

PHYSICOCHEMICAL CONDITIONS OF COMPLEX DIFFUSION SATURATION OF METAL SURFACES WITH TITANIUM AND CHROMIUM

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Theoretical calculations of physical and chemical conditions have been carried out for the process of diffusion saturation of steels and solid solution alloys with titanium and chromium in the presence of carbon. An equilibrium composition of the reaction medium in the temperature range 600–1500 K has been determined. The optimum temperature interval of the saturation process has been established.

KEY WORDS: *coatings, diffusion saturation, condensed phase, gas phase, carbide, solid solution alloys, steels*

1. INTRODUCTION

The application of carbide protective coatings is accompanied by mass transfer between the processed material and the active gas medium formed in the reaction medium. This is due to the fact that in the system that combines the active gas phase and the processed material certain chemical reactions are taking place during the process. These reactions proceed simultaneously or sequentially in the volume of the gas phase, at the boundary with the material, and inside of the material. These processes can have a different effect on the mass transfer, and as a result influence the process of coating formation. For the mass transfer of great importance

for the mass transfer is the diffusion of the saturation element from the active gas phase into the material's substrate (Loskutov et al., 1991; Pogrebniak et al., 2012; Azarenkov et al., 2007; Petukhov et al., 2006).

By applying carbide coatings in a closed reaction medium using carbide-forming transition metal's powders and halide compounds as the starting reagents, the following basic stages of mass transfer can be singled out: formation of a carrying component of the saturation element; diffusion of this component to the surface of the processed material; component chemisorption by the surface of the material; occurrence of chemical reactions in the chemisorbed layer, accompanied by the separation of the atomic state saturation element and the removal of the reaction products into the gas phase; adsorption of the saturation element by the surface of the material; interaction of the diffused element with the components of the material's substrate; formation of solid solutions or chemical compounds (Kopeikina et al., 2008; Harchenko et al., 2014; Shmatov and Poberezhnyj, 2007; Berladir et al., 2016; Pogrebniak et al., 2016).

The rate of the mass transfer is influenced by both chemical and physical factors. Therefore, the data on mass transfer are obtained by a detailed study of the chemical reactions occurring in the reaction medium and determining their number. This fact allows one to find the ways of exerting an influence on the individual stages of the saturation process in order to improve it, as well as to develop rational compositions of reaction medium and create scientifically grounded technology for obtaining protective coatings with needed properties (Degula et al., 2015; Beresnev et al., 2008; Hizhnjak et al., 2012; Zaulychny et al., 2016; Olemskoi et al. 2012).

The aim of this work is to analyze the dependence of the gas and condensed phase composition on the quantitative component ratio in a certain temperature range. The possibility of the process of complex diffusion saturation of the metal surface with titanium and chromium is considered and the optimal conditions for the conduction of the process are determined and proposed.

2. EXPERIMENTAL PROCEDURE

It is known that during coating deposition by the method of transport chemical reactions, several processes may occur in different reactor's zones (Hizhnjak et al., 2003; Krauze-Rejberg et al., 2013). In order to substantiate the choice of technological parameters for the process of the deposition of protective coatings, in this work we carried out an analysis of the physical and chemical conditions of saturation based on the thermodynamic approach, as well as theoretical determination of the equilibrium state of the reaction medium.

For determining the composition of the reaction medium, an analysis of the thermodynamic equilibrium between the various components of a closed multicomponent system based on the second law of thermodynamics was made. The advantage of this technique over others is based on the possibility of taking into account all constituent components and substances formed in this system (Loskutova et al., 2006; Sigova et al., 2007).

The equilibrium was evaluated in the temperature range 600–1500 K for systems consisting of saturated metals, titanium and chromium, as well as chlorine, carbon, oxygen, and nitrogen as the raw components; iron, carbon, tungsten, and cobalt as the components of the substrate.

In the given temperature range in the reaction medium, chlorides of saturated metals of different valences are present. Also taken into account should be the appearance of oxides,

nitrides, and carbides of these elements. The formation of oxides and nitrides occurs as a result of the interaction of metal powders with the oxygen and nitrogen of air that remain after the evacuation of the reaction chamber. The carbide phases are formed due to the interplay of transition metals with carbon from the original alloy and dissociated from the carbon tetrachloride. The introduction of the CCl_4 carbonaceous additive into the reaction medium increases the degree of chlorination of transition metals, reduces the probability of formation of oxide films and prevents carbonization of the metal surfaces.

To carry out the calculations, it should be taken into account that the reaction medium in terms of the possibility of deposition of carbide coatings requires:

- 1) A sufficiently high partial pressure of saturation of metal's chlorides in the temperature range 1173–1373 K;
- 2) The presence, in the gas phase of the reaction medium, of chlorides of saturation metals of different valences, which make possible the occurrence of reverse transport reactions;
- 3) The absence of chlorides of saturation metals in the condensed state in the temperature range investigated;
- 4) The ability to form condensed state carbides and other phases corresponding to the type of coating at required temperatures;
- 5) The absence, in the gas or condensed phase, of ballast substances that reduce the activity of the gas phase and worsen the properties of coatings.

For the calculations, the applied program package "Astra" was used, which allows one to predict the formation of certain phases in the reaction medium under given conditions (Hizhnjak et al., 2008). To determine the most probable reactions of carbonization, the change of the thermodynamic potential ΔG_T^0 per one molecule of the resulting carbide was calculated using the HSC CHEMISTRY program.

3. RESULTS AND DISCUSSION

As a result of treatment, the chromium adsorbed by the metal surface interacts with carbon of the steel substrate, as well as with the carbon from the gas medium and forms Cr_{23}C_6 or Cr_7C_3 chromium carbides. Titanium is also a carbide-forming element, and in contact with carbon it composes TiC carbide. Thus, on the surface of carbon steels and solid solution alloys a diffusion zone based on chromium and titanium carbides appears. As a result of the chromium interaction with the iron from the steel base, the formation of the σ -phase is also possible (Gol'dshtejn et al., 1999).

The reaction medium must satisfy the following requirements: the partial pressure of the chloride of saturated metals (CrCl , CrCl_2 , CrCl_3 , CrCl_4 , TiCl_2 , TiCl_3 , TiCl_4) should be sufficiently high; the corresponding substances (Cr_{23}C_6 , Cr_7C_3 , TiC) should be present in a condensed state in the range of saturation temperatures; no ballast substances should be present in the gas and condensed phases should be.

The equilibrium of the phases was estimated at a constant pressure of 10^2 Pa in the temperature range from 600 to 1500 K. The chosen system pressure and the temperature range of the study correspond to the real conditions of saturation. The results of investigations of the studied systems, where the saturate elements are chrome and titanium, are given in Table 1 and Figs. 1–3.

TABLE 1: Equilibrium phase composition of systems for diffusion metallization ($T = 600\text{--}1500 \text{ K}$, $p = 10^2 \text{ Pa}$)

System Composition, mole		Composition of the Reaction Medium	
		Gas Phase	Condensed Phase
1	Ti–Cr–C–Cl = 1–4–2–2	TiCl ₂ , TiCl ₃ , TiCl ₄ , CrCl, CrCl ₂ , CrCl ₃	TiC, Cr ₇ C ₃ , Cr ₃ C ₂
2	Ti–Cr–C–Cl = 4–1–2–2	TiCl ₂ , TiCl ₃ , TiCl ₄ , CrCl, CrCl ₂	TiC, Ti
3	Ti–Cr–C–Cl–W–Co = 2–2–2–2–2–0.5	TiCl ₂ , TiCl ₃ , TiCl ₄ , CrCl, CrCl ₂ , CrCl ₃ , CoCl, CoCl ₂ , WCl	TiC, WC, Cr ₂₃ C ₆
4	Ti–Cr–C–Cl–Fe = 2–2–2–2–2	TiCl ₂ , TiCl ₃ , TiCl ₄ , CrCl, CrCl ₂ , CrCl ₃ , FeCl, FeCl ₂	TiC, Cr ₂₃ C ₆
5	Ti–Cr–C–Cl–W–Co–O–N = 2–2–2–2–0.5–0.3–0.8	TiCl ₂ , TiCl ₃ , TiCl ₄ , CrCl, CrCl ₂ , CoCl, WCl ₂ , CO, CO ₂ , N ₂ , TiOCl ₂	TiC, Ti ₂ O ₃ , TiN, Cr ₂₃ C ₆
6	Ti–Cr–C–Cl–W–Co–O–N = 2–2–2–2–2–0.5–1–3	TiCl ₂ , TiCl ₃ , TiCl ₄ , CrCl, CrCl ₂ , WCl ₂ , CO, CO ₂ , N ₂ , TiOCl ₂	TiN, Ti ₄ O ₇ , WN, Cr ₂₃ C ₆
7	Ti–Cr–C–Cl–Fe–O–N = 2–2–2–2–2–0.3–0.8	TiCl ₂ , TiCl ₃ , TiCl ₄ , CrCl, CrCl ₂ , FeCl, FeCl ₂ , FeCl ₃ , CO, CO ₂ , N ₂ , TiOCl ₂	TiC, Fe ₃ C, Ti ₄ O ₇
8	Ti–Cr–C–Cl–Fe–O–N = 2–2–2–2–2–1–3	TiCl ₂ , TiCl ₃ , TiCl ₄ , CrCl ₂ , CrCl ₃ , FeCl, FeCl ₂ , FeCl ₃ , CO, CO ₂ , N ₂ , TiOCl ₂	TiN, Fe ₃ C, Cr ₂ N, Ti ₄ O ₇

In the case of the interaction of the Ti–Cr–C–Cl system components in the temperature range 600–1500 K, titanium and chromium chlorides are formed in the gas phase, Fig. 1. The gas phase consists of titanium chlorides TiCl₂, TiCl₃, TiCl₄ and chromium chlorides CrCl, CrCl₂, CrCl₃; in the condensed state such carbides as TiC, Cr₇C₃, and Cr₃C₂ were found. With increase in the quantitative ratio of titanium, the titanium chlorides begin to prevail in the gas phase, while the condensed chromium carbide disappears and only TiC is formed. Therefore, the optimal ratio of saturated metals can be considered equal to 1/1.

Taking into account the presence of W and Co base elements in the reaction medium (for solid solution alloys), the appearance of chlorides of these metals (Fig. 2), namely, CoCl, CoCl₂, and WCl₂ is possible in the gas phase, except for the chromium and titanium chlorides. In a condensed state, WC, Cr₂₃C₆, and TiC carbides have been detected.

For steel samples, where the main component is Fe, the iron chlorides FeCl, FeCl₂ are present in the gas phase in addition to chromium and titanium chlorides. The condensed phase contains Cr₂₃C₆ chromium carbide and TiC titanium carbide. In the case of the participation of air components in the reaction medium, the carbon dioxide and molecular nitrogen appear in the gas phase in addition to the metal chlorides (Fig. 3). In a condensed state, the nitrides and oxides of metals are formed.

The theoretical calculations show that the partial pressure of chlorides increases significantly at temperatures above 900 K, and only for TiCl₄ chloride at a temperature of 1000–1100 K it is reduced. For most chlorides, the stabilization of the partial pressure at temperatures above 1300 K is observed, which means that a further increase in the temperature would not lead to

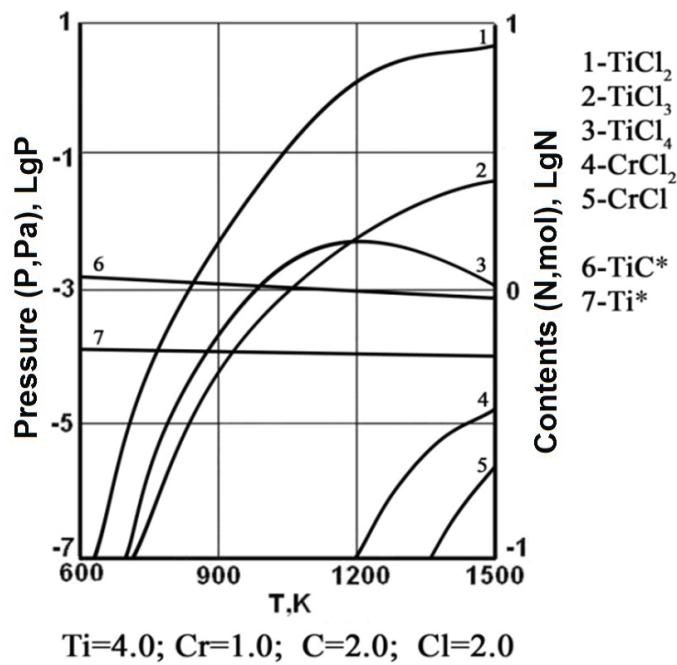
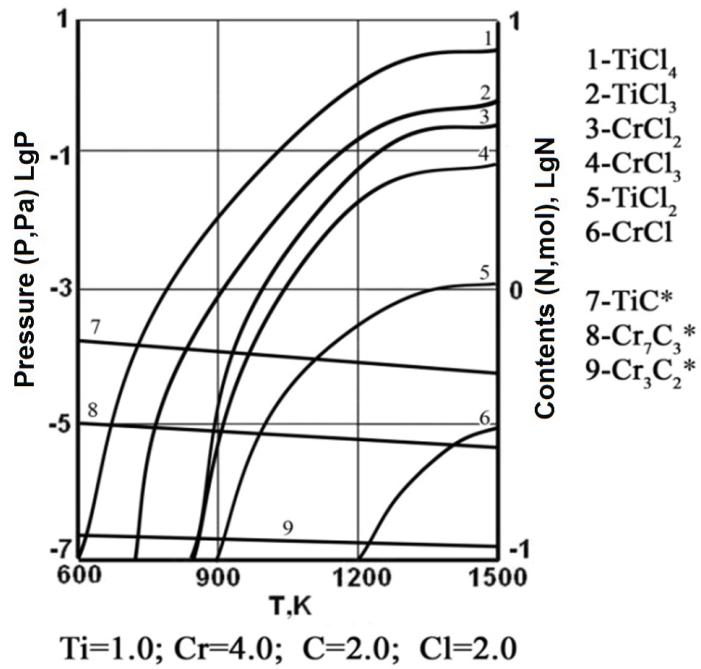


FIG. 1: Equilibrium phase composition of systems of saturated components (*-condensed phase)

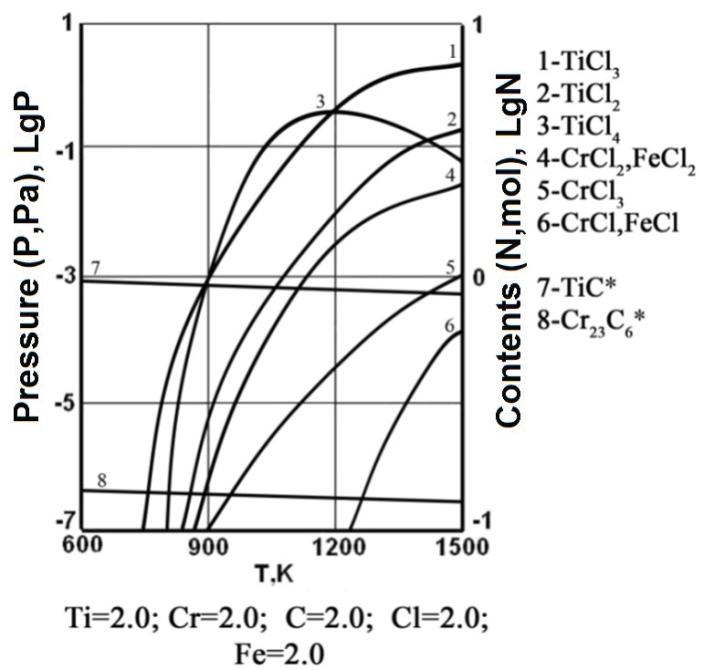
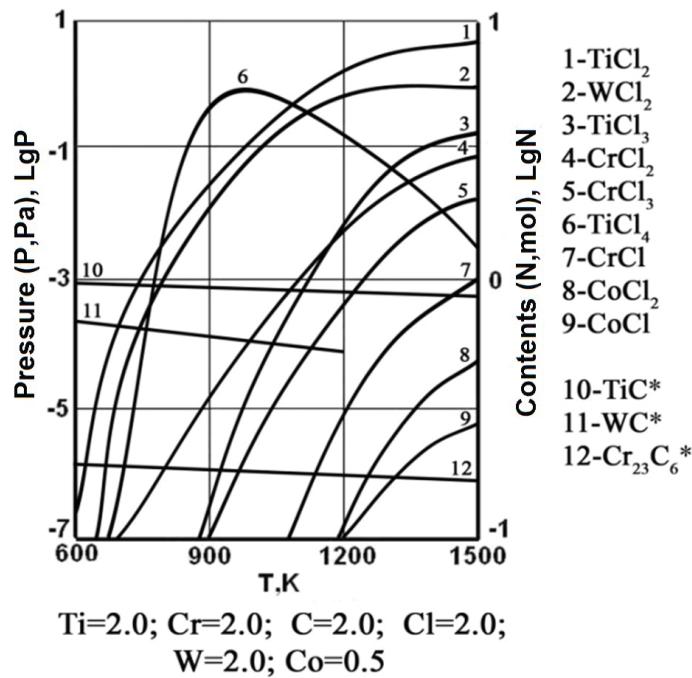


FIG. 2: Equilibrium phase composition of systems involving base components (*-condensed phase)

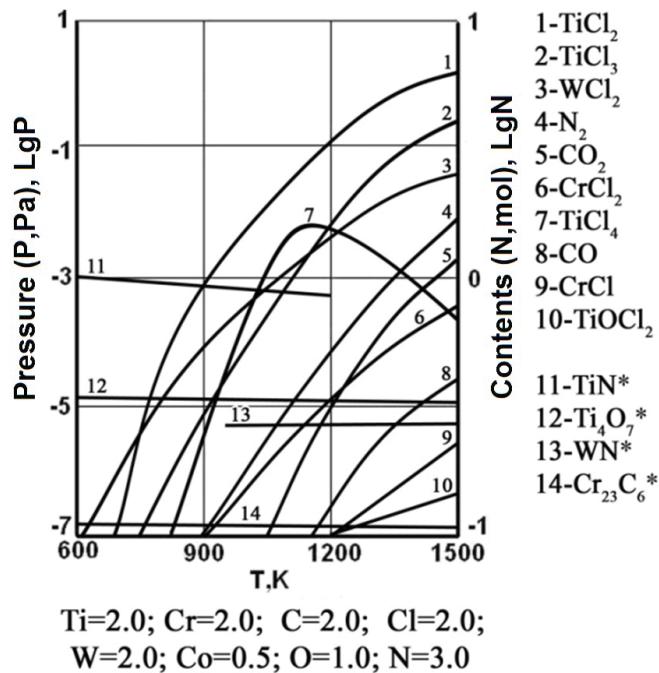
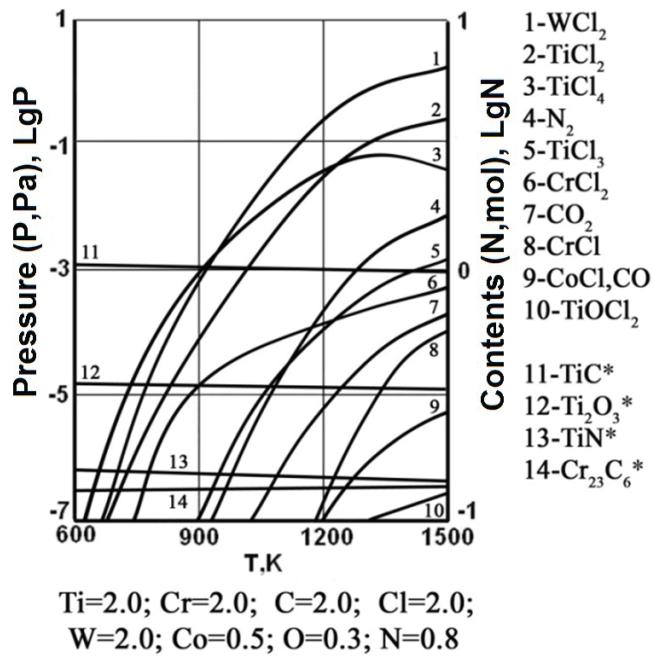


FIG. 3.

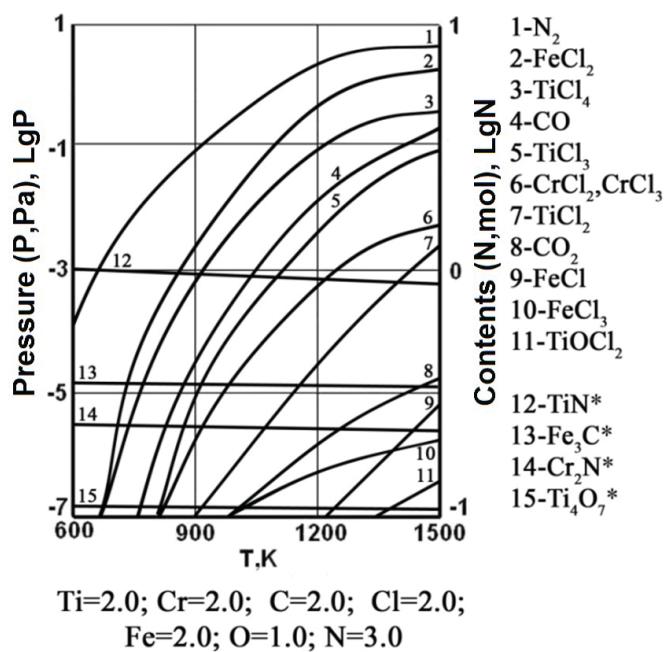
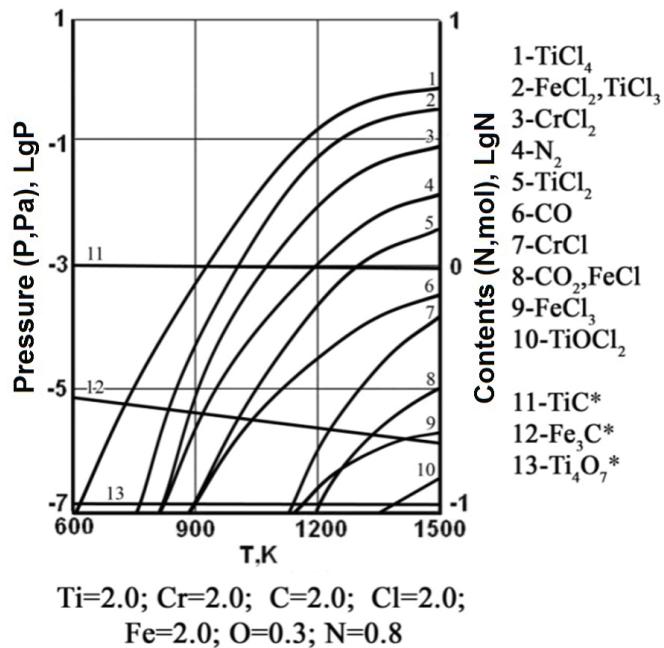


FIG. 3: Equilibrium phase composition of systems with participation of air components (*-condensed phase)

its significant increase. From this it can be concluded that the optimum temperature range for the processes of diffusion saturation in the chlorine medium will be temperatures of 1200–1300 K.

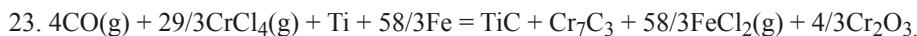
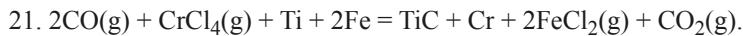
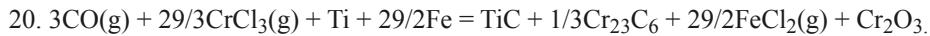
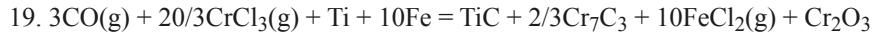
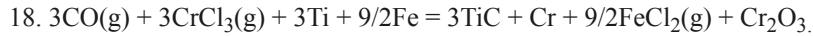
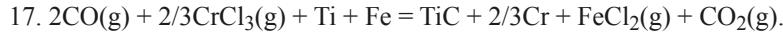
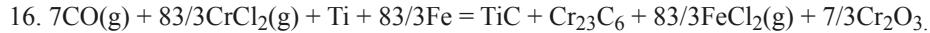
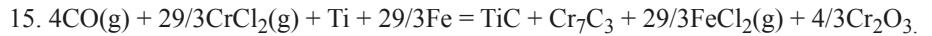
The specified temperature interval also ensures the formation and existence of carbides and nitrides in the form of a condensed phase.

It is known that carbon tetrachloride dissociates at elevated temperatures by the reaction $\text{CCl}_4 \rightarrow \text{C} + 2\text{Cl}_2$. In the case, where in addition to carbon tetrachloride the reaction medium also has CO compounds that are guaranteed to be formed by an excess of carbon and lack of oxygen in the reaction chamber, the appearance of the COCl_2 compound is very probable. The dissociation degree of COCl_2 is at a temperature of 1073 K.

In this case, active atomic chlorine appears, which forms chromium chlorides of different valences (CrCl_4 , CrCl_3 , CrCl_2) during the interaction with the chromium powders. After the introduction of titanium powders into the reaction medium, it becomes thermodynamically possible to form titanium carbides and chromium carbides of different stoichiometric compositions as reaction products.

The most thermodynamically possible reactions of carbide formation in the process of diffusion saturation of steels with chromium are given below:

1. $2\text{COCl}_2(\text{g}) + \text{CrCl}_2(\text{g}) + \text{Ti} + 3\text{Fe} = \text{TiC} + \text{Cr} + 3\text{FeCl}_2(\text{g}) + \text{CO}_2(\text{g})$.
2. $\text{COCl}_2(\text{g}) + 5/3\text{CrCl}_2(\text{g}) + \text{Ti} + 8/3\text{Fe} = \text{TiC} + \text{Cr} + 8/3\text{FeCl}_2(\text{g}) + 1/3\text{Cr}_2\text{O}_3$.
3. $7\text{COCl}_2(\text{g}) + 83/3\text{CrCl}_2(\text{g}) + \text{Ti} + 104/3\text{Fe} = \text{TiC} + \text{Cr}_{23}\text{C}_6 + 104/3\text{FeCl}_2(\text{g}) + 7/3\text{Cr}_2\text{O}_3$.
4. $4\text{COCl}_2(\text{g}) + 29/3\text{CrCl}_2(\text{g}) + \text{Ti} + 41/3\text{Fe} = \text{TiC} + \text{Cr}_7\text{C}_3 + 41/3\text{FeCl}_2(\text{g}) + 4/3\text{Cr}_2\text{O}_3$.
5. $2\text{COCl}_2(\text{g}) + \text{CrCl}_3(\text{g}) + \text{Ti} + 7/2\text{Fe} = \text{TiC} + \text{Cr} + 7/2\text{FeCl}_2(\text{g}) + \text{CO}_2(\text{g})$.
6. $3\text{COCl}_2(\text{g}) + 3\text{CrCl}_3(\text{g}) + 3\text{Ti} + 15/2\text{Fe} = 3\text{TiC} + \text{Cr} + 15/2\text{FeCl}_2(\text{g}) + \text{Cr}_2\text{O}_3$.
7. $3\text{COCl}_2(\text{g}) + 20/3\text{CrCl}_3(\text{g}) + \text{Ti} + 13\text{Fe} = \text{TiC} + 2/3\text{Cr}_7\text{C}_3 + 13\text{FeCl}_2(\text{g}) + \text{Cr}_2\text{O}_3$.
8. $7\text{COCl}_2(\text{g}) + 83/3\text{CrCl}_3(\text{g}) + \text{Ti} + 97/2\text{Fe} = \text{TiC} + \text{Cr}_{23}\text{C}_6 + 97/2\text{FeCl}_2(\text{g}) + 7/3\text{Cr}_2\text{O}_3$.
9. $2\text{COCl}_2(\text{g}) + \text{CrCl}_4(\text{g}) + \text{Ti} + 4\text{Fe} = \text{TiC} + \text{Cr} + 4\text{FeCl}_2(\text{g}) + \text{CO}_2(\text{g})$.
10. $3\text{COCl}_2(\text{g}) + 3\text{CrCl}_4(\text{g}) + 3\text{Ti} + 9\text{Fe} = 3\text{TiC} + \text{Cr} + 9\text{FeCl}_2(\text{g}) + \text{Cr}_2\text{O}_3$.
11. $3\text{COCl}_2(\text{g}) + 20/3\text{CrCl}_4(\text{g}) + \text{Ti} + 98/6\text{Fe} = \text{TiC} + 2/3\text{Cr}_7\text{C}_3 + 98/6\text{FeCl}_2(\text{g}) + \text{Cr}_2\text{O}_3$.
12. $3\text{COCl}_2(\text{g}) + 29/3\text{CrCl}_4(\text{g}) + \text{Ti} + 134/6\text{Fe} = \text{TiC} + 1/3\text{Cr}_{23}\text{C}_6 + 134/6\text{FeCl}_2(\text{g}) + \text{Cr}_2\text{O}_3$.
13. $2\text{CO}(\text{g}) + \text{CrCl}_2(\text{g}) + \text{Ti} + \text{Fe} = \text{TiC} + \text{Cr} + \text{FeCl}_2(\text{g}) + \text{CO}_2(\text{g})$.
14. $\text{CO}(\text{g}) + 5/3\text{CrCl}_2(\text{g}) + \text{Ti} + 5/3\text{Fe} = \text{TiC} + \text{Cr} + 5/3\text{FeCl}_2(\text{g}) + 1/3\text{Cr}_2\text{O}_3$.



The possibility of the occurrence of the above-mentioned exchange-type carbonization reactions is confirmed by the change of the thermodynamic potential ΔG_T^0 of these reactions (Fig. 4).

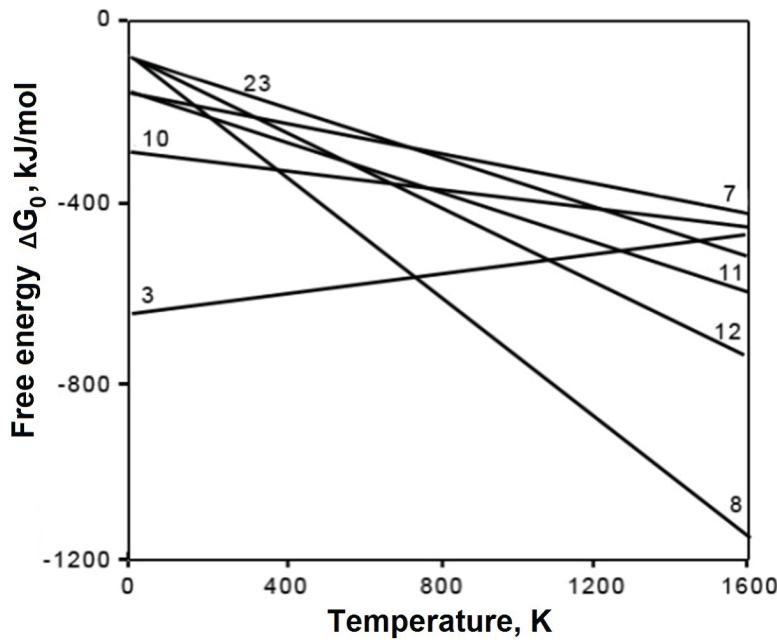


FIG. 4: Dependence of the free energy of the formation of chromium and titanium carbides on temperature

As could be seen from Fig. 4, the reactions of carbide formation 3, 7, 8, 10, 11, 12, and 23 are the most thermodynamically probable under the accepted conditions of saturation.

4. CONCLUSIONS

The analysis of the results of theoretical studies showed that:

- An increase in the ratio of metal/chlorine in the investigated temperature range 600–1500 K is accompanied by the increase in the partial pressure of higher chlorides. The chlorides of metals of different valences are found in the gas phase, and their partial pressure increases with temperature;
- The probable formation of metal carbides TiC , Cr_3C_2 , Cr_7C_3 , and $Cr_{23}C_6$ in a condensed state for systems containing Ti, Cr, and C is evident. Titanium and chromium carbides are stable in the investigated temperature range;
- The presence of oxides Ti_2O_3 , Ti_4O_7 , and Cr_2O_3 in a condensed state, as well as the formation of nitrides in the systems that involve oxygen and nitrogen is observed;
- Oxides of titanium and chromium are stable at 600–1500 K for oxygen to chlorine ratio 1:6. With increase of the chlorine amount and a reduction of oxygen, the oxides of the transition metal exist in a condensed state in the low temperature region;
- The deposition of the carbide and oxide coatings on the base of titanium and chromium on the surface of steels and solid solution alloys is possible.

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