

THE EFFECT OF ATMOSPHERE FLOW RATE ON CARBURIZATION PROCESS OF POROUS IRON

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Abstract

The effect of CH_4 - H_2 - N_2 atmosphere flow rate on the carburization process of porous DV 0.40 steel was studied with the purpose of quantifying this effect. The experiments were performed at 900°C for 3h in cracked ammonia containing 4, 7 and 10 vol.% of methane and with carbon activities of 3.76, 6.90 and 10.50. Flow rates in the operating section of furnace ranged from 0.03 to 3.72 mm/s, which correspond to total flows of 0.70 – 96.88 l/h. Carbon concentration in the sample surface layers depended linearly on the flow rate, and parabolically on the carbon activity in the atmospheres. The flow rate had no effect on the decrease of carbon concentration in the sample volume, which depended only on the carbon activity in the specimens. On the basis of experimental data, mathematical equations were proposed to describe these dependences. During the cooling period the atmosphere flow rate also influenced the decarburization degree of already carburized surface layers of samples. Determining influences on decarburization of these layers were the decrease of carbon activity in the atmosphere during cooling, the high dew point in the atmosphere, and mainly the open porosity of the samples, which allows rapid exchange of carbon between the atmosphere and the surface layers of the sample.

Keywords: powder metallurgy, sintered steels, controlled atmospheres, sintering atmospheres, carburization

INTRODUCTION

A saturant element quantity, which an atmosphere can offer to a processed material in the processes of chemical-heat treatment of steels in controlled atmospheres (carburization, nitriding, nitrocarburization), is given mainly by its concentration in that atmosphere and on the atmosphere flow. Carbon transfer into the part's surface depends on the atmosphere flow rate inside the furnace, which can be calculated after considering the cross-section of the furnace operating part and the known rate at which the atmosphere is flowing into this furnace [1,2,3]. The gas flow rate should be high enough to guarantee that no depletion of reactive species will occur as well as to prevent gas stagnation. At the same time, the gas flow should be slow enough to allow the gas mixture to pre-heat and to reach equilibrium, as is required in many applications. Usually, gas flow between 1 and 10 mm/s satisfies both requirements [4].

In order to intensify and accelerate the process, carburizing atmospheres frequently have carbon potential higher than the carbon potential, which corresponds to the solubility limit of carbon in iron [5,6].

At the present time, the carburization process of wrought steels is considered to be a very well understood area of chemical-heat treatment from both the theoretical and

practical points of view. During the last 30 years enormous progress has been made in the field of computer processing, modelling and calculations of the chemical-heat treatment of wrought steels. By the linkage of phase diagrams with the kinetic models of individual processes [3,7-13], after setting various technological parameters (atmosphere composition, atmosphere carbon potential, flow, temperature, chemical composition of steel, process duration, dimensions of carburised object, etc.), computer is able to predict e.g. a resultant carbon profile in the sample and the corresponding hardness course gradient from sample surface into the core, etc. This progress continues, and will continue to do so, as improved and more precise descriptions of specific systems and their models are developed and innovative mathematical computer modelling techniques are brought into use. In practice, the computerised "know-how" procedures are often asserted [25].

All these simulating programs were made and are made with the intention to use them for wrought steels, not for porous sintered steel [14].

Past experience has shown that many failures occur when the conditions considered valid for carburization of wrought steels are applied to the carburization of porous steels. Compacts from PM steels, as a consequence of their so-called open porosity, are characterized by reaction surfaces some hundreds of times larger than that of compact (wrought) materials [15-17] and consequently have a correspondingly higher reactivity. The "case-depth" is generally deeper and less sharply defined than in fully dense steels, but this is generally an advantage rather than a disadvantage [18].

The effect of selected technological parameters on carburization behaviour of sintered components based on DV 0.40 (RZ 400, Demag-Meer) iron powder, and on carbon distribution in samples volume has been studied in some papers, e.g. [19-24]. In this paper, the attention was focused on the influence of flowing atmospheres with different carbon potentials upon the carburization process of the porous iron. The main aim was to quantify the relation between the flow of carburizing atmosphere and carbon content in the individual layers of samples in order to obtain the additional knowledge to understand the carburization process of porous iron in endo-atmospheres and microstructure formation within the carburising components volume.

EXPERIMENTAL

Experiments were realized on the compacts prepared from the powder DV 0.40 steel which were sintered at 1100°C for 2 h in cracked ammonia (dew point DP \approx -50°C). Their chemical composition was: 0.086 % C; 0.300 % Mn; 0.010 % S; 0.010 % P; 0.020 % Si; 0.050 % Al; 0.100 % O. The dimensions of compacts after sintering were $\varnothing 13 \times 13$ mm and their total porosity ranged within the interval of 17.5 – 18.5 %.

For investigation of the flow rate effect on the carburizing of porous iron in the CH₄ - H₂ - N₂ atmosphere equipment was used that allowed a regulation of atmosphere flow rate in the range of 0 - 100 l/h. In the experiment it was possible to change the flow rates continually and to regulate them using regulation flowmeters. The equipment scheme was published in [20]. The flows of 0.7, 24.22, 48.44, 72.66 and 96.88 l/h were used in the realized experiments, so that the retort calibre of 96 mm responded to the flow rates of 0.03, 0.93, 1.86, 2.79 and 3.72 mm/s in an empty retort.

Carburization was carried out at the temperature of 900°C for 3 h. Atmospheres with contents of 4, 7 and 10 vol.% CH₄ in cracked ammonia were used as carburizing atmospheres. The atmosphere dew point (DP) at the furnace chamber input was \approx -14°C at a total pressure of 101 kPa. The atmospheres were not dried. Their chemical compositions at both the furnace input and output were chromatographically monitored. The carbon

activities in atmospheres, determined by the methods published in [24], were 3.76, 6.90 and 10.50.

The samples were placed in the operating section of the furnace on the chamotte grate that permitted carbon diffusion into the total sample's surface, and also control of the sample cooling rate. The samples, after carburizing, were cooled within the temperature interval of 900 - 650°C at a rate of ca 25°C /min in the operating atmosphere.

By the chemical analyses of chips from layers of 0-0.5, 0.5-1.0, 1.0-1.75, 1.75-3.5 and 3.5-6.5 mm from samples surface, it corresponded to distances of 0.25, 0.75, 1.375, 2.625 and 5 mm from the sample surface, the average carbon contents in the layers were determined. Obtained results were completed by metallographic analyses of the investigated layers by light microscope.

RESULTS OF CHEMICAL AND METALLOGRAPHICAL ANALYSES

The results of chemical analyses of chips, corresponding to the distances of 0.025, 0.075, 0.1375, 0.2625 and 0.5 cm from surface of samples, including the experimental flows data and flow rates and carbon activities in atmospheres, are listed in Tab.1.

Tab.1. Total carbon concentrations in the individual samples layers in the dependency on the flow rate and the carbon activity of the atmospheres (carbon concentrations expressed in wt.%, distance from surface in cm).

a _C	v [mm/s]	F [l/h]	c _{0.025}	c _{0.075}	c _{0.1375}	c _{0.2625}	c _{0.5}
	0.03	0.70	0.29	0.40	0.37	0.35	0.34
	0.93	22.22	0.46	0.43	0.39	0.33	0.35
3.76	1.86	48.44	0.59	0.47	0.41	0.34	0.31
	2.79	72.66	0.61	0.50	0.46	0.41	0.40
	3.72	96.88	0.65	0.50	0.49	0.46	0.43
	0.03	0.70	0.40	0.52	0.47	0.45	0.44
	0.93	22.22	0.50	0.52	0.52	0.48	0.48
6.90	1.86	48.44	0.57	0.58	0.60	0.58	0.51
	2.79	72.66	0.64	0.65	0.65	0.63	0.57
	3.72	96.88	0.68	0.71	0.70	0.66	0.62
	0.03	0.70	0.49	0.69	0.66	0.57	0.54
	0.93	22.22	0.76	0.78	0.72	0.64	0.54
10.50	1.86	48.44	0.78	0.80	0.73	0.72	0.64
	2.79	72.66	0.84	0.92	0.89	0.83	0.76
	3.72	96.88	0.88	0.99	0.91	0.89	0.78

These values are graphically marked by dots in Figs.1-3, in dependence upon the distance from sample surfaces, for individual atmosphere flow rates, and for particular carbon activities in atmospheres, resp. Lines represent the samples' carbon concentration profiles calculated on the basis of mathematical processing of experimental data according to formula (7).

As can be seen from the experimental points, except for the ~0.5 mm layer immediately at the surface, carbon concentration decreased with an increasing distance from the sample's surface, and this decrease is approximately exponential. This dependence can be observed in all samples carburized in an atmosphere with a carbon activity of 3.76 or 6.90 or 10.50. With an increase of carbon activity in atmospheres, the carbon concentration proportionally increased not only at surfaces but also within internal layers of samples.

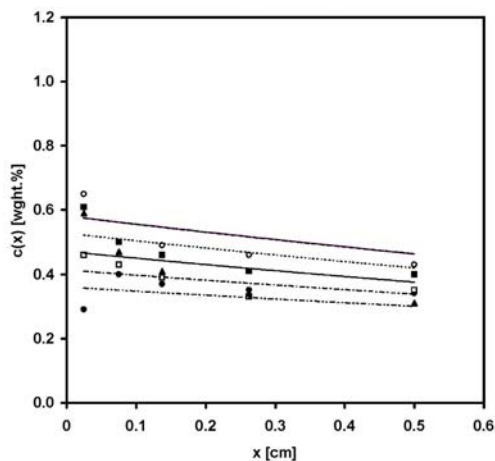


Fig.1. The carbon content in the individual sample layers for various flow rates of atmospheres with 4 vol. % CH_4 + cracked NH_3 .

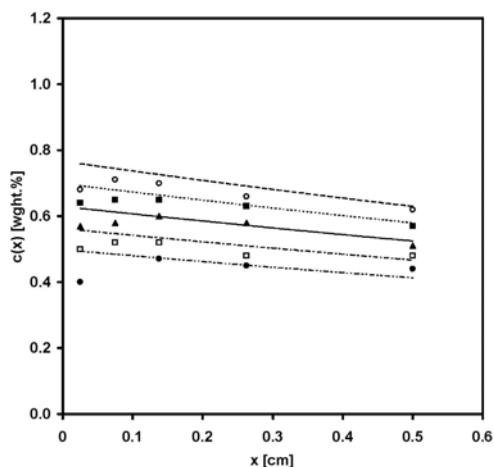


Fig.2. The carbon content in the individual sample layers for various flow rates of atmospheres with 7 vol. % CH_4 + cracked NH_3 .

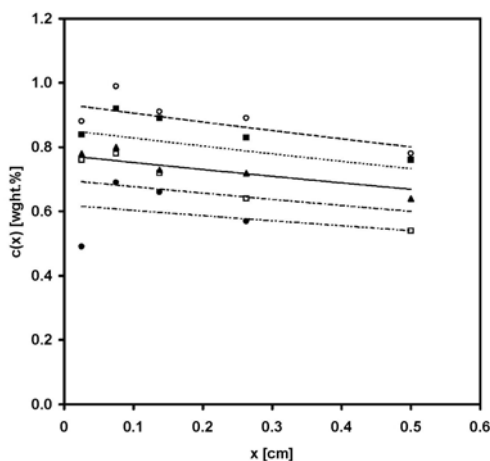


Fig.3. The carbon content in the individual sample layers for various flow rates of atmospheres with 10 vol. % CH_4 + cracked NH_3 .

In the samples carburized in a stationary atmosphere with 4 vol.% CH_4 and also in the samples carburized in an atmosphere with 7 vol.% CH_4 , a thin layer started to occur on samples surface. The thin layer was at the moment only moderately decarburized in regard to carbon concentration upon the following subsurface layer. In the samples carburized in an atmosphere with 10 vol.% CH_4 , the presence of this decarburized layer was already apparent. For the samples carburized in stationary atmospheres, the presence of this decarburized layer was observed not only in the atmosphere with 4 % CH_4 , but also with 7 and 10 vol.% CH_4 .

The metallographic study of carburized samples confirmed the results of chemical analyses of chips removed (sampled) from their individual layers. The layer with a thickness of ca 0.5 mm was visible on the samples surfaces carburized in stationary atmosphere with 4 vol.% CH_4 , and carburized in atmospheres with 7 and 10 vol.% CH_4 . This layer in regard to

pearlite content in following subsurface layer, was moderately decarburized (Fig.4). At a distance of about 0.75 mm from the sample surface, the most carburized layers occurred, but also in the case of carburization in the atmosphere with 10 vol.% CH₄ and with a flow ca 100 l/h, clearly pearlitic layers were presented without the presence of secondary cementite. The microstructures of the samples internal layers, carburized in the atmosphere with a content of 4 vol.% CH₄, were pearlite-ferritic (Fig.5), with 7 vol.% CH₄, also pearlite-ferritic up to ferrite-pearlitic (Fig.6), and with 10 vol.% CH₄ ferrite-pearlitic up to pearlitic (Fig.7). For comparison, the microstructure of a green compact is shown in Fig.8 and it was composed of ferritic grains with locally occurring pearlite islands.



Fig.4. The samples surface layers microstructure after carburizing ($a_c = 10.5$; $v = 3.72$ mm/s) (Nital etched).

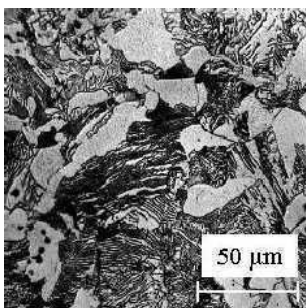


Fig.5. The inner layers microstructure of samples carburized in atmospheres containing 4 vol. % CH₄ ($v = 3.72$ mm/s) (Nital etched).

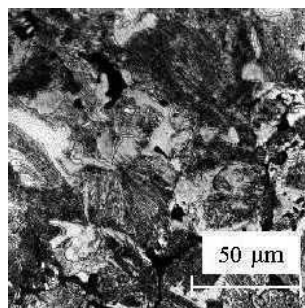


Fig.6. The inner layers microstructure of samples carburized in atmospheres containing 7 vol. % CH₄ ($v = 3.72$ mm/s) (Nital etched).

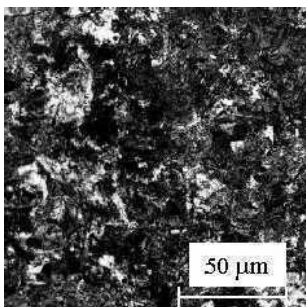


Fig.7. The inner layers structure of the samples carburized in atmospheres containing 10 vol.% CH₄ ($v = 3.72$ mm/s) (Nital etched).

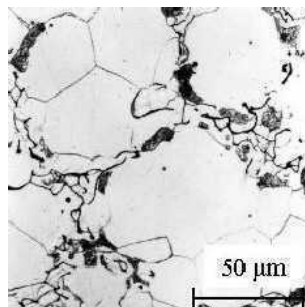


Fig.8. The microstructure of sintered parts (Nital etched).

MATHEMATICAL PROCESSING OF RESULTS

The main aim of the presented paper was to quantify the intensity of carburizing not only in surface layers, but also in the internal layers of samples prepared from sintered DV 0.40 steel, with constant geometry and porosity, in dependence upon the flow rate and the carbon activity in the carburizing atmospheres. The result processing was done by the method of a separation of variables and by multiple regression analysis, using the technique developed for evaluating the experimental data of heterogeneous reactions in progress in the systems solid - gas [26].

$$\text{As seen from the formula: } c(x) - c_0 = (c_p - c_0) \cdot \exp(-k \cdot x) \quad (1)$$

where $c(x)$ is the carbon content [wt.%] at the distance x [cm] from samples surface, c_0 - initial carbon content in samples [wt.%] - in this case 0.086 wt.%, c_p - carbon content on the sample surface [wt.%], k - a coefficient expressing the slope of carbon concentration decrease with regard to the distance from samples surface, the values of expressions $(c_p - c_0)$ and coefficient k were calculated for individual flow rates of atmospheres and carbon activities in atmospheres as well. The dependence of $(c_p - c_0)$ values on the atmosphere flow rates for atmospheres with a given carbon activity is presented in Fig.9 by experimental points. These dependencies are shown by lines according to formula (5).

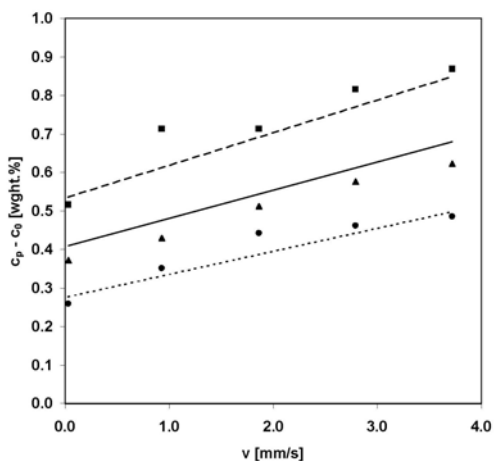


Fig.9. Dependence of carbon concentration $(c_p - c_0)$ in the specimen surface on flow rates of atmospheres with various carbon activities.

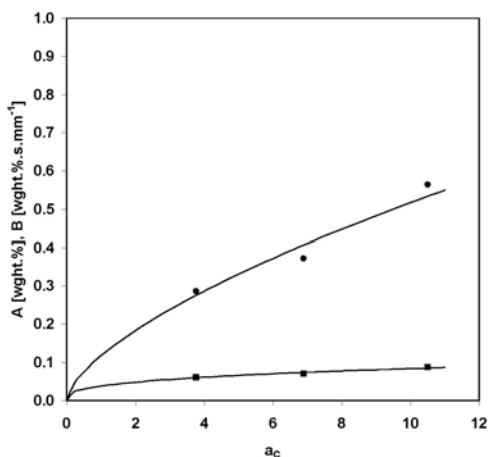


Fig.10. The dependence of the constant A and B factors on the atmosphere carbon activity.

In the second stage of the mathematical processing of experimental data, the values of A and B constants for atmospheres with given carbon activities a_c were determined from the dependency:

$$c_p - c_0 = A + B \cdot v \quad (2)$$

where v is the atmosphere flow rate [mm/s]. These values are plotted in Fig.10 by experimental points. After multiple regression analysis, it was possible to express their dependency on the carbon activity in atmosphere by the equations:

$$A = 117.6 \cdot 10^{-3} \cdot (a_c)^{0.643} \quad (3)$$

$$B = 37.0 \cdot 10^{-3} \cdot (a_c)^{0.342} \quad (4)$$

By these dependencies are represented in Fig.10 by lines.

The values of expressions $(c_p - c_0)$ it was possible to express by the equation:

$$(c_p - c_0) = 117.6 \cdot 10^{-3} \cdot (a_C)^{0.643} + 37.0 \cdot 10^{-3} \cdot v \cdot (a_C)^{0.342} \quad (5)$$

The values of coefficient k [cm^{-1}] at flow rates in the range of 0 - 4 mm/s did not express a dependency on the stated parameter. The average values of this coefficient were calculated for atmospheres with various carbon activities. The average values of k decreased with activity increase, but as a result of a low number of experimental points, it was not possible to determine a final functional dependence k on a_C . In regard to the results and mathematical processing of data obtained during carburization of the same material at similar conditions [21-23], their dependence on carbon activity in the atmosphere was expressed by a similar formula, which was after mathematical processing in the form:

$$k = 0.732 \cdot \exp(-71.6 \cdot 10^{-3} \cdot a_C) \quad (6)$$

The result of this processing are formula that express the distribution of carbon content in the individual layers of samples in dependence upon flow rate of atmosphere and on carbon activity within it:

$$c(x) = c_0 + [117.6 \cdot 10^{-3} \cdot (a_C)^{0.643} + 37.0 \cdot 10^{-3} \cdot v \cdot (a_C)^{0.342}] \cdot \exp[-0.732 \cdot x \cdot \exp(-71.6 \cdot 10^{-3} \cdot a_C)] \quad (7)$$

The final step of the mathematical processing of data obtained was a comparison of the values of carbon content in the individual layers of samples determined by chemical analyses $c(x)_{\text{exp}}$ with the values of carbon content calculated from the equation (7) - $c(x)_{\text{cal}}$. Graphically, this dependency is shown in Fig.11. As it can be seen from the figure, among the experimental and a calculated value there is a good agreement (the coefficient of correlation equals 0.9948).

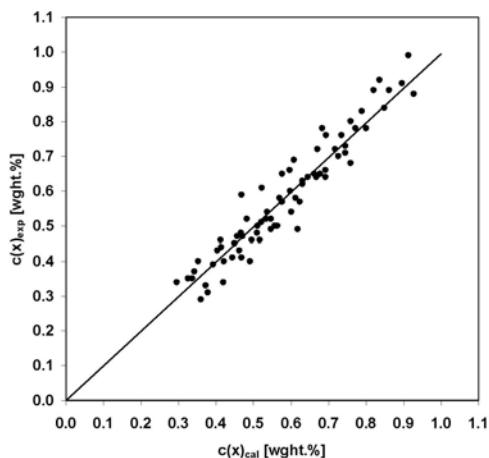


Fig.11. The comparison of the individual layers carbon concentration values experimentally determined - $c(x)_{\text{exp}}$ and calculated via the equation (7) - $c(x)_{\text{cal}}$.

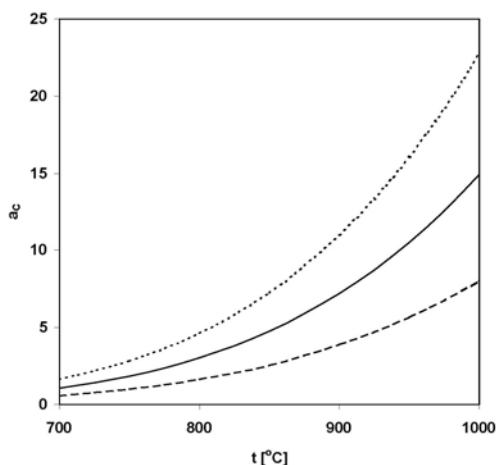


Fig.12. The dependence of the atmospheres carbon activity on the temperature T [$^{\circ}\text{C}$] of carburization for various contents of methane in the atmospheres $\text{CH}_4 + \text{H}_2 + \text{N}_2$ (input dew point $\approx -14^{\circ}\text{C}$) [24].

DISCUSSION

As follows from the experimental results, carbon content in samples was increased along with both the flow rate of atmospheres and carbon activity in atmospheres. The extrapolated values of carbon content at the samples surface c_p were linearly dependent on atmospheres' flow rate, and parabolically dependent on carbon activity in the atmospheres

(Figs.9,10). These dependencies may be described by the formula (5). The dependencies do not rise from the beginning of the coordinate system. It is effected by the fact that applied atmospheres, as a consequence of their strong carburizing ability, and hence the high carbon activity, carburized the materials even though they were stationary, each one according to its carbon activity.

Contrary to factor c_p , the coefficient k , which specifies the measure of decrease of carbon concentration with an increasing distance from samples surface, was independent of the atmospheres flow rate. Its values were influenced only by carbon activity in atmospheres.

The investigated facts were verified, the mechanism of processes taking place in samples surfaces had a quite different character than the mechanism of processes taking place in the samples inner layers. The dependency of c_p values on the flow of atmospheres and on the carbon activity in atmospheres confirms that the carburizing of surface layers is controlled by absorption – desorption processes. Compared to this fact, the independence of coefficient k values on the atmospheres flow rate confirms that the carburizing in the internal layers is controlled by diffusion.

As was already mentioned above, the effect of decarburization at the process temperature of carburized layers during sample cooling was observed in their surface layers. A tendency to form decarburized surface layers was observed, first of all, on the samples carburized and cooled in atmospheres with low atmosphere flow, hence in quasi-stationary atmospheres and with a high methane concentration, i.e. with high carbon activity. Whereas in the case of carburizing in atmospheres with 4 vol.% CH_4 , the differences between the atmosphere activity at holding time on temperature and activity at cooling were not markedly expressed on decarburizing of surface layers - except in the case of the stationary atmosphere, these differences were already more expressed at an atmosphere with 7 vol.% CH_4 . In the case of atmospheres with 10 vol.% CH_4 , the temperature decrease caused such differences between atmosphere carbon activity at the holding time, and at cooling, that significant decarburization occurred in surface layers. The atmosphere carbon activity decrease during the cooling period was thereby higher, the higher the methane content in atmosphere [22,24,27]. As is seen in Fig.12, where the dependence of carbon activity in atmospheres on temperature (calculated on the basis of [24] for given experimental conditions) is plotted, carbon activity during cooling of samples carburized in atmospheres with 10 vol.% CH_4 decreased from the value ca 11 to a value ca 3, whereas the carbon activity of atmospheres within the temperature range of 900 - 750°C during a cooling of samples carburized in atmospheres with 4 vol.% CH_4 decreased from a value ca 4 to a value ca 1. Consequently, decarburizing already carburized surface layers is also greater at cooling in atmospheres containing 10 vol.% CH_4 , compared with cooling in atmospheres with 4 vol.% CH_4 .

Surface layers decarburization was also increased as a result of the relatively high dew point of atmospheres used ($\text{DP} \approx -14^\circ\text{C}$) [20].

Another factor accelerating the decarburization of samples surface layers was their open porosity, which allowed the atmospheres to operate to a sizeable depth under the samples surface by their decarburizing effect. As is seen from the experimental points plotted in Figs.1-3, these depths achieved values of ca 0.5 mm in the case of used porosity ($P_c \approx 18\%$), also in the cases of carburizing in stationary atmospheres. Up to the mentioned depths, the interconnected pores allowed decarburization of "already carburized layers" during cooling.

The final effect of these factors, i.e. decreasing carbon activity in atmosphere at decreasing temperature, a high dew point of carburizing atmospheres and the high porosity

of samples, was the fact that decarburized thicknesses were much greater than would be predicted on the basis of a decrease of carbon diffusion coefficient during the cooling stage in compact materials.

On the basis of data obtained by mathematical processing of experimental data, it is possible also to state that the final equation (7) well represents the carbon distribution in the samples volume, and maximal differences between calculated and measured values were within the range $\pm 10\%$.

CONCLUSIONS

The paper is focused on the examination and quantification of effect of the flow of atmospheres CH_4 - H_2 - N_2 , resp. of the rate by which these atmospheres flowed in the operating section of the furnace, on the carburizing course of porous DV 0.40 steel. On the basis of the experimental results at given experimental conditions (cylinder $\varnothing 13 \times 13$ mm, total porosity $P_c \approx 18\%$ of cylinder specimen, diffusion by the whole sample surface, a dew point of atmosphere at the furnace input $\approx -14^\circ\text{C}$) it is possible to make the following conclusions:

1. During the mathematical processing of experimental data, for the carbon distribution in samples volume, we came out with the equation (1): $c(x) - c_0 = (c_p - c_0) \cdot \exp(-k \cdot x)$.
2. In a realized set of experiments, the carbon concentration at the sample surface, in the range of 0 - 4 mm/s, increased with the atmosphere flow rate linearly. This rise was more intensive at a higher carbon activity in atmosphere. It was possible to express the dependence of carbon content at the sample surface on the atmosphere flow rate and on the atmosphere carbon activity by using the formula (5): $(c_p - c_0) = 117.6 \cdot 10^{-3} \cdot (a_C)^{0.643} + 37.0 \cdot 10^{-3} \cdot v \cdot (a_C)^{0.342}$.
3. The carbon distribution in the sample volume depended, first of all, on its concentration in the surface layer. The degree of the carbon content decrease with increasing the distance from samples surface did not depend on the atmosphere flow rate, it was moderate, dependent on the carbon activity in atmospheres. The coefficient k , characterizing this decrease, was possible to express using the formula (6): $k = 0.732 \cdot \exp(-71.6 \cdot 10^{-3} \cdot a_C)$.
4. The dependency of the carbon content on the distance from samples surface, on the atmosphere flow rate, and on the atmosphere carbon activity was quantified by the formula (7).
5. After comparison of the values for carbon content in the individual sample layers determined experimentally and calculated via the equation (7), a good agreement was determined to be between them, with a tolerance $\pm 10\%$.
6. The partial decarburization occurred in the sample surface layers during cooling. The degree of decarburization depended on the flow rate - the lower, the more extensive the decarburization - and on the atmosphere carbon activity - the higher it was during the carburization, the higher was the decarburization during cooling.

On the basis of the above mentioned facts, it was possible to state that carburization of surface layers was controlled by absorption-desorption processes taking place at the samples surface, and depending on the atmosphere flow rate and on the carbon activity within them. The carbon distribution in the sample volume was controlled by carbon diffusion in the component, and it was independent on the atmosphere flow rate.

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