

## Nanostructure-based Processes at the Carbonizing Steels

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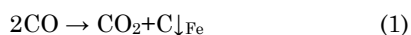
The studies of nanostructure-based processes carburizing steels showed that oxidizing atmosphere when carburizing steel contains along with carbon dioxide ( $\text{CO}_2 + \text{C} = 2\text{CO}$ ) molecular and atmospheric oxygen ( $\text{O}_2 + 2\text{C} = 2\text{CO}$ ;  $\text{O} + \text{C} = \text{CO}$ ) released from the carbonate  $\text{BaCO}_3$  during its thermal dissociation. Intensive formation of CO provides high carbonizing ability of carbonate-soot coating and steel.

**Keywords:** Nanostructure-based processes, Carbonization, Steel, Thermodynamic calculations.

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### 1. INTRODUCTION

Cementation is the most common process of thermochemical treatment of steel products. The main source of carbon in most solid and gas carburizing agents is carbon monoxide. Its carbonizing activity is carried out as a result of the decomposition on the steel surface with the release of atomic carbon which is absorbed by this surface



It should be noted that for steel carburizing (for reaction 1) less than 1 % of carbon monoxide, which is part of a carburizing atmosphere, is consumed. The main part of CO partially burns out at the furnace outlet and partially leaves the furnace unburnt that causes uneconomical and environmentally unfriendly process [1, 2].

Studies [3, 4] found out that a substantial increase in carburizing ability and in carburizing environmental friendliness can be achieved using a carbonate-carbon coating, applied to the surface which is to be carburized.

### 2. RESEARCH OBJECT AND TECHNIQUES.

Nanostructure-based processes occurring on the surface of the carburized steel during its carburizing in pasty soot carburizing agents are the object of the study. Thermodynamic calculation is the method of the study.

### 3. RESULTS DESCRIPTION AND ANALYSIS.

The mechanism and kinematics of the reaction at the interface between the carburizing environment and steel change in the thin coating on the surface of carburized steel. In this case, not chemisorption of CO molecules from the gas environment on the steel surface but the reaction of CO formation and then decomposition at the interface of the contacting surfaces of soot particles and steel starts to play the main role in the carburization. Due to this, the independence of the speed of carburization from the speed of the gas flow passing

through the working area of the furnace is practically provided.

Active carbon monoxide in the face-hardening coating is formed as a result of thermal dissociation of barium carbonate [5, 6]



and subsequent reacting of  $\text{CO}_2$  with carbon on the surface of hot soot particles



However, taking into account high carbonizing ability of carbonate-soot coating it can be assumed that an additional amount of carbon monoxide is formed in the coating due to BaO dissociation.

Barium oxide dissociates into its components Ba,  $\text{O}_2$  and O resulting in providing oxygen required for the formation of carbon when it reacts with soot:



This assumption can be verified by thermodynamic calculations, in particular by the calculation of the equilibrium partial pressures of molecular and atomic oxygen above BaO.

According to the theory of thermal dissociation of compounds, in most cases considerations for metals are limited to monatomic vapours [4, 5].

In such reduction for the partial pressure of barium vapour in BaO dissociation products, the balance equation is as follows:

$$P_{\text{Ba}} = P_{\text{O}} + 2P_{\text{O}_2} \quad (6)$$

(barium vapour partial pressure is equal to the sum of the partial pressures of oxygen reduced to a monatomic gas).

The pressure at which barium vapour is in equilibrium with the condensed barium is taken as the standard state. In this case, the thermodynamic activity of barium vapour  $a_{\text{Ba}}$  in BaO dissociation products is equal to one [7].

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If, as a result of the oxide dissociation the pressure of the saturated metal vapour is provided, i.e. the following condition is fulfilled:

$$P_M = P_o^M, \quad (7)$$

then the change of the free energy  $\Delta G^{oT}$  in the dissociation reactions of the oxide is the same as  $\Delta G^{oT}$  of the reaction of oxide forming from metal in the condensed state, the values of which are available in reference literature, including [8].

The fulfillment of the condition (7) makes it possible to calculate the partial pressure of molecular oxygen using  $\Delta G^{oT}$  of the formation of the oxide BaO from the components in standard conditions, i.e. from metal in the condensed state and molecular oxygen, according to the reaction:



To calculate the partial pressure of atomic oxygen  $P_o$  according to  $\Delta G^{oT}$  for reaction



is not possible, since the change of free energy for this reaction is not given in reference literature. However,  $P_o$  can be calculated using well-studied reaction of thermal dissociation of molecular oxygen [5, 6]



with equilibrium constant

$$K_{\text{O}_2} = P_o^2/P_{\text{O}_2} \quad (11)$$

Having expressed  $P_{\text{O}_2}$  through  $K_{\text{O}_2}$ , in accordance with (11), the balance equation (6) can be written as follows:

$$P_{\text{Ba}} = P_o + 2/K_{\text{O}_2} \cdot P_o^2 \quad (12)$$

If we take into account the equilibrium constant for the reactions (8):

$$K_{\text{BaO}} = P_{\text{Ba}} P_{\text{O}_2} = P_{\text{Ba}} \cdot P_o^2 / K_{\text{O}_2} \quad (13)$$

and express  $P_{\text{Ba}}$  through  $K_{\text{BaO}}$ ,  $K_{\text{O}_2}$  and  $P_o$  in accordance with (13)

$$P_{\text{Ba}} = (K_{\text{BaO}} \cdot K_{\text{O}_2})^{0.5} / P_o \quad (14)$$

(it is possible to rewrite the balance equation 12):

$$(K_{\text{BaO}} \cdot K_{\text{O}_2})^{0.5} = P_o^2 + 2P_o^3 \quad (15)$$

Expressing the value of the equilibrium constants through  $\Delta G^{oT}$ :

$$LqK = -\Delta G^{oT}/4,576T, \quad (16)$$

According to the equation (15), using the reference values  $\Delta G^{oT}$  [8] it is possible to calculate the partial pressure of atomic oxygen at a temperature of BaO dissociation. Taking into account all the gases in the dissociation products, which influence significantly the overall pressure, the balance equation

$$\sum P_c = \sum P_o$$

takes the form:

$$P_c + 2P_{c_2} + 3P_{c_3} = P_o + 2P_{\text{O}_2} + P_{\text{CO}_2} \quad (17)$$

The critical pressure of CO, i.e. corresponding to the pressure of the saturated vapour of carbon above graphite in the dissociation products (not  $P_{c_0} = 1$  atm) is taken as a standard state of carbon monoxide in order to compare directly the reducing ability of carbon with respect to the condensed metal oxides. The critical pressure of carbon monoxide in the temperature range of 1000-2000 K is expressed by the equation [4, 5]:

$$LqP_{c_0} = 9,27 - 23730/T \quad (18)$$

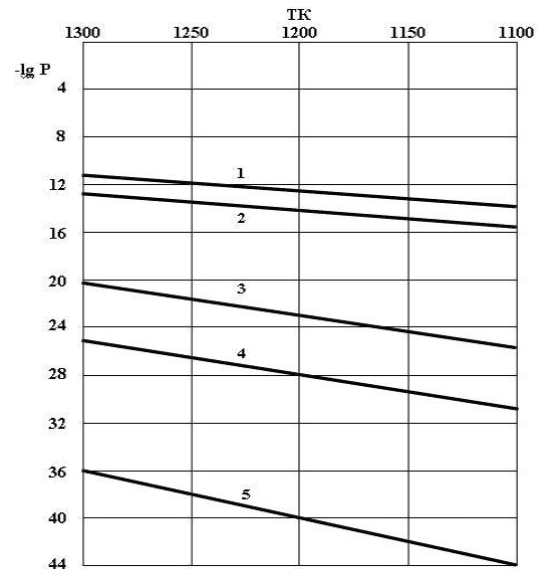
The partial pressures of the components of the gas phase in equilibrium with graphite are expressed [4, 5] by the following equations:

$$LqP_{\text{CO}_2} = 9,60 - 38794/T; \quad (19)$$

$$LqP_{\text{O}_2} = 9,58 - 59454/T; \quad (20)$$

$$LqP_o = 8,24 - 42986/T. \quad (21)$$

Figure 1 shows the results of the calculation of the partial pressures for BaO and CO dissociation products at 1100-1300 K, corresponding to the equilibrium with barium and graphite. Computer calculations are performed using equations (11), (15), (16) and (18-21) and reference data [8]. As it can be seen in the figure, the reduction of Ba from BaO using carbon is possible over the entire studied temperature range because the equilibrium curves  $P_o$  and  $P_{\text{O}_2}$  for the system C-CO are located below (by 15-25 orders) the equilibrium curves  $P_o$  and  $P_{\text{O}_2}$  for the system Ba-BaO.



**Fig. 1** – Partial pressures for BaO and CO dissociation products at 1100-1300 K in equilibrium with condensed barium and graphite, respectively. 1 –  $P_{\text{O}_2}(\text{BaO})$ , 2 –  $P_o(\text{BaO})$ , 3 –  $P_{\text{CO}_2}(\text{Co})$ , 4 –  $P_o(\text{Co})$ , 5 –  $P_{\text{O}_2}(\text{Co})$

#### 4. CONCLUSION

Thus, the thermodynamic analysis showed that in the carbonate-soot mixture on the surface of steel the oxidizing atmosphere for carbon contains molecular and atmospheric oxygen along with carbon dioxide. A

significant increase in the rate of carburizing using carbonate-soot coating is achieved because on the surface of steel not chemisorption of CO molecules from gas environment but the reaction of CO formation and

then its immediate decomposition at the interface of the contacting surfaces of soot particles and steel take place.

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