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Thermodynamic Analysis of Equilibrium Condition of Carbon-containing Atmospheres in Nanosized Carbide Structures Formation

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The paper discusses the processes of the formation of nanosized carbide structures at the interaction of the gas atmospheres components with carbon of α-and γ- solid solutions of iron. Calculations show that the equilibrium content of water vapor in relation to carbon in γ-iron under the influence of the increasing hydrogen concentration significantly shifts to the zone of higher values.

Keywords: Carbide structures, Carbon potential, Heat treatment.

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The purpose of this work is to analyze of the equilibrium conditions of multicomponent gas atmospheres with steels with different carbon content at the formation of nanosized carbide structures. Such analysis will be useful in developing effective technological heat treatment processes as well as carburizing and nitrocarburizing of steel parts.

The object of the research is gas endothermic controlled atmosphere which mostly consists of nitrogen, hydrogen and carbon monoxide, as well as minor impurities (< 1 %) CO_2, H_2O, and CH_4.

One of the important advantages of the endothermic atmosphere is the simplicity of its composition (carbon potential) regulation for moisture, which characteristic feature is the dew point. Condensation hygrometers allow measuring the dew point temperature with high accuracy. Usually, the amount of methane added to endogas to increase its carbon potential is set for each type of steel experimentally, that causes some inconvenience; however, there is a technique developed by E.L. Gyulikhandanov [1] which allows by means of calculation determine atmospheric composition for processing a particular type of steel.

Interaction of the components of gas atmospheres with carbon of α-and γ-iron solid solutions is one of the most important issues for heat treatment practice. The main reactions that occur on the surface of steels heated in endothermic atmosphere, are as follows:

$$C_{s.sol.} + CO_2 \leftrightarrow 2CO \quad (1)$$

$$C_{s.sol.} + H_2O \leftrightarrow CO + H_2 \quad (2)$$

$$C_{s.sol.} + H_2 \leftrightarrow CH_4 \quad (3)$$

where *s sol.* is solid solution.

Moreover, in the gas mixture the following exchange reactions between the components may take place:

$$CO_2 + H_2 \leftrightarrow H_2O + CO \quad (4)$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 ; \quad (5)$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 . \quad (6)$$

The equilibriums of three most important reactions (1) ... (3) are defined as the equations describing the equilibrium state of the atmosphere and carbon of steel. The equilibriums constants:

$$K_1 = \frac{P_{CO}^2}{P_{CO_2} \cdot a_c} ; \quad (7)$$

$$K_2 = \frac{P_{CO} \cdot P_{H_2}}{P_{H_2O} \cdot a_c} ; \quad (8)$$

$$K_3 = \frac{P_{CH_4}}{P_{H_2}^2 \cdot a_c} . \quad (9)$$

where P_{CO}, P_{CO_2}, P_{H_2}, P_{H_2O} are the partial pressure of the corresponding components in gas mixture; a_c is the thermodynamicc activity of carbon in solid solution contacting with atmosphere.

Having five factors determining the equilibrium in the 'gas atmosphere − carbon of steel' system it is necessary to have two more equations. The balance equation, which determines the constancy of the composition of the gas mixture, and the equation which determines the constancy of the gas pressure can be used:

$$\frac{P_{CO} + P_{CO_2} + P_{CH_4}}{P_{H_2} + P_{H_2O} + 2P_{CH_4}} = b ; \quad (10)$$

$$P_{CO} + P_{CO_2} + P_{H_2} + P_{H_2O} + P_{CH_4} = P . \quad (11)$$

Equation (10) is the ratio of total of carbon to hydrogen in the original / feed gas / исходный, which in principle should not be changed at proceeding of all the reactions. Equation (11) represents the total of all par-

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tial pressures of the components of the mixture except for nitrogen which is not involved in the reactions. The total of all partial pressures of the components of the mixture together with nitrogen is 1at ($P + P_{N2} = 1$ at).

Thus, non-linear equations (7), (8), (9), (10), (11) are a mathematical model using which it is possible to calculate the composition of the gas mixture which is in equilibrium with carbon dissolved in iron.

Thermodynamic activity of carbon in unalloyed austenite can be calculated with sufficient accuracy by the empirical formula [2, 3]:

$$\ln a_C = \frac{2105}{T} - 0{,}6735 + \frac{317}{T} \cdot \frac{N_C}{1 - N_C} + \lg , \qquad (12)$$

where T is the temperature; N_c is the concentration of carbon in austenite (compared to the standard state – graphite).

The analysis of the resulting model shows that the high content of methane introduced into endogas to increase its carbon potential causes a considerable increase of hydrogen content in the atmosphere (see reaction 2 and 3). Wherein the equilibrium contents of water vapor in relation to carbon in γ-iron under the influence of increasing hydrogen concentration shifts to the zone of high carbon potential of the atmosphere for neutral (non-decarburizing) heating or for steel carburizing; careful drying of the atmosphere is required.

Using this model thermodynamic calculations have been carried out for the gas atmosphere of 20% H_2; 9,5 % CO; 0,15 % CO_2; 0,3 % H_2O; 69,05 % N_2, 1 % CH_4. It is most commonly used in industry and shows the equilibrium concentration of carbon with respect to the γ-solid solution depending on the content of water vapor (dew point, °C). The calculations show that the maximum amount of carbon that may be in the steel surface layer in equilibrium with the atmosphere carbon at temperature of ≈ 900 °C is ≈ 1,2 %. The reduction of the heating temperature for a given composition of the saturating environment will cause sooting on the surface of component parts. The increase of the atmospheric humidity (dew point temperature increase) will also lead to sooting. In poor atmospheres with high degree of dehydration ($t_p \approx -60$ °C), decarburization of steel should occur from the standpoint of thermodynamics. The experimental studies on carbon saturation of the armco iron samples in endothermic atmosphere generated by the industrial generator ЭН-16, showed that at high additions of methane sooting on the surface of the samples rather than increased carbon satu. in γ-Fe for en dothermic industrial processing ration of metal occurs. This process corresponds to a shift beyond the zone of γ-solid solution to the zone of graphite. The results are represented in Fig. 1 in a diagram.

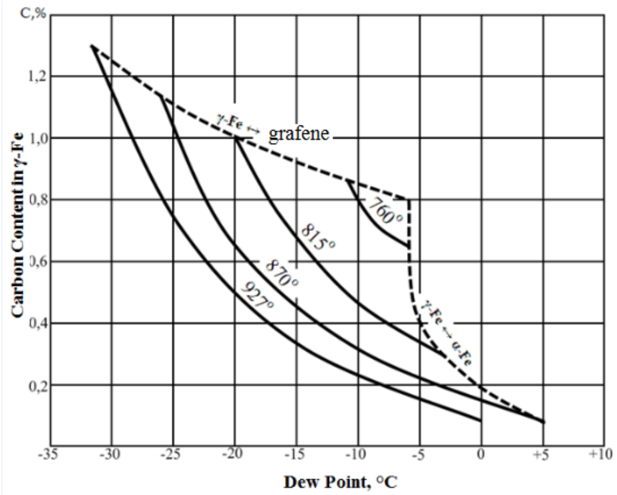

Fig. 1 – The calculated curves of water vapor equilibrium with respect to carbon

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