Calculation of Physicochemical Conditions of the Formation of Protective Coatings Based on Carbides and Nitrides of Chromium

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Theoretical calculations of physical and chemical conditions of the process of diffusion saturation of carbon steels with nitrogen, carbon and chromium in the conditions of low pressure in the chlorine environment are carried out. The probable phase composition as a result of diffusion saturation is determined. The temperature interval for the existence of carbides and nitrides was established. The main probable condensed and gas phases that are formed as a result of saturation of carbon steels with carbon, nitrogen and chromium are identified. It is analyzed how the number of condensed and gas phases changes depending on the temperature of the diffusion coating process. It is theoretically established that two chromium nitrides CrN and Cr_2N and chromium carbide Cr_3C_2 will be the main condensed phases as a result of deposition of the protective coating. The temperature interval for the existence of the main strengthening phases is established. Systems with oxygen content are analyzed. The formation of chromium oxides in the gas state is noted. It is determined that in the first and final stages of saturation (the initial and final temperatures of the saturation process), the main chromium-containing phase is chromium carbide and the almost complete absence of Cr_2N nitride. The temperature of 1300 K is the optimum temperature at which a complex chromium carbide-nitride coating is formed. This combination of protective coating layers will have optimum properties in terms of wear and corrosion protection.

Keywords: Thermodynamic calculations, Coatings, Diffusion saturation, Condensed phase, Gas phase, Carbon steels.

1. INTRODUCTION

Chemical vapor deposition (CVD) and diffusion saturation processes are controlled by chemical reactions of the decomposition of transition metal chlorides on the substrate surface. Thermodynamic analysis of closed systems makes it possible to predict the phase composition of steel surfaces after sequential saturation with nitrogen and chromium in chlorine medium and to determine the technological parameters of the process.

The powders of the saturating elements react in reverse with the chlorine gas phase. In this case, light compounds are formed that enter the zone with other chemical equilibrium conditions. As a result, the saturating metal is deposited on the metal surface. The process of transporting the alloying element in the reaction medium is due to the pressure gradient of chlorides in the zones of their formation and in the deposition zone. This is achieved by the temperature gradient between the area of the original components and the area of the saturating surface.

Both chemical and physical factors influence the rate of component transfer. Saturation proceeds in several stages: formation of the transfer components of the saturating elements; then diffusion through the gas phase to the alloy's surface; adsorption of the saturating elements by the material's surface; diffusion into the interior of the material; interaction of the diffusing element with the components of the material accompanied by the formation of solid solutions or chemical compounds [1-3].

The aim of this work is to conduct a thermodynamic analysis: to determine a phase composition of proposed coating and a phase quantity under defined temperature conditions in a certain ratio of starting reagents. These calculations allow to spot the optimal amount of starting reagents for the successful implementation of the process of carbon steels saturation with chromium.

2. MATERIALS AND METHODS

In this paper, an evaluation of the physicochemical conditions of the sequential saturation of carbon steels with nitrogen and chromium was carried out. The diffusion saturation process was implemented in two successive stages. In the first stage, nitriding was carried out using known technology in a camera furnace in ammonia environment at its dissociation degree of 47-55 % at 540 °C for 36 h. The second stage of chromium saturation was carried out in a closed reaction medium under conditions of a reduced gas phase pressure in a camera furnace at 1050 °C for 4 h. As saturation components, chromium powder (100-300 μm) and carbon tetrachloride (CCl_4) were used. Charcoal was added to the saturation medium to increase carbonation ability.

It is known that during transportation of the alloying elements as a result of chemical transport reactions several processes may occur in different zones of reactor [4, 5]. To substantiate the choice of technological parameters for coatings deposition an analysis of the physicochemical conditions of the saturation process was applied based on the thermodynamic approach of determining the phase equilibrium in the reaction medium.

The method of thermodynamic equilibrium between different components of a closed multicomponent system was used to determine the composition of the reaction medium on the basis of the second law of thermo-

dynamics. The necessity of using this technique was initiated by an inability to apply other methods, considering all the constituent components and substances formed in the closed reaction medium [6, 7].

To analyze the physicochemical conditions of the saturation process a thermodynamic approach was applied, which allows a theoretical determination of the equilibrium composition of a closed isolated system. The equilibrium in a closed system differs from the real conditions of a saturation process. At the same time, the literature review [8, 9] showed the feasibility of the proposed approach in different branches of metallurgy. The possible phase composition of the coating is determined by the probable composition of the condensed phase for a particular equilibrium system, the ratio of components in which may vary.

Systems with a high nitrogen content relative to carbon, equal and insignificant ones, were considered. The condensed phase estimation allows to determine the expected phase composition of the coating.

The equilibrium composition was determined in the temperature range of 500-150 K at the constant pressure $p = 10^2$ Pa for systems involving C, N, Cl, Fe, O and Cr (see Table 1).

In a given temperature range in the reaction medium, the presence of chlorides of saturating metals of different valence is evident. It must be taken into account the formation of oxides, nitrides and carbides of the reacting elements as a result of the metal powders interaction with oxygen and nitrogen, which are left after a chamber evacuating. Carbide phases are formed due to chromium interaction with the carbon of the original alloy, and carbon form tetrachloride CCl_4 as a result of its dissociation. Dissociation of carbon tetrachloride increases the degree of chlorination of chromium, reduces the probability of oxide films formation and prevents a steel surface upon decarburization.

For the thermodynamic calculations, the applied program package «Astra» was used, which allows to predict the formation of condensed and gas phases in the reaction medium under given conditions [10].

3. RESULTS AND DISCUSSION

Systems with the participation of Cl, N, C, Fe and Cr in the temperature range of 500-1500 K (Table 1, systems 1, 2) with a predominant nitrogen and carbon content were considered. In systems, where nitrogen content prevails carbon content, the chromium carbide is not formed in the condensed phase (system 2). With the increase of carbon in the system, the main condensed phases are C, $CrCl_2$, CrN, Cr_2N, Cr_3C_2 (Fig. 1).

It was found that there are no significant differences from the nitriding process in systems with a predominant nitrogen content. In this case, system 1 produces two known nitrides of the saturation element CrN and Cr_2N [11].

It is established that chromium carbides are not formed. It is noted that chromium carbide Cr_3C_2 is formed by reducing the amount of nitrogen and increasing the carbon content in the systems.

The chemical reactions of system 3 (Table 1) result in the condensation of the following phases: chromium nitrides CrN and Cr_2N, chromium carbide Cr_3C_2 and
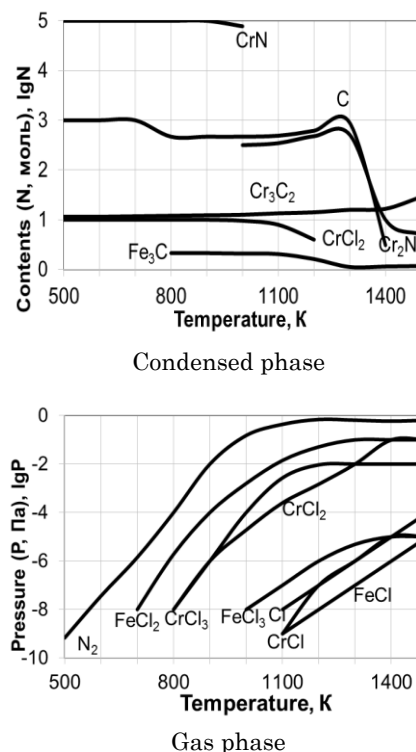

Condensed phase

Gas phase

Fig. 1 – Equilibrium phase composition of the Cl-N-C-Fe-Cr = 2-5-3-1-6 (mole) systems, $p = 10^2$ Pa

carbon C, iron Fe, iron carbide Fe_3C, chromium chloride $CrCl_2$ and a small amount of Cr_2O_3 oxide (Fig. 2).

Chromium chlorides of different valences and small amounts of iron chlorides are formed in the gas phase. It should be noted that chromium oxides are not formed in the gas phase. In turn, the system contains carbon oxides of CO and CO_2. Theoretical calculations of the processes that occur during the application of protective carbonitride coatings on the basis of transition metals of IV-VI groups can provide an information not only about the probability of the phase formation, but also about the distribution of system components among these phases in the temperature range of 500-1500 K. The iron in the Cl-N-C-Fe-Cr = 2-2-9-1-6 system at a temperature of 500 K is mainly concentrated in the free state (Fig. 3). In the temperature range of 800-1100 K iron is combined with carbon to form iron carbide Fe_3C. At temperatures above 1300 K, the amount of Fe_3C decreases due to the formation of iron chloride $FeCl_2$ in the system.

The nitrogen distribution is presented in Fig. 3. At 500-800 K, nitrogen binds to CrN chromium nitride. With further increase in temperature, the phase of CrN disappears, thus forming a new chromium nitride Cr_2N.

Since the temperature of 1200 K thermodynamically advantageous is the existence of free nitrogen N_2, the amount of which slowly increases with increasing temperature from 5.28 % at 1200 K to 100 % at 1400 K.

The main carbon-containing phases (Fig. 3) in the temperature range 500-800 K are free carbon and chromium carbide Cr_3C_2. Subsequently, as the temperature increases, another phase is formed, containing carbon carbide Fe_3C. At temperatures of 1400-1500 K, the predominant phase is chromium carbide Cr_3C_2.

Table 1 – Equilibrium phase composition of systems for diffusion saturation of steels ($T = 500\text{-}1500$ K, $p = 10^2$ Pa)

| System components and their amount, mole	Phases in the reaction medium	
	Condensed phase	Gas phase
Cl-N-C-Fe-Cr = = 2-8-3-1-6	C, Fe, Fe_3C, $CrCl_2$, CrN, Cr_2N	Cl, N_2, FeCl, $FeCl_2$, $FeCl_3$, CrCl, $CrCl_2$, $CrCl_3$
Cl-N-C-Fe-Cr = = 2-5-3-1-6	C, Fe, Fe_3C, $CrCl_2$, CrN, Cr_2N, Cr_3C_2	Cl, N_2, FeCl, $FeCl_2$, $FeCl_3$, CrCl, $CrCl_2$, $CrCl_3$
O-Cl-N-C-Fe-Cr = = 1-2-2-5-0.6-6	C, Fe, Fe_3C, $Cr_2O_3 \cdot CrCl_2$, CrN, Cr_2N, Cr_3C_2	Cl, N_2, CO, CO_2, FeCl, $FeCl_2$, $FeCl_3$, CrCl, $CrCl_2$, $CrCl_3$

Condensed phase

Gas phase
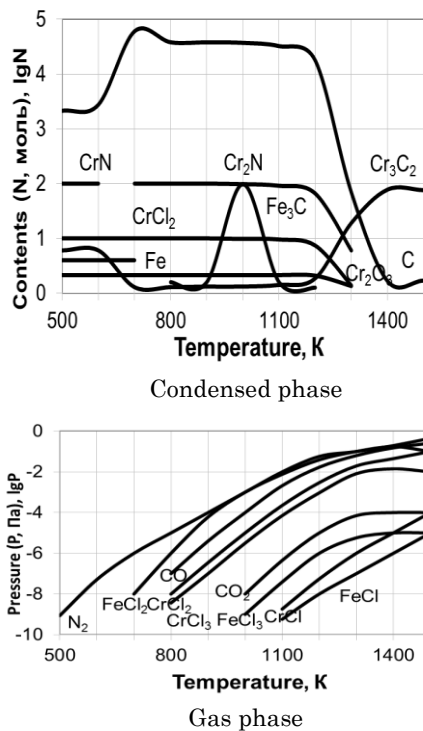
Fig. 2 – Equilibrium phase composition of the O-Cl-N-C-Fe-Cr = 1-2-2-5-0.6-6 (mole) systems, $p = 10^2$ Pa

4. CONCLUSIONS

Investigations of the physicochemical conditions of the process of diffusion saturation of carbon steels in closed systems with the participation of chromium, carbon, nitrogen, chlorine and oxygen in the temperature range 500-1500 K at a constant pressure $p = 10^2$ Pa showed that:

– the main condensed phases are CrN, Cr_2N, Cr_3C_2,
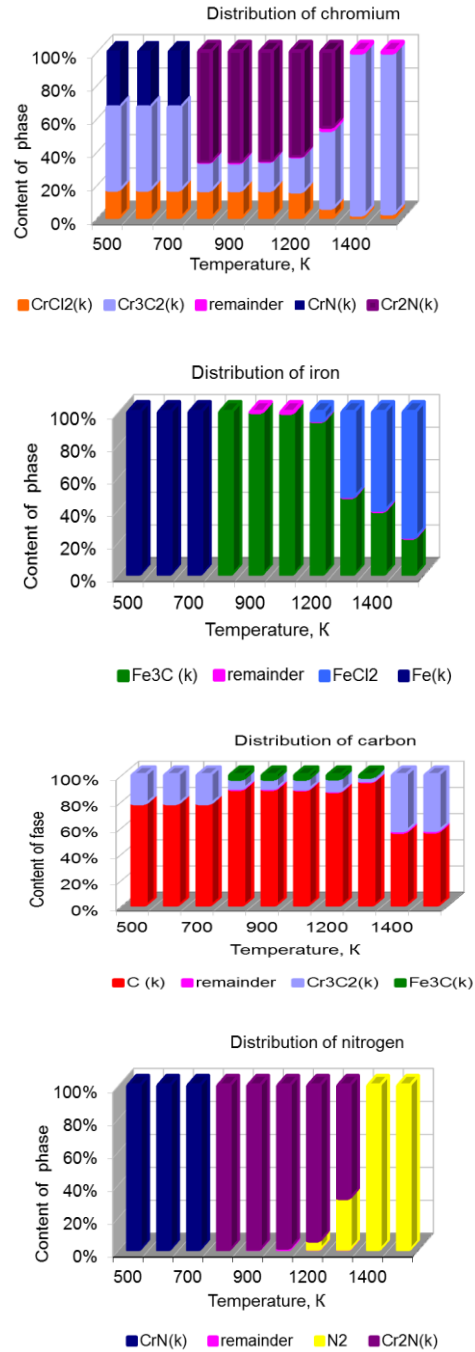
Fig. 3 – The distribution of elements of the Cl-N-C-Fe-Cr = 2-2-9-1-6 (mole) system by chemical compounds

the amount of which depends on the content of nitrogen, carbon in the initial state and a temperature;

– the main components of the gas phase are chlorides of saturating elements of different valences;

– in the presence of oxygen in the system the oxides of the saturation element Cr_2O_3 are formed, the existence of which is limited by low temperatures.

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Розрахунок фізико-хімічних умов процесу формування захисних покриттів на основі карбідів та нітридів хрому

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Проведено теоретичні розрахунки фізико-хімічних умов процесу дифузійного насичення вуглецевих сталей азотом, вуглецем та хромом в умовах низького тиску в середовищі хлору. Визначено ймовірний фазовий склад в результаті дифузійного насичення. Встановлено температурний інтервал існування карбідів та нітридів. Визначено основні ймовірні конденсовані та газові фази, що утворюються в результаті насичення вуглецевих сталей вуглецем, азотом та хромом. Проаналізовано, як змінюється кількість конденсованої та газової фаз залежно від зміни температури процесу дифузійного насичення. Теоретично встановлено, що в результаті нанесення захисного покриття основними конденсованими фазами будуть два нітриди хрому CrN, Cr_2N та карбід хрому Cr_3C_2. Встановлено температурний інтервал існування основних зміцнюючих фаз. Проаналізовано системи з вмістом кисню. Відзначається утворення оксидів хрому в газовому стані. Визначено, що на першій та заключній стадіях насичення (початкові та кінцеві температури процесу насичення) основною фазою, що містить хром, є карбід хрому та майже повна відсутність нітриду Cr_2N. Температура 1300 К – оптимальна температура, при якій утворюється комплексне покриття нітрид-карбід хрому. Таке поєднання шарів захисного покриття буде мати оптимальні властивості з точки зору захисту від зносу та корозії.

Ключові слова: Термодинамічні розрахунки, Покриття, Дифузійне насичення, Конденсована фаза, Газова фаза, Вуглецеві сталі.