Particularities of carburising kinetics in different media

D. DRAGOMIR[*a], M. O. COJOCARU[b], L. N. DRUGA[c]
[a]*UTTIS, Vidra, Ilfov, 077185, Romania*
[b]*"Polytehnica" University, Faculty of Materials Science and Engineering, 060032, Bucuresti, Romania*
[c]*Romanian Academy for Technical Sciences, Bucuresti, Romania*

The kinetics of the carburising processes in media which are relatively rare used in the thermochemical treatments practice (paste, paste-urban fuel gas, urban fuel gas) for specific applications or in case of inappropriate endowment of thermochemical treatments facilities is less addressed in the technical literature in the field. In this sense, this paper attempts to bring further knowledge in the field of carburising processes kinetics in these types of carburising media, in particular, and of the ways of accelerating of the carburising layers growth kinetics, in general. The experimental researches performed on basis of a non compositional programme aimed to study the kinetics differences developed during carburising of a low alloyed case hardening steel in various media: paste, paste-urban fuel gas in comparison with carburising in urban fuel gas in the presence of the fluidization state of the media with a view of highlighting of the process parameters (carburising temperature and holding time at the carburising temperature) influences, respectively the assessment of the fluidization state on the carburising kinetics changes. The results of the carburising experiments performed at temperatures in the range of 900 ... 1000° C and times in the range of 30 ... 90 min confirm that the paste provides a carburising kinetics superior to that assured by urban fuel gas and the carburising kinetics in combined media (paste-urban fuel gas) has an intermediate value. The paper presents also the possibility to accelerate the kinetics of carburising process in urban fuel gas by using of the fluidized bed, the carburising kinetics recorded in this case being the most intense for the treatment temperatures and times investigated.

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1. Introduction

The carburizing is one of the processes often used in industry to increase the lifetime of metallic products.

Carburizing process particularities, kinetics and mechanisms in different media have been addressed in various technical literature references [1-20], among these, the mass transfer phenomena in the thermochemical processing media and metallic products being subject to analysis in [4-8], either based on the analysis of kinetic models of specific carburizing reactions, developed primarily for gas carburizing by Grabke, Madsac et. al, Kasperma et. al, other or in terms of defining, estimating and calculating of the carbon mass transfer coefficient by Hoffmann et al, Wunning, Madsac et. al, Munts et al., other, respectively studying the influencing factors on the carbon mass transfer coefficient.

Also different studies of other authors dedicated to carburizing process kinetics, approached the possibilities of carburizing process accelerating using low pressure [9], addition of rare-earth in the metallic product under thermochemical processing [10] or in the gaseous media [11], in the presence of electrolytic plasma [12] or fluidization state [13-16].

The kinetics of carburising in pastes is less addressed in the more recent technical literature in the field, some concerns regarding the solid carburizing kinetics being presented in [17].

The purpose of this paper is a comparative analysis of a carburizing kinetics of a low alloyed case hardening steel, 21NiCrMo2, processed in relatively rare used carburizing media - paste, paste-urban fuel gas, urban fuel gas, on basis on the study of the influences exerted by the process parameters - carburizing temperature and holding time at carburizing temperature on carburizing case depth and rate attained in these media.

In the paper are also shown the effects of the fluidization state on the kinetics of the carburizing process of alloyed case hardening steels, the results being compared with that obtained at carburizing in relatively rare used carburizing media.

2. Experimental procedure

The carburizing experiments in relatively rare used carburizing media were performed in electrical ovens on 21NiCrMo2 (W 1.6523) steel samples of Φ15 x 20 mm. The carburizing paste consists in certain amounts of fine divided charcoal, calcium and sodium carbonates, potassium ferrocyanide and heat treatment oil as an appropriate consistency to be assured.

Fluidized bed carburizing experiments in urban fuel gas were carried out in a vertical electric furnace having the fluidized layer consisting of sand particles on 17MoCr10 (W 1.7131) and 17MoCrNi14 (W 1.6587) steels samples of Φ15 × 20 mm. Chemical compositions of the investigated steels determined by chemical analysis were: 21NiCrMo2(0.2%C, 0.76%Mn, 0.027%S, 0.027%P, 0.43%Cr, 0.26%Si, 0,51%Ni, 0.22%Mo); 17MnCr 10 (0.19%C, 1.29%Mn, 0.017%S, 0.021%P, 1.26%Cr); 17MoCrNi14 (0.19%C, 0.82%Mn, 0.040%S, 0.021%P, 1.4%Cr, 0.32%Si, 1.5%Ni, 0.20%Mo). The thermochemical processing was performed at temperatures in the range of 900 - 1000°C and holding times at carburizing temperatures in the range of 30 - 90 min.

3. Results and discussion

3.1 Results and discussion on carburising in relatively rare used carburising media

The graphical expressions of the mathematical models of interdependences between the effective case depths of the carburized layers, respectively the momentary carburizing rates in terms of thermal and time parameters of thermochemical processing (carburising) for the different media taken in analysis are shown in fig. 1 a, b, c.

The layers growth kinetics in the analyzed carburizing media led to distinct differences that can be explained both by media activities and mass transfer processes intensities occurring there. The intensity of mass transfer processes expressed by the variation in time at different temperatures of the effective case depth of the carburising layer, respectively carburising rate is decreasing: paste, combined media, urban fuel gas.

The case depth variation with the holding time in the above mentioned media is unusual for temperatures of 900°C and 950°C for paste, respectively for all temperatures investigated for urban fuel gas, showing a maximum in the range 60-75 min; at temperatures above 950°C, the variation is parabolic for paste carburizing. In the case of carburizing in combined media, the case depth variation with holding time is a result of both carburizing media influences and generally respects the parabolic trend.

Regarding the evolution of the carburizing rate with holding time in the temperature range investigated, in the first moments of the carburizing up to times of 30 min, due to the fact that the medium - paste is high chemically active, the differences between its carburizing capabilities at the carburizing temperatures and the concentration gradients at the medium – metallic products interface will not lead to noticeable variations in the carburizing rates.

By the increasing of the holding time at the carburizing temperatures, the carbon availability in pastes decreases, both due to the transfer in the metallic matrix and also due to the losses in the enclosure where the thermochemical process is performed. The modifying of the activity of the carburizing paste is more intense as the temperature is increasing, phenomenon leading to the proportional decreasing of the saturation rates.

In the case of carburizing in urban fuel gas, the decreasing of the carburized layer growth kinetics is given by the appearance of soot at exceeding of saturation concentration of carbon in austenite at a certain temperature with negative effects on carburizing rates (after 60 - 75 min); the decreasing in time of carburizing rate is due to lowering of the general capacity of carburizing of the atmosphere generated by the combustion of urban fuel gas with about 0.5% at temperature variation in the range 900÷1000°C [19].

In the case of combined media, the carburizing rates variation with the holding times for the investigated temperatures is a resultant of the two media influences, their values being lower than those determined for paste.

Regarding the assessment of the carbon transfer mechanisms during paste carburizing, these are governed by the carburizing reactions leading to the formation of carbon in active state and which are occurring predominantly in the gaseous phase: decomposition of Ba and Ca carbonates with release of carbon dioxide, reaction of carbon dioxide (both from carbonates decomposition and also from the reaction of excess carbon with oxygen) with existing paste excess carbon with formation of carbon monoxide and active carbon release, decomposition of potassium ferrocyanide with release of active carbon; other carbon source is represented by the micron particles of charcoal also available in the paste used for carburizing.

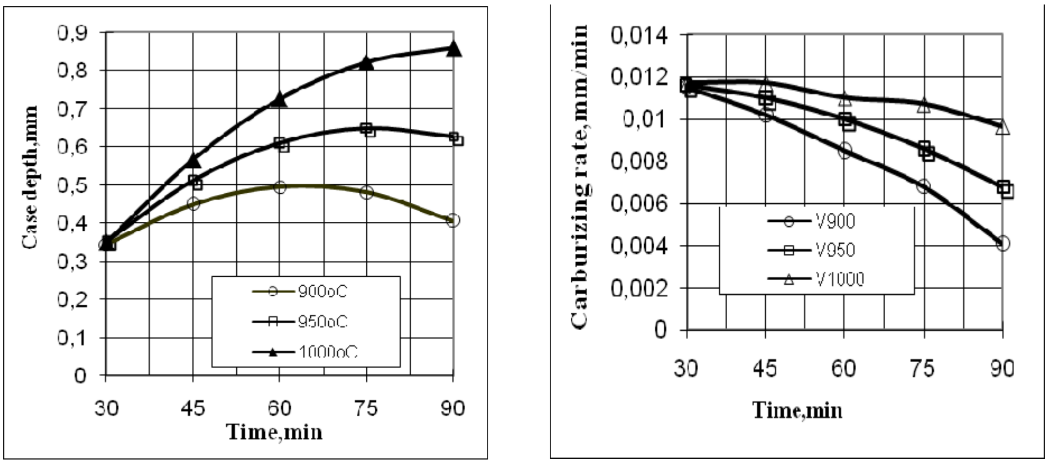
3.2 Results and discussion on carburising in fluidized bed

The comparative analysis of carburising kinetics in relatively rare used carburising media of 21NiCrMo2 steel and of kinetics of alloyed case hardening steels processed in fluidized bed using as active media the urban fuel gas, has provided the following aspects:

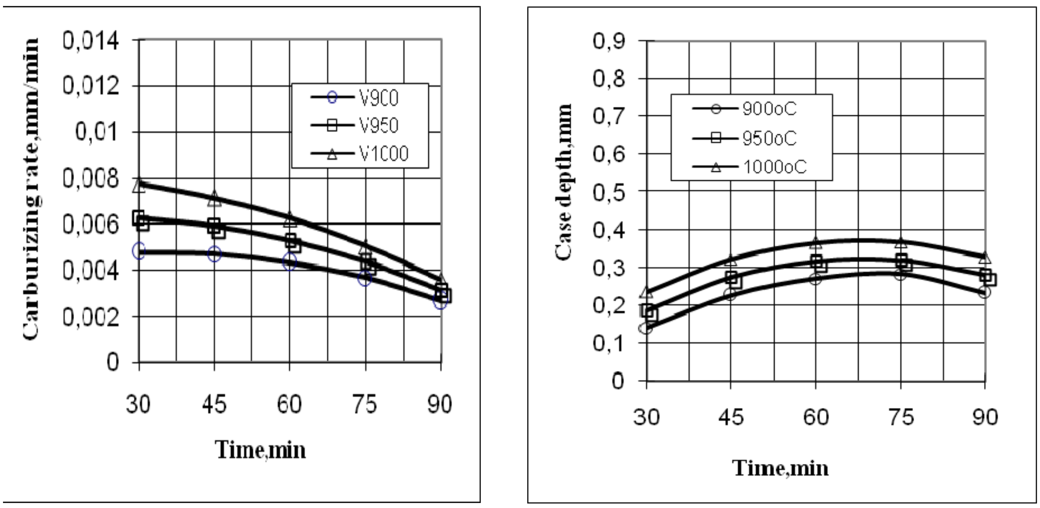
- the intensity of mass transfer processes in fluidized bed expressed by the same factors as for the kinetics in relatively rare used carburizing media, is quite similar for the two alloyed case hardening steels - 17MnCr10, 17MoCrNi14 (steels with close proportions of the elements with carbon affinity – Mn, Cr, Mo: $\sum(\%Mn + \%Cr)_{17MnCr10} = 2{,}55$ compared with $\sum(\%Mo + \%Cr + \%Mn) = 2{,}42$) and superior to that of 21NiCrMo2 steel, carburised at the same thermochemical processing parameters (T, t) in relatively rare used carburising media;
- the 17MoCrNi14 steel has fluidized bed carburizing kinetics superior to those of 21NiCrMo2 steel (both steels have the same alloying elements but in different proportions) and the case depths and carburizing rates are about 2.2 ... 2.8 times higher in comparison with those obtained in urban fuel gas carburizing respectively about 1.2 …1.5 times higher in comparison with those obtained in paste, respectively in combined media (paste – urban fuel gas).

The explanation of different carburizing kinetics in fluidized bed, under the same thermochemical processing parameters, achieved on similar steels in terms of chemical composition but still different in content and combination of alloying elements is both related to the carbon mass transfer particularities in fluidized bed and also in the metallic products.

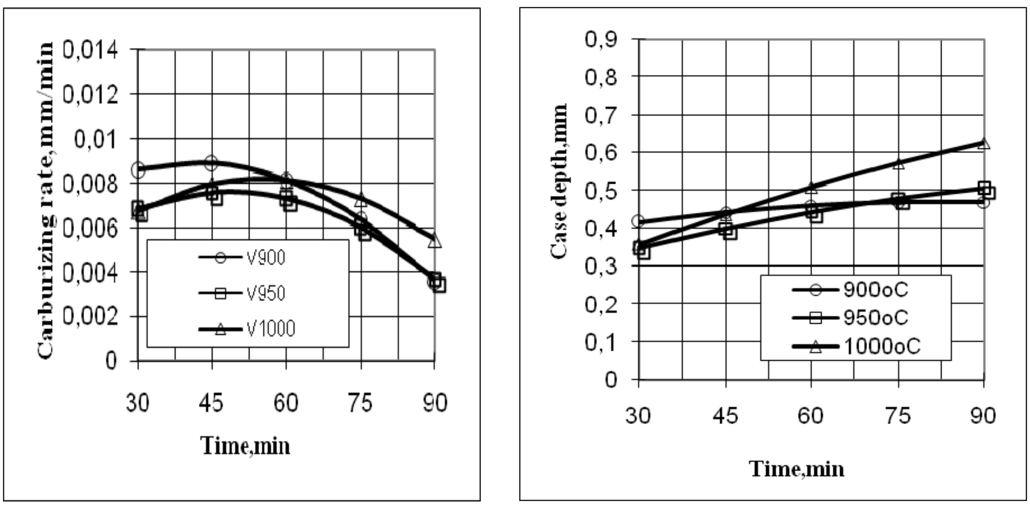
The fluidized bed carburising process is a non equilibrium process and basically is an extension of conventional gas carburising, the reactions in the gas phase and gas - solid are identical in principle, ones of the major differences being the carburising rates and overall carbon mass transfer coefficient (the carbon mass transfer coefficient in fluidized bed is at least twice times higher than that achieved in conventional carburising for the same type of atmosphere [13-16]).



a) paste

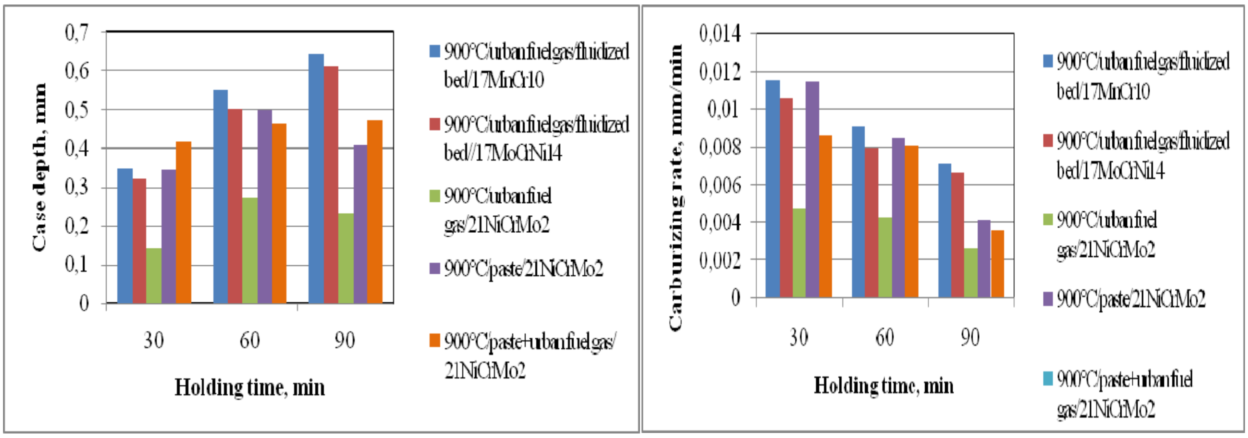


b) urban fuel

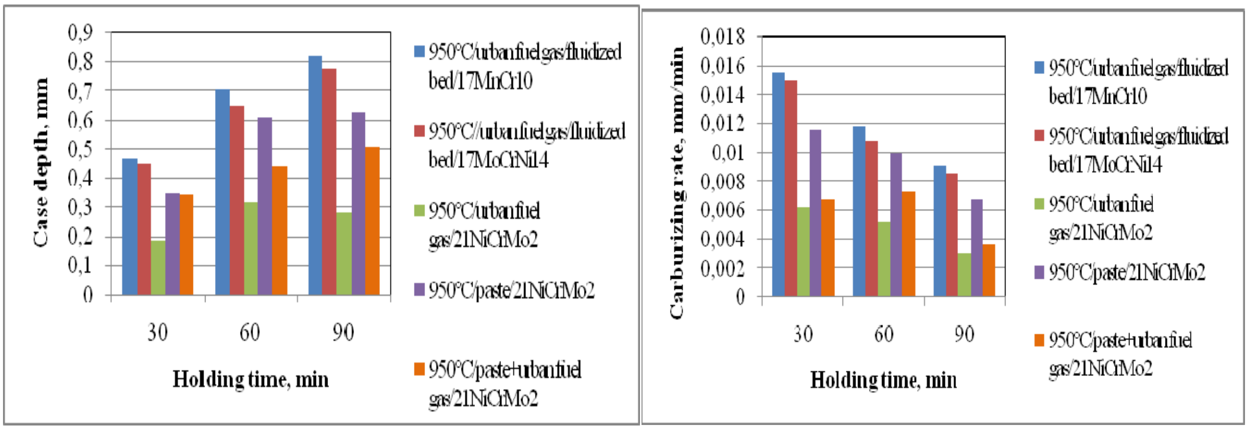


c) paste + urban fuel gas

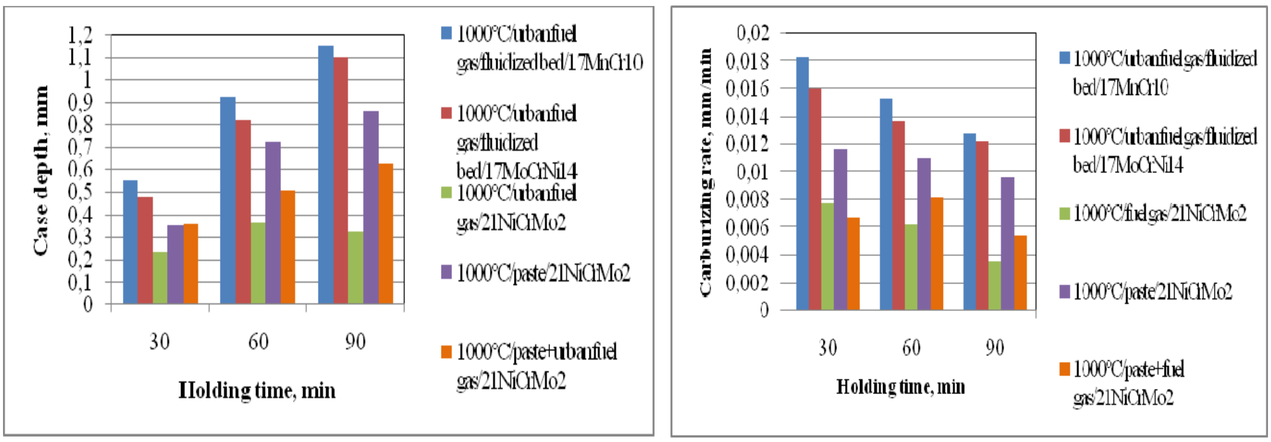
Fig. 1. The carburizing layers kinetics in relatively rare used carburizing media for 21NiCrMo2 steel.



a) T=900°C/30, 60, 90 min



b) T=950°C/30, 60, 90 min



c) T=1000°C/30, 60, 90 min

Fig. 2. The carburising layers growth kinetics in fluidized bed in comparison with the carburizing layers growth kinetics in relatively rare used carburising media.

The intensifying of the mass transfer in the fluidized bed and the higher values of carbon mass transfer fluxes and coefficients in fluidized bed carburising compared with other carburising media are explained by the following particularities:

- the fluidized bed hydrodynamics and intense heat transfer accelerate the catalytic dissociation of urban fuel gas (gas composition: 85%-95% CH_4, approx. 10%H_2, more than 2% CO, CO_2, O_2 and N_2), change the chemical reactions rates both in the fluidized bed and also at interface; the excess carbon formed in the fluidized bed is either burned or recombined, resulting increased carbon mass transfer coefficients in the fluidized bed and also at interface;

- due to activation and permanently "washing" of the surface metallic products by the fluidized bed particles, a significant increase in the active gaseous elements concentration results, fresh carbon atoms carrier gas and chemically active particles arrive on the metallic products surface, the adsorption and diffusion change in interface and as result the mass transfer flux in the surface of the metallic product is accelerated (the interface boundary layer decreases or disappears);

- the carburising medium is more uniform by chemical point of view and has a higher chemical potential than that assured by the conventional carburising gaseous medium also due to hydrodynamics and greater temperature uniformity; this also lead to acceleration of adsorption and surface diffusion, allowing a high surface carbon concentrations in short times to be achieved.

In addition to the mentioned particularities, a great influence on the mass transfer coefficient value at the interface is also due to the hydrodynamic parameters of fluidized bed (solid particles characteristics - nature, size, specific gravity, shape; fluidization gas characteristics - specific gravity, temperature; shape and dimensions of the enclosure where the fluidization takes place; flow characteristics of fluidized bed - loss of pressure, specific gravity, viscosity, bubble size, fluidization velocity; size and position of parts immersed in the fluidized bed other) involved in the transfer of carbon.

As is well known from the theory and practice of carburising processes, after initial period, the carburizing kinetics elements that govern the carbon mass transfer are the interface carbon mass transfer coefficient and carbon diffusion coefficient in steel [7].

It was found that the 17MnCr10 or 17MoCrNi14 steels, that contain carbides forming elements in approx. equal proportions (~2,5%) that decrease the carbon activity in austenite, have the fluidized bed carburising kinetics more intense than the 21NiCrMo2 steel carburising kinetics in any of the relatively rare used carburising media taken in analysis, although the proportion of the carbides forming elements in the latest is of only 1,41% (41,5% of that related to the first category of steels).

Thus for temperature of 950^{o}C and 60 min holding time, the effective case depth, respectively the carburising rate in the case of 17MnCr10 (and close to this, for 17NiCrMo14) is 0.71 mm, respectively 0.018 mm/min, compared to 0.62 mm and 0.065 mm/min, in the case of 21NiCrMo2 steel carburised in the more active media – paste from the relatively rare used carburising media investigated.

The relatively low kinetics differences between the fluidized bed carburising kinetics recorded for the two steels 17MnCr10 and 17MoCrNi14, can be explained by the rapport of the proportions of the carbides forming elements and austenite stabilizing elements, with direct implications on the carbon mass transfer through diffusion, respectively on the atoms flux transferred through the medium – metallic matrix interface [20].

4. Conclusions

The experimental research aimed at studying of growth kinetics in relatively rare used carburizing media and of the possibility of acceleration of mass transfer processes in urban fuel gas in the presence of fluidization state.

The kinetics of mass transfer processes in relatively rare used carburizing media of 21NiCrMo2 steel expressed by the variation in time at different temperatures of effective case depth of carburized layer, respectively carburizing rate is decreasing: paste, combined media, urban fuel gas.

The kinetics of mass transfer processes in fluidized bed expressed by the same factors as for the kinetics in relatively rare used carburizing media for investigated steels 17MnCr10, 17MoCrNi14 is superior to that recorded for the 21NiCrMo2 steel, carburized at the same thermochemical processing parameters (T, t) in relatively rare used carburizing media.

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* Corresponding author: dana_dragomir@hotmail.com