25CrMnSiNiMo are given in Table 4.

**Table 4.** Results from the study on materials for corrosion resistance

Steel	E <sub>cor.</sub> , mV	i <sub>A</sub> , mA/cm <sup>2</sup>	δ <sub>c.z.</sub> μm	δ <sub>tot.</sub> μm
25CrMnSiNiMo - core	-403	0.04÷85	-	-
25CrMnSiNiMo - carbonitrided surface - mode 1, table 3. (corgon)	- 423	0.005÷0,2	8	240
25CrMnSiNiMo - carbonitrided surface - mode 2, table 3 (propane-butane)	11	0.45÷6,3	4,5	180

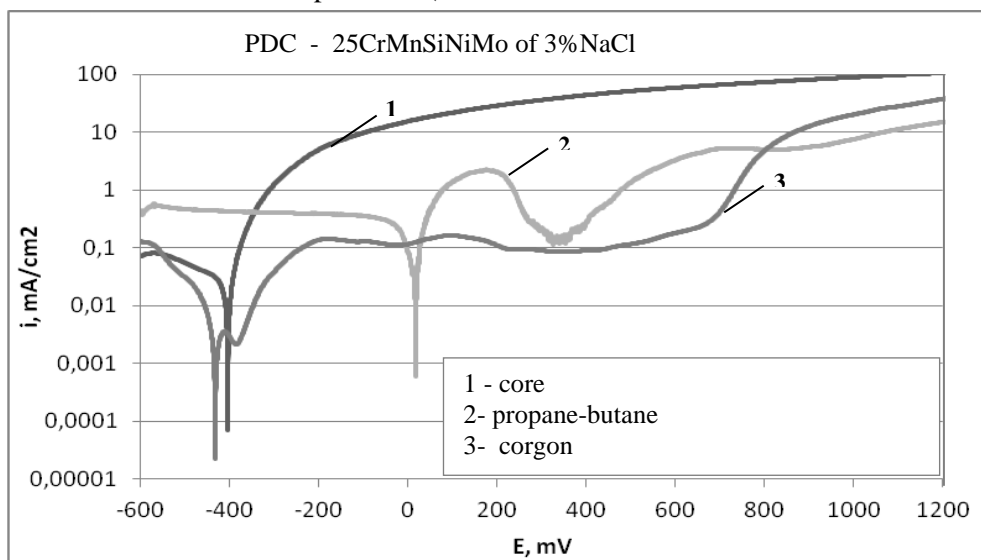
Ion carbonitriding of steel 25CrMnSiNiMo in saturating media of ammonia-corgon or ammonia and propane-butane leads to improvement of its electrochemical properties (fig.2). The corrosion

potential of the core of the sample is 403 mV. The anodic part of the potentiodynamic curve of the core only shows an area of active anodic dissolution, in which the current density changes from 0,05mA/cm<sup>2</sup>

до  $90\text{mA/cm}^2$ . Carbonitriding does not lead to a considerable change in the potential of corrosion  $E_{\text{cor}}$ , so that the measured value is  $423\text{ mV}$ . In the anodic part of the potentiodynamic curves (PDC) of the carbonitrided surface, the current density  $i_A$  is almost constant and it changes from  $0,05\text{ mA/cm}^2$  to  $0,2\text{mA/cm}^2$  to  $703\text{mV}$ . The passive state is characterized by small density of the anodic current  $0,21\text{ mA/cm}^2$  and a wide zone of the passive state – from  $-205\text{ mV}$  to  $703\text{ mV}$ . More active anodic dissolution is observed at values over  $703\text{mV}$ , and the current density  $i_A$  reaches up to  $48,2\text{ mA/cm}^2$  at  $E_{\text{cor}}=1200\text{ mV}$ . A different picture of the potentiodynamic curves is observed after carbonitriding in a medium of ammonia and propane-butane – fig. 2. The cathodic process is hindered compared to the combined zone process (the

cathodic curve is less steep). A very small passive zone is registered. The anodic current at the core is bigger by a few orders than the passive current for the carbonitrided surface in a medium of ammonia and corgon.

It can be noted that the current density  $i_A$  in the anodic part of the potentiodynamic curves (PDC) of the carbonitrided surface considerably changes from  $0,45\text{ mA/cm}^2$  to  $7,1\text{ mA/cm}^2$  to  $800\text{ mV}$ . The higher current density  $i_A$  leads to an active anodic dissolution, which indicates reduction of the corrosion resistance of the carbonitrided surface. Carbonitriding of materials in a medium of ammonia and corgon shows better electrochemical properties, than the same process but in a medium of ammonia and propane-butane.

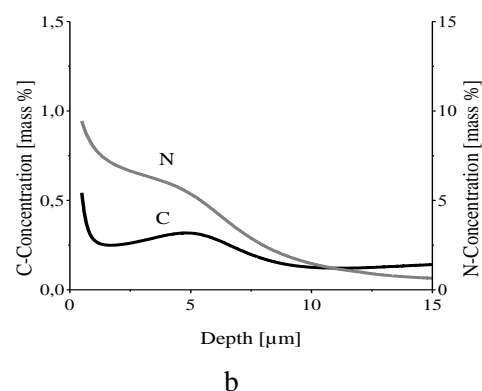
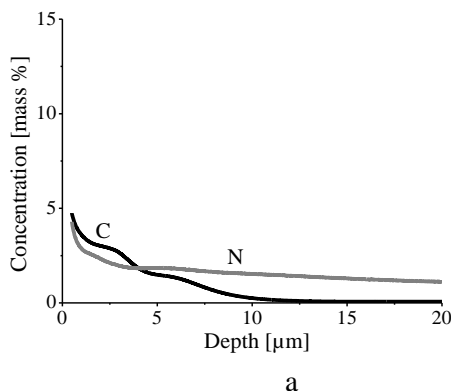


**Figure.2.** Potentiodynamic curves of steel 25CrMnSiNiMo as a core and after carbonitriding at: 2-  $t = 550\text{ }^\circ\text{C}$ ,  $P_{\text{NH}_3} = 200\text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 200\text{ Pa}$ ,  $\tau = 4\text{ h}$ ; 3-  $t = 550\text{ }^\circ\text{C}$ ,  $P_{\text{NH}_3} = 360\text{ Pa}$ ,  $P_{\text{propane-butane}} = 40\text{ Pa}$ ,  $\tau = 4\text{ h}$

This is due to the small concentration of carbon in the combined zone (fig. 3b), which gives rise to the more homogeneous and dense carbonitrided zone without cementite in it.

The conducted X-ray structure analysis shows that when the surface is saturated with propane-

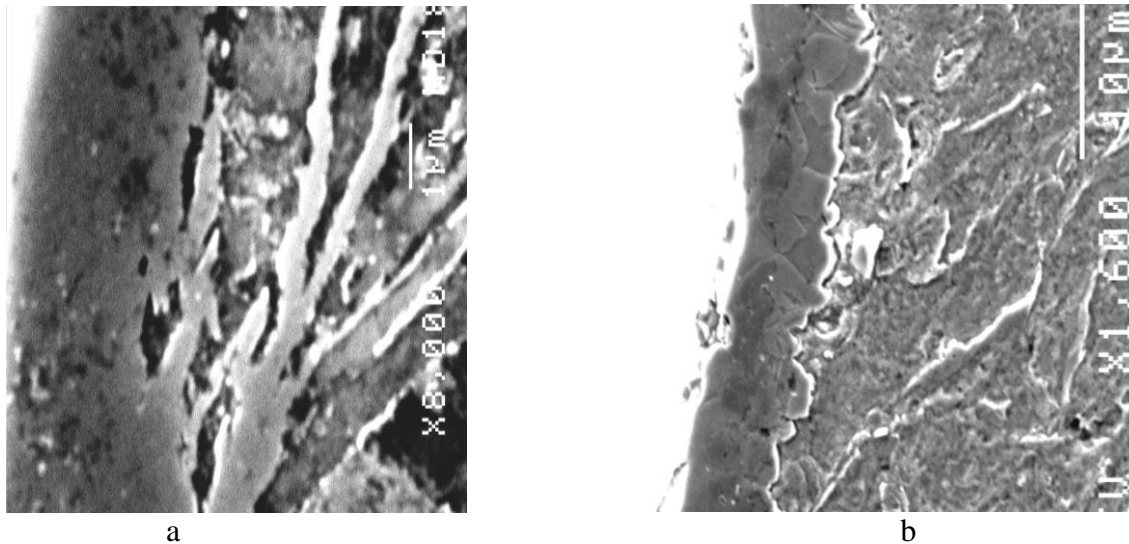
butane, certain amount of cementite is also observed except for the phases  $\epsilon$ ,  $\gamma'$  and  $\alpha$ . This is explained by the bigger concentration of carbon in the combined zone – fig. 3a.



**Figure.3.** Distribution of carbon (C) and nitrogen (N) in depth after carbonitriding of steel 25CrMnSiNiMo at:  $t = 550^{\circ}\text{C}$ , a-  $P_{1\text{NH}_3} = 360\text{ Pa}$ ,  $P_{2\text{C}_3\text{H}_8-\text{C}_4\text{H}_{10}} = 40\text{ Pa}$ ;  $\tau = 4\text{ h}$ , b-  $P_{1\text{NH}_3} = 200\text{ Pa}$ ,  $P_{2\text{82\%Ar} + 18\%\text{CO}_2} = 200\text{ Pa}$ ,  $\tau = 4\text{ h}$

This, in turn, leads to an increase in the heterogeneity of the carbonitrided zone, what results in accelerated corrosion of the surface layer. More

pores are also observed in the carbonitrided zone after treatment in a medium of ammonia and propane-butane – fig. 4.



**Figure.4.** Microstructure after carbonitriding of steel 25CrMnSiNiMo at:  $t = 550^{\circ}\text{C}$ , a-  $P_{1\text{NH}_3} = 360\text{ Pa}$ ,  $P_{2\text{C}_3\text{H}_8-\text{C}_4\text{H}_{10}} = 40\text{ Pa}$ ;  $\tau = 4\text{ h}$ , b-  $P_{1\text{NH}_3} = 200\text{ Pa}$ ,  $P_{2\text{82\%Ar} + 18%\text{CO}_2} = 200\text{ Pa}$ ,  $\tau = 4\text{ h}$  at:  $t = 550^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 360\text{ Pa}$ ,  $P_{\text{corgon}} = 40\text{ Pa}$ ,  $\tau = 4\text{ h}$

### 3.2. Medium, composed of 0.1 $\text{MNa}_2\text{SO}_4$

Potentiodynamic curves were captured for all studied carbonitrided samples and the core (the basic

material). The results from the studies for corrosion resistance are given in Table 5.

**Table 5.** Results from the study on the corrosion resistance of steel 25XГCHMA

Steel	$E_{\text{cor.}}$ , mV	$i_A$ , mA/cm <sup>2</sup>	$\delta_{\text{c.z.}}$ µm	$\Delta_{\text{tot.}}$ µm
25CrMnSiNiMo - core	-478	0.03÷48	-	-
25CrMnSiNiMo - carbonitrided surface - mode 1, table 3 (corgon)	-482	0.03÷0.38	7	210
25CrMnSiNiMo - carbonitrided surface - mode 2, table 3 (propane-butane)	-443	0.03÷30	6,5	200

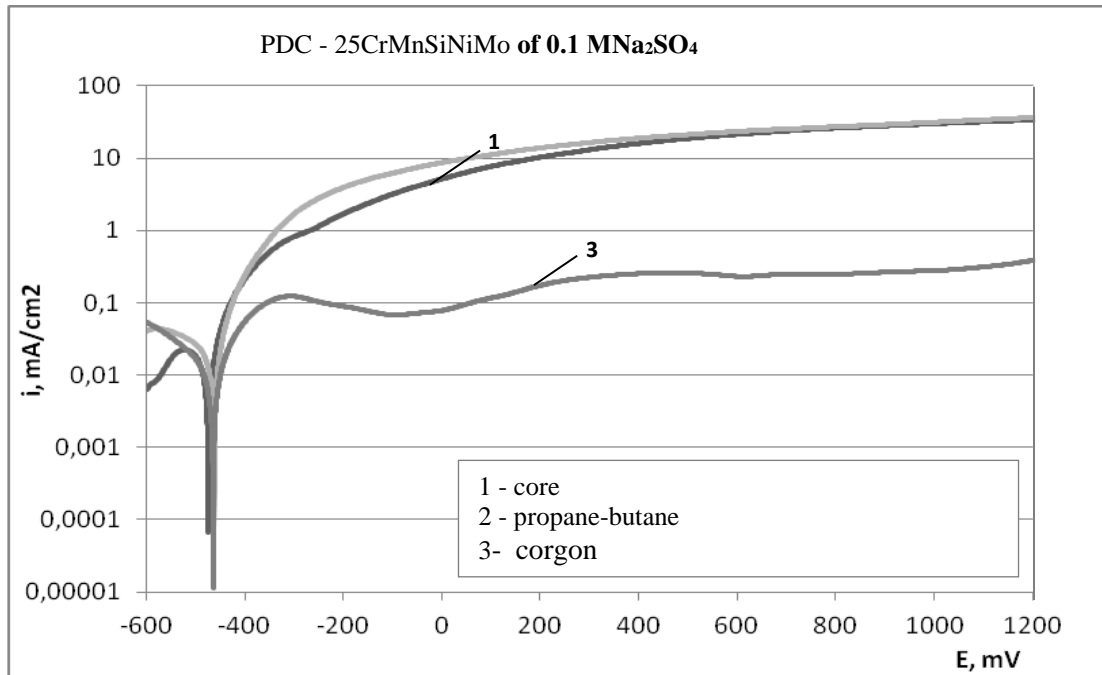
The process of ion carbonitriding of steel 25CrMnSiNiMo in saturating media of either ammonia-corgon or ammonia and propane-butane also leads to improvement of its electrochemical properties in 0.1  $\text{MNa}_2\text{SO}_4$  - fig.6. From Table 5 it can be noted that the potential of corrosion of the sample core is - 478 mV. Carbonitriding, on the other hand, does not lead to considerable displacement of the potential of corrosion  $E_{\text{cor.}}$ , so the measured value is - 482mV. In the anodic part of the potentiodynamic curves (PDC) of the carbonitrided surface (in a medium of corgon) the current density  $i_A$  is almost constant and changes from 0,03 mA/cm<sup>2</sup> to 0,38 mA/cm<sup>2</sup>. In carbonitriding in a medium of ammonia and propane-butane, the current density  $i_A$  strongly changes from 0.03 mA/cm<sup>2</sup> to 30 mA/cm<sup>2</sup>.

This leads to an active anodic dissolution, which indicates reduction in the corrosion resistance of the carbonitrided surface – fig. 6.

It is necessary to underline that in conducting the tests both in 3%NaCl, and in 0.1 $\text{MNa}_2\text{SO}_4$ , ion carbonitriding in a medium of ammonia and corgon shows better electrochemical properties than the same process but in a medium of ammonia and propane-butane. This is due to the more homogeneous and dense carbonitrided zone, formed in a medium of ammonia and corgon. The conducted X-ray structure analysis shows that when the surface is saturated with propane-butane, a certain amount of cementite is observed in addition to the phases  $\epsilon$ ,  $\gamma^I$  and  $\alpha$ . This is explained by the bigger concentration of carbon in the combined zone. The availability of



cementite in the carbonitrided zone leads to increase in its heterogeneity, what results in speeding up the corrosion of the surface layer.



**Figure.6.** Potentiodynamic curves of steel 25CrMnSiNiMo as a core and after carbonitriding at: 3-  $t = 550\text{ }^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 200\text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 200\text{ Pa}$ ,  $\tau = 4\text{ h}$ ; 2-  $t = 550\text{ }^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 360\text{ Pa}$ ,  $P_{\text{propane-butane}} = 40\text{ Pa}$ ,  $\tau = 4\text{ h}$

The increase of the corrosion resistance of the carbonitrided layers is due to the  $\epsilon$ -phase, formed on the surface, which has a higher electrode potential (-0.1 to -0.13mV) than the other phases -  $\gamma'$  and  $\alpha + \gamma'$  and  $\alpha$  [5].

#### IV. Conclusions

The applied modes of carbonitriding allow for improving the corrosion behavior of steel 25CrMnSiNiMo.

The process of ion carbonitriding of steel 25CrMnSiNiMo in a medium of ammonia and corgon<sup>®</sup> 18 shows a better corrosion resistance in a medium of 3% NaCl and 0.1  $\text{MNa}_2\text{SO}_4$ , than in the saturating medium of ammonia and propane-butane.

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## INVESTIGATION OF EXTRACTS FROM SAGE (*Salvia officinalis* L.) FOR APPLICATION IN COSMETIC

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**Abstract:** It has been studied the influence of two main technological factors, temperature and duration, upon the composition of ethanol extracts from sage (*Salvia officinalis* L.) for cosmetics application. The equations of extraction with respect to tannins have been derived.

**Keywords:** leaves from sage, ethanol extracts.

### I. Introduction

The genus *Salvia* from the Lamiaceae family is represented by 900 species in world.

Sage (*Salvia officinalis* L.) is an aromatic and ornamental herb common herbal plant, which is widely cultivated in various parts around the world, but it is native in the Mediterranean region. Phytochemical investigation of sage revealed a great number of bioactive compounds (polyphenols, essential oil and flavonoids). The plant has been used in folk medicine for the treatment of inflammatory processes, common cold and nervous diseases [7].

Essential oil and extracts from sage have been shown to possess antimicrobial, antioxidant, anti-inflammatory and other properties [2 – 5].

In Bulgaria, from the approximately about 20 species of the genus *Salvia* and sage is one of the most popular medicinal drugs [5].

From the leaves of sage, growing in Bulgaria, extracts with 70 % ethanol and propylene glycol for cosmetics application have been obtained [1].

There is no scientific evidence for obtaining extracts for cosmetics application from leaves of sage (*Salvia officinalis* L.), which is set as the aim of the current work.

### II. Material and methods

**Plant material:** Leaves from sage (*Salvia officinalis*) from the Bulgarian market were used in the investigation. The raw material was characterized in terms of: moisture content by drying it up to constant weight, at 105 °C [6] and content of tannins by titration of hot water extract with potassium permanganate solution using indigo carmine as indicator [6].

**Obtaining of extracts:** Extraction was carried out in laboratory conditions as a process in a batch static mode by maceration in the solvent at ratio of raw material to solvent = 1 : 10. Four solvents were used for the extraction: 95, 70, 50 and 30 vol. % ethanol.

The solvents, their concentration and the weight ratio of the raw material were chosen on the basis of authors' own unpublished data.

The influence of the technological factors: temperature (20, 40 and 60 °C) and duration of extraction (1, 3 and 5 h), was examined by mathematical modeling of the experiment as a two-factor analysis on three levels (3<sup>2</sup>).

As a criterion for effectiveness of the process the quantity of tannins was determined. On the basis of the experimental data, the equations of extraction were worked out for tannins, whose coefficients were estimated for significance by Student's test and for adequacy by Fisher's test.

### III. Results and discussion

The analyzed sage leaves and fruits were with 12,16 % moisture level, and contained 8,04 % tannins, respectively. Figures 1 - 4 present the schemes of the experiments that have been carried out and the obtained results.

Data presented on the figures prove that the highest amounts of tannins are extracted with 50 % ethanol. Parallel to the increase in the temperature and the duration of the process there is an increase in the content of the extracted tannins (the difference in the amount of tannins after 5 h and 7 h extraction was not statistically proven).

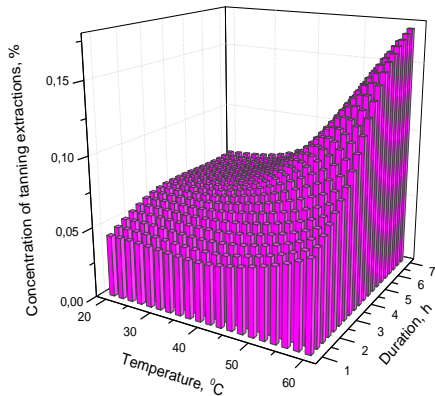


Figure 1. Content of tannins in extracts with 95% ethanol

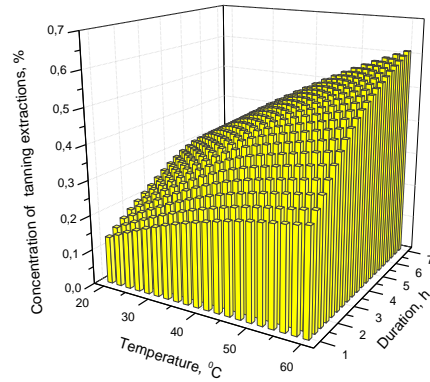


Figure 3. Content of tannins in extracts with 50% ethanol

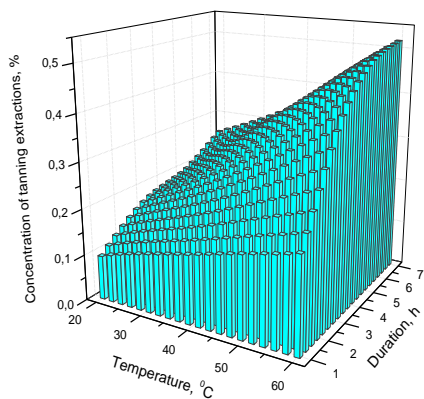


Figure 2. Content of tannins in extracts with 70% ethanol

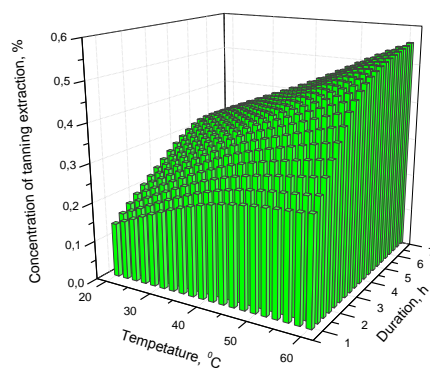


Figure 4. Content of tannins in extracts with 30% ethanol

The equations of extraction, which have been worked out, were proved adequate and with significant coefficients, as follows:

95 % ethanol

$$y = 0,061 + 0,023x_1 + 0,024x_2 + 0,018x_1x_2 + 0,017x_1^2, \quad (1)$$

70 % ethanol

$$y = 0,282 + 0,107x_1 + 0,099x_2 + 0,051x_1x_2 + 0,003x_1^2 - 0,037x_2^2, \quad (2)$$

50 % ethanol

$$y = 0,385 + 0,105x_1 + 0,107x_2 + 0,022x_1x_2 - 0,033x_1^2 - 0,035x_2^2, \quad (3)$$

30 % ethanol

$$y = 0,366 + 0,092x_1 + 0,104x_2 + 0,019x_1x_2 - 0,012x_1^2 - 0,041x_2^2, \quad (4)$$

where:  $y$  – content of tannins, %;  
 $x_1$  – duration of the process, h.  
 $x_2$  – temperature, °C;

#### IV. Conclusion

The optimal conditions for extraction procedure of the sage leaves were determined.

The extracts contain tannins and have prospective for possible application in different cosmetic products, but of course additional investigations are a must.

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