

## THE EFFECT OF CHANGE OF CARBURIZING MEDIA NATURE ON GROWTH KINETICS OF LAYERS

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*Utilizarea pastelor ca medii furnizoare de carbon în stare activă pentru carburare nu constituie o nouă tehnică, inconvenientele legate de acestea limitând nivelul lor de aplicabilitate. Devin deosebit de interesante în cazurile în care apare necesitatea carburării unor porțiuni strict limitate și reduse ca amplitudine de pe suprafața produselor, sau în cazurile în care este necesară realizarea unor diferențieri în ceea ce privește dimensiunea straturilor carburate la nivelul același reper, caz în care carburarea poate avea loc în prezența a două medii, pasta și respectiv un gaz carburant.*

*În lucrare sunt prezentate rezultatele experimentale ale carburării în diferite medii, mai puțin uzuale (solid-pastă, gazos-gaz combustibil urban: gazul din rețeaua orășenească cu un conținut cel mai frecvent de aproximativ (65÷75)%CH<sub>4</sub> și respectiv un mediu mixt care combină efectele prezenței pastei și ale gazului urban) a unui oțel aliat de cementare, oțel cu ereditate granulară fină și călăbilitate bainitică corespunzătoare.*

*The use of pastes as media that supply active carbon for carburizing is not representing a new technique; the inconveniences related to these are limiting their practicability. They become particularly interesting when strictly limited and reduced zones from the surface products have to be carburized, or on areas where different case depths of the same workpiece are to be obtained. In this situation carburizing can occur in the presence of two media, paste and a carburizing gas.*

*The paper shows the results of carburizing experiments performed in less commonly used carburizing media (solid-paste, gas – urban fuel gas: the gas from the urban gas network which contains frequently (65...75)% CH<sub>4</sub> and respectively a mixed medium that combines the effects of the paste and urban gas) on a case hardening, hereditary fine-grained alloy steel having an appropriate bainitic hardenability.*

**Keywords:** growing kinetics, carburizing media nature

### 1. Introduction

The media used for carburizing are available in a large diversity and in all aggregation states: solid, liquid, gas, vacuum, plasma.

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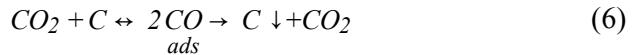
The granular or pasty solid media are applicable for small series production, unique parts. They are also used when lacking appropriate endowment for realizing a high efficiency and control possibilities of the carburizing process.

The gaseous media are mostly used for carburizing, between them the fuel gas from the urban gas network (unlike the natural gas that contains about 92% ... 97% CH<sub>4</sub>, the urban gas is a diluted natural gas having a methane content which varies in large limits, between 65%...75% CH<sub>4</sub>, as lower limit and 90...95% CH<sub>4</sub>, as upper limit) represents the most simple and usable solution for the carburizing process developing [1, 2].

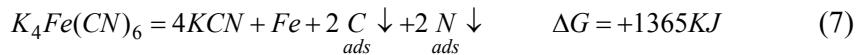
The pastes used for carburizing can be considered as a very convenient way of carbon enrichment of the metallic workpieces surface layers;

The carburizing pastes can be obtained in a large composition variety, but as a whole, their composition is similar to that corresponding to the carburizing granular solid media – wood coal, also, extremely fine powdered, together with activators as barium, sodium and calcium carbonates; all components are maintained in a binder introduced in a suitable amount as to provide the required consistency and viscosity of pastes [3, 4].

The reactions that lead to the formation of active carbon atoms (for solid media in general and for pastes in particular) occur preponderantly in gaseous phase. The specific reactions for these media, at 1000°C are as follows:



In the presence of potassium (or sodium) ferrocyanide in the composition of the carburizing paste, at the processing temperature, further reactions will appear:



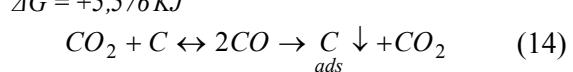
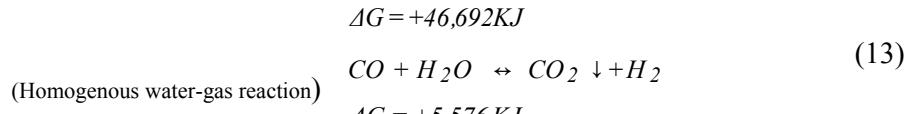
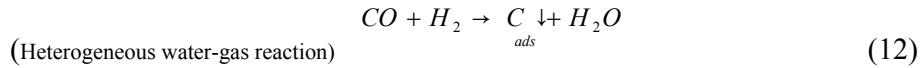
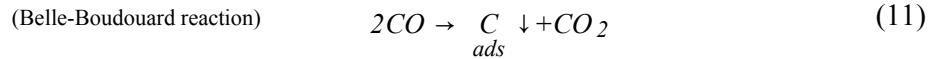
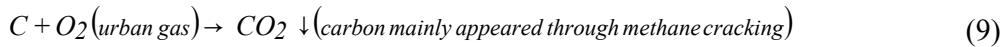
and will also generate elements in an active state. At this temperature, the carbon adsorption and diffusion take place preponderantly, the adsorbed nitrogen generates an extremely thin zone of carbonitrides on the products surface.

The carbon generated by the micron particles of wood coal from the carburizing paste is also added to these carburizing sources.

In the case of urban gas (from the urban gas network), the methane, the main carbon donor, decomposes at the carburizing temperature and provides carbon according to the relation:



The saturation with carbon when using urban fuel gas become possible also due to other reactions caused by the urban gas components (in the urban gas composition, besides the methane, are also available more than 10% hydrogen, more than 2% carbon monoxide and also carbon dioxide, oxygen and nitrogen [1]):



Obviously, the growth kinetics of case hardened layers in specific media – solid, gaseous or combined (in the presence of pastes and gas) are different; these differences are determined by the media activities and the mass transfer intensity.

## 2. Materials and experimental techniques

The purpose of the experimental research was to quantify the differences in kinetics obtained on steels carburizing in various media (with more limited use, but which are often practicable when the facilities are inadequate, or when small series of parts have to be carburized; the carburizing pastes as solid media and the urban fuel gas are included in this media category) and to particularize these differences for the 21NiCrMo2 case hardened alloy steel; on the other hand, assuming these kinetics differences reported in the technical literature, an attempt to determine whether these differences can be exploited was done.

To achieve these objectives, the experiment programming method was used [5]: the orthogonal compositional central programming of second order was

taken into consideration, the independent variables being the process temperature and the holding time at processing temperature.

The equipment used for carburizing was equipped with a trap for a rapid entrance/exit of the samples from the enclosure without changing the gas flow regime (for the case of carburizing in urban gas or in pastes and urban gas).

The samples were  $\Phi 15 \times 20$  mm cylinders - annealed rods of 21NiCrMo2- having the composition determined through complete chemical analysis: 0,2%C; 0,26%Si; 0,76%Mn; 0,43%Cr; 0,22%Mo; 0,51%Ni; P and S below 0,027% (in the W 1.6523 grade limits).

The estimation of case depths of carburized and quenched layers (directly in water from the carburizing temperature) were achieved considering the microhardnesses values, accepting the following rule - the effective (carburized and quenched) layer's case depth is given by the distance between the surface and the zone where the microhardness is  $550\mu\text{HV}_{0,1}$ .

A Reichart microhardness tester was used, with a load of 100 g; the microscopy investigations were performed with a Neophot 21 microscope.

The paste was produced from common components: fine powdered wood coal, a mixture of sodium carbonate, calcium carbonate and potassium ferrocyanide, extremely well homogenized, at which heat treatment oil was added in order to provide a composition having a required consistency and viscosity.

The thermochemical treatment was performed in an automatic temperature control electric furnace: in the case of urban gas usage, a constant overpressure in the workspace of about  $500 \text{ mmH}_2\text{O}$  and a constant gas flowrate during the isothermal holding were assured.

The experiments in urban gas took place in a relatively narrow time range, in which the urban gas composition was kept relatively constant.

### **3. Results and discussions.**

The processing conditions, according to the adopted programming method, are shown in table 1.

The meaning of the coded values, respectively the natural values corresponding to the independent parameters of the carburizing processes taken into analysis is given in table 2.

The quantification of the effects of independent parameter's discreet variation in their specific variation ranges (table 2) was ensured by modelling the interdependences between sizes that define the growth and formation kinetics of different media carburized layers, for the 21NiCrMo2 steel (ec.15...20, fig.1), thus opening the way of process managing in optimal conditions.

Table 1

## The matrix of orthogonal central compositional program of the second order

No.	Temperature, °C X <sub>1</sub> /Z <sub>1</sub>	Time, min X <sub>2</sub> /Z <sub>2</sub>	Dependent variables, Y					
			Carburizing in paste		Carburizing in paste and urban gas		Carburizing in urban gas	
			δ, mm Y <sub>1</sub>	V <sub>carb</sub> , mm/min (mm/h) Y <sub>2</sub>	δ, mm Y <sub>1</sub>	V <sub>carb</sub> , mm/min (mm/h) Y <sub>2</sub>	δ, mm Y <sub>1</sub>	V <sub>carb</sub> , mm/min (mm/h) Y <sub>2</sub>
1	(+) 1000 90	(+) 90	0,875	0,0095 (0,57)	0,510	0,00526 (0,31)	0,375	0,00363 (0,21)
2	(+) 1000 30	(-) 30	0,275	0,0116 (0,69)	0,160	0,00683 (0,41)	0,150	0,00785 (0,47)
3	(-) 900 90	(+) 90	0,462	0,0044 (0,26)	0,380	0,00354 (0,21)	0,280	0,00258 (0,15)
4	(-) 900 30	(-) 30	0,330	0,0118 (0,70)	0,247	0,00886 (0,53)	0,140	0,00469 (0,28)
5	(0) 950 90	(+α) 90	0,550	0,0069 (0,41)	0,260	0,00394 (0,23)	0,150	0,00310 (0,18)
6	(0) 950 30	(-α) 30	0,450	0,0117 (0,70)	0,260	0,00646 (0,38)	0,240	0,00627 (0,37)
7	(+α) 1000 60	(0) 60	0,745	0,012 (0,72)	0,520	0,00848 (0,50)	0,350	0,00609 (0,36)
8	(-α) 900 60	(0) 60	0,412	0,0082 (0,49)	0,420	0,00768 (0,46)	0,170	0,0045 (0,27)
9	(0) 950 60	(0) 60	0,675	0,010 (0,6)	0,475	0,0074 (0,49)	0,400	0,0053 (0,31)

Note: In table no.1,  $X_i/Z_i$  are the coded values, respectively natural values of the independent process parameters (temperature and isothermal holding time).

Table 2

## Base level and variation ranges of independent parameters

Factors	Z <sub>1</sub> (Temperature, °C)	Z <sub>2</sub> (Time, minutes)
Codes	X <sub>1</sub>	X <sub>2</sub>
Base level, Z <sub>10</sub>	950	60
Variation range, ΔZ <sub>i</sub>	50	30
Superior level, (+1); Z <sub>10</sub> +ΔZ <sub>i</sub>	1000	30
Inferior level, (-1); Z <sub>10</sub> -ΔZ <sub>i</sub>	900	90

The processing of the experimental data and the statistical verification of the regression equations coefficients, respectively of the concordance between the adopted models, led to the following particular forms of the regression equations (coded forms), namely their graphical aspects (Fig. 1):

- for the case of paste carburizing:

$$\delta = f(T; t)$$

$$Y = 0,61 - 0,12X_2^2 + 0,115X_1 + 0,138X_2 + 0,117X_1X_2 \quad (15)$$

$$V_{carb} = f(T; t) \\ Y = 10^{-3}[10 - 0,75X_2^2 + 1,45X_1 - 2,38X_2 + 1,32X_1X_2] \quad (16)$$

- for the case of urban gas carburizing:

$$\delta = f(T; t) \\ Y = 0,318 - 0,084X_2^2 + 0,0475X_1 + 0,0458X_2 \quad (17)$$

$$V_{carb} = f(T; t) \\ Y = 10^{-3}[5,29 - 0,61X_2^2 + 0,96X_1 - 1,58X_2 - 0,52X_1X_2] \quad (18)$$

- for the case of pastes and urban gas carburizing:

$$\delta = f(T; t) \\ Y = 0,444 + 0,041X_1^2 - 0,1688X_2^2 + 0,0238X_1 + 0,0805X_2 + 0,054X_1X_2 \quad (19)$$

$$V_{carb} = f(T; t) \\ Y = 10^{-3}[7,29 + 0,84X_1^2 - 2,038X_2^2 - 1,57X_2 + 0,94X_1X_2] \quad (20)$$

The analysis of particular forms of regression equations and of their graphical expressions revealed a series of issues, particularly interesting, on carburizing kinetics:

- the most intense kinetic occurs in the case of carburizing pastes application; in descending order, the mixed media (used when dimensional gradients of layers case depths in different zones of the same workpiece have to be obtained) will follow and the urban fuel gas exhibits the less intense one.

- at high temperatures (greater than 950°C), in the case of pastes, the evolution over time of carburized layer case depth shows a parabolic dependence; at 950°C, or below this temperature level, the dependence has an extreme characteristic, respectively has a maximum that moves at greater holding times, with temperature increasing (from 60 min at 900°C, it reaches 75 min at 950°C). The tendency above described is valid also for urban fuel gas carburizing, regardless temperature. In the case of mixed media, the estimation of carburized layer case depth was carried out in the zone placed in direct contact with the paste.

The evolution over time, at different temperatures, of the carburized layers total case depth represents in this case a combination of effects generated by the action of the two media; the general trend is a parabolic variation.

- the carburized layers case depths, obtained in the case of use of carburizing pastes at holding times less than or equal to 30 min, are very close (in statistical terms) for all tested temperatures between 900°C and 1000°C; they are slightly different in the case of urban fuel gas carburizing, respectively in mixed carburizing media;

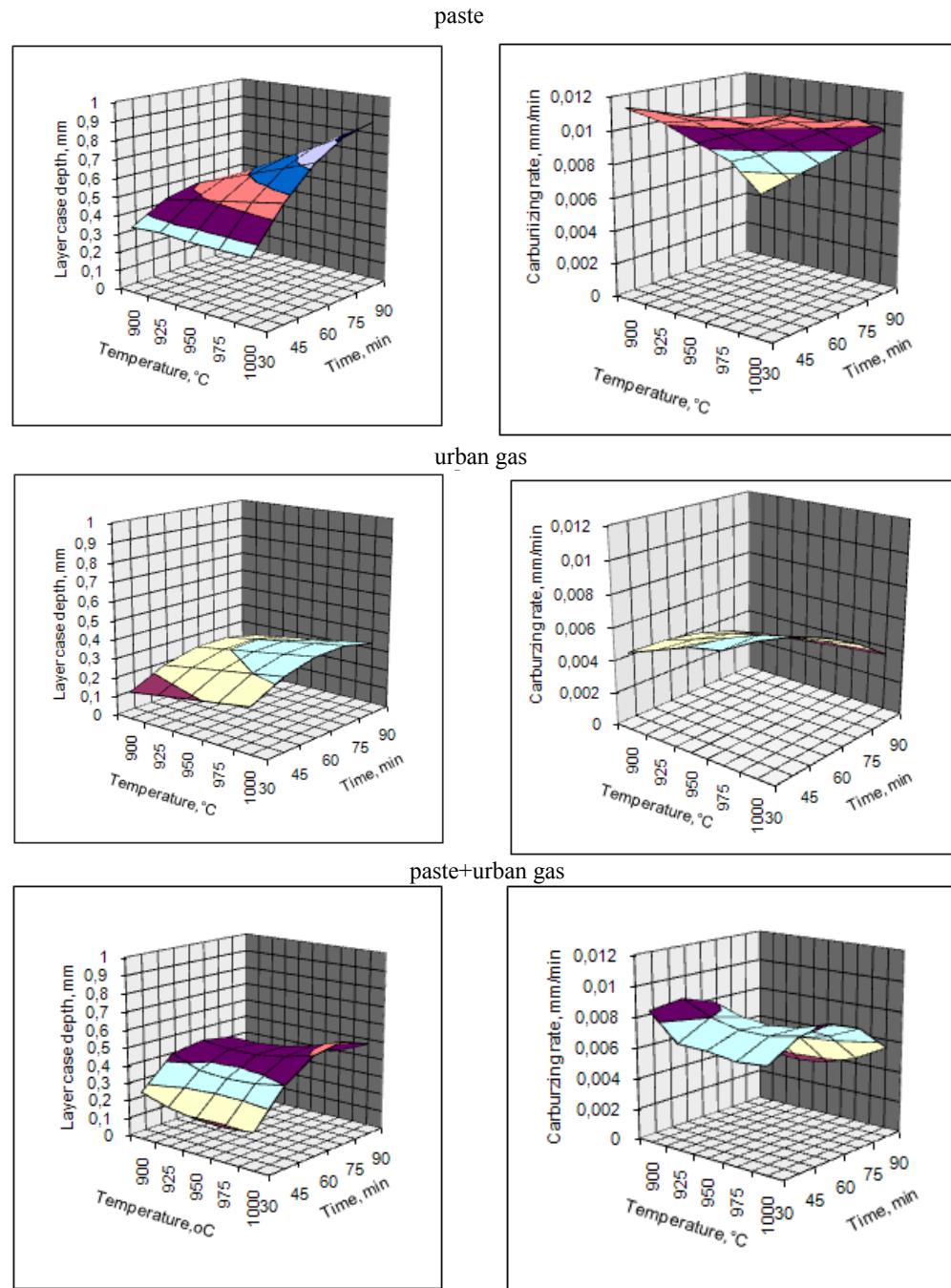


Fig. 1. Kinetics comparisons (case depths-carburizing rates) between results obtained on carburizing of 21NiCrMo2 steel in different media

- in the case of urban fuel gas carburizing, the dependences of the carburized layer case depth on isothermal holding time are similar (dependence with extreme characteristic, with a maximum in the range 60-75 min), for different temperatures in the tested range (900°C...1000°C);

The mode of variation of carburized layer case depth in time at different temperatures has to be corroborated with the mode of variation of the boost rates (the rates of obtaining of carburized layers). Thus:

- in the case of pastes carburizing, the carburizing rates are close for low isothermal holding times (below 30 min), regardless of the processing temperature, but are clearly differentiated at the increase of the isothermal holding times: at high temperatures, these carburizing rates become superior to those recorded at lower temperatures;

- in the case of urban fuel gas carburizing, a reverse evolution of the carburizing rate can be observed, as compared to the evolution of pastes carburizing rate: at different holding times, the carburizing rates regardless the thermochemical processing temperature are close;

- in the case of mixed media, pastes + urban fuel gas, one can notice the resultant of the two variation mode of carburizing rates, specific to the two tested media.

These claims can be substantiated as follows:

The process kinetics expressed by the variation in time at different temperatures of the effective carburized layer's case depths, respectively of the carburizing rates, is the result of several elementary processes taking place in turn with different rates:

- the decomposition of the components of the carburizing medium, accomplishes at a certain rate (reaction rate); in time, there is a change in the medium activity – the case of carburizing pastes as a result of their consumption;

- the adsorption of the carburizing element in the workpiece's surface, characterized by the adsorption rate;

- the diffusion of the adsorbed element in the metallic matrix, process characterized by a certain mass transfer rate.

In the case of pastes carburizing, the adsorption rate at the beginning of the process is very high especially at great temperature values (over 950°C), the losses are minimal, so that a very large proportion of the media's components decomposition products (which are in direct contact with the workpiece's surface) are adsorbed; in time, the rate decreases slightly due to the lowering of the concentration gradient at the interface medium - carburized metallic workpiece.

At lower temperatures ( $\leq 950^{\circ}\text{C}$ ) the adsorption rate is lower, the carburizing rate decreases due, on the one hand, to the increase in losses of active state elements in the medium and, on the other hand, due to the concentration gradient's decrease at the interface medium - metallic workpiece.

At the same time, how can be explained the way in which the differences between carburizing rates at different temperatures and isothermal holding times (very low for relatively reduced holding times and very high for long holding times) varies?

During the process first stage (the first 30 min of isothermal holding), the paste medium is very active, the differences between its carburizing ability at  $900^{\circ}\text{C}$  respectively  $1000^{\circ}\text{C}$  and implicitly the concentrations gradients at the medium – metallic workpiece interface are not significantly influencing the carburizing rates. In time, due to the reduction of the medium activity (paste consumption), a diminution of the active carbon atoms availability at the interface takes place, with implications on the concentration gradient; the different temperatures and diffusion coefficients ( $D=f(T; \frac{\partial c}{\partial x})$ ) lead to a higher gradient in the range of high temperatures and thus determine higher carburizing rates.

The question one could ask is why in the case of urban gas the carburized layer case depth versus time dependence, at a certain temperature, is different from the parabolic one? The reason is the appearance of the soot when exceeding the carbon saturation concentration in austenite at a certain temperature.

The high methane carburizing ability has a negative influence on the carburizing process developing, because the atomic carbon, in active state augments in the duplex micro layer between the methane Nernst boundary layer and solid austenite superficial layer, phenomenon that favours the re-combining of the carbon active atoms in solid molecular carbon under the form of soot [6].

At a constant urban fuel gas flowrate during the process, this phenomenon is initiated when the limit  $C_{\text{boost}} = 0.00322 T - 1.686$  [6] is exceeded, or more exactly, in the real experimental conditions,  $1.2\% \text{C}$  at  $900^{\circ}\text{C}$ ,  $1.37\% \text{C}$  at  $950^{\circ}\text{C}$  and respectively  $1.53\% \text{C}$  at  $1000^{\circ}\text{C}$ . Thus, a decrease of the carburizing growing kinetics is observed.

To avoid these situations it is necessary to reduce the atmosphere's carbon potential below the saturation limit, problem that can be solved through an advanced dilution of the carburizing atmosphere, after 60-75 min of isothermal holding, or through using a processing regime in two stages – boost and diffusion.

Wyss [7] indicates that a 95%  $\text{N}_2$  dilution of methane reduces its carburizing ability to 5% of that recorded at  $900^{\circ}\text{C}$ , keeping it approximately constant when temperature increases in the range  $900^{\circ}\dots 1000^{\circ}\text{C}$ .

In the case of gaseous carburizing media - urban fuel gas - the carburizing rate has a significant diminution in time, when temperature varies in the range  $900^{\circ}\dots 1000^{\circ}\text{C}$ .

The phenomenon is related to the mode in which the atmosphere carburizing ability is changing.

Thus, while the methane - the main atmosphere component (often between 60-75%) - rises its carburizing ability with 0.95% at a temperature increase from 900°C to 1000°C (from 525.6 to 530.6 °C/m<sup>3</sup>CH<sub>4</sub>), the carbon monoxide in the direct decomposition reaction, specific to the Belle-Boudouard equilibrium, decreases its carburizing ability with 69% (from 13.9 to 4.3 °C/m<sup>3</sup>CO), and in the heterogeneous water gas reaction with about 68.2% (from 10.7 to 3.4 °C/m<sup>3</sup>CO) [6,8].

A reduction of about 0.5% of the general carburizing ability of the atmosphere generated by the combustion of the urban gas can be observed, when temperature varies in the testing range.

In conclusion, the differences in carburizing rates obtained at various temperatures, in time, are mainly determined by the concentration gradient at the medium –metallic workpiece interface, which is high in the first moments of the isothermal holding time and decreases with time.

Also, the possibility of appearance of the soot on the surface of the metallic workpieces when the saturation limit of carbon in austenite is exceeded (for a certain temperature) has to be taken into consideration; this phenomenon has major negative implications on the case hardened layer's growing rate.

In the case of mixed media - pastes + combustion products of the urban gas - the growth kinetics of the layers combine the effects of the two media, the resultant being weaker as compared to the level obtained for pastes.

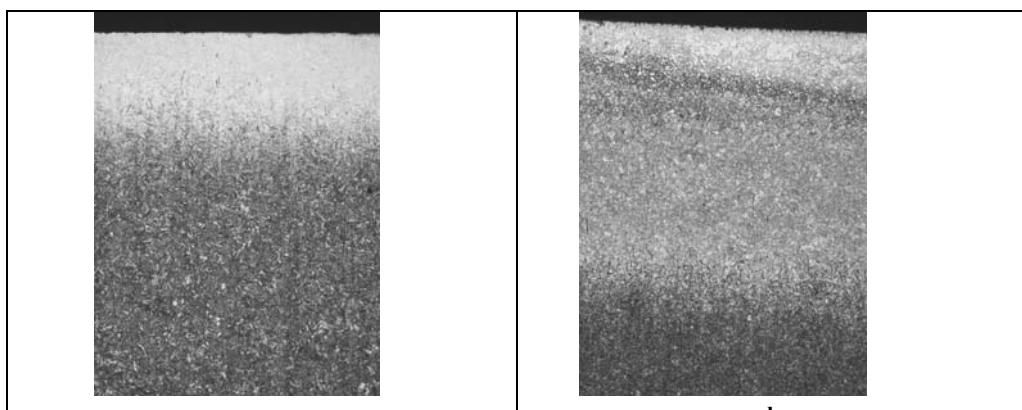


Fig.2. Micrographs of the carburized and water - quenched layers for the 21NiCrMo2 steel.  
Carburizing media: pastes, with maintaining in air; carburizing parameters: t = 30min;  
T = 950°C (a), 1000°C (b). Etching reagent: nital 2%; Magnification:100:1

The reason can be the “washing” effect of the urban gas decomposition components, gas which is permanently circulated in the workspace from the entrance (the bottom of the retort) to the exit (the upper side of the retort).

The phase composition of the carburized layers for the analyzed steels is identical for each regime, the differences being caused exclusively by the level of the processing temperatures and times and are reflected only in the total effective case depth of the carburized and quenched layer (Fig. 2).

One can observe in the carburized layer the cryptocrystalline martensite (for both **a** and **b** micrographs) and in the transition zone and core, martensite + lower bainite, respectively lower bainite. The maximum microhardness in the layer was  $733 \mu\text{HV}_{0,1}$  respectively about  $440 \mu\text{HV}_{0,1}$  in the core.

## 6. Conclusions

The experimental researches aimed to study the carburized layers growth kinetics in different media, with more limited use, which are applicable when small batches of workpieces have to be treated, or where the heat treatment facilities do not allow the use of other carburizing methods, more efficient in terms of control of processing parameters.

A case hardening alloy steel, 21NiCrMo2 with fine granular heredity and appropriate bainitic hardenability was used for the researches.

The carburizing was performed in pastes and respectively in urban gas, the selection of processing parameters being in accordance with a programme that allowed the subsequent statistical processing of the experimental data and conception of the regression equations that in turn can provide the optimal choice of parameters  $T$ -  $t$  -  $\delta$ , according to immediate needs.

The following conclusions can be drawn:

-the pastes assure a high carburizing rate, superior to that attained for the urban gas;

-the composition of the tested paste (extremely fine powdered wood coal together with a mixture of carbonates plus potassium ferrocyanide) provides higher carburizing rates than those recorded in other carburizing processes in pastes commonly used in practice [1, 2];

-the kinetics of the pastes carburizing is superior to the kinetics of urban gas carburizing, medium where the methane proportion varies in relatively large limits, fact that lead to difficulties in predicting with reasonable accuracy on the processing results;

- in the case of urban fuel gas carburizing in a single stage of isothermal holding, the possibility that after 60-75 min of maintaining to appear soot on the products surface was created; this phenomenon causes a change in the growth kinetics of carburized layers. To avoid the soot, due to exceeding of the saturation concentration of carbon in austenite at a certain temperature, it is necessary to use an advanced atmosphere dilution, or to realize the carburizing process in two stages, boost and diffusion;

- by combining the two carburizing media, solid – paste and gaseous – urban gas (or any other active carburizing media) we can obtain carburized layers with different thicknesses on the lateral surface of the same workpiece, due to different growth kinetics of layers in these carburizing media: in the zones where the carburizing paste is available and the holding is done in carburizing gas, the growth kinetics of the carburized layer is slightly inferior to that obtained during pastes carburizing, where the technological holding takes place in air, and not in an active carburizing media;

- the phase composition of carburized and water quenched layers is the same for all thermochemical processing methods tested, the differences consisting in the thicknesses of the carburized layers (their effective case depths).

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