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Thermodynamic modeling of processes in carbide-forming systems Ti–C–H–N and Ti–O–C–H–N

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Abstract. Thermodynamic analysis of high-temperature interactions in Ti–C–H–N, Ti–O–C–H–N systems was carried out, corresponding to the processes of titanium carbide synthesis in the conditions of plasma flow using various titanium-containing raw materials. Modeling processes in these carbide-forming systems showed that the formation of titanium carbide is possible in equilibrium and quasi-equilibrium conditions, at temperatures below 3500 K, with stoichiometric and excess carbon according to gas-phase reaction involving titanium and cyanide vapour. The possibility of achieving a high yield of titanium carbide in real synthesis conditions is predicted.

1. Introduction

The objects of thermodynamic modeling are plasma-metallurgical jet processes of for the carbides production, which unlike traditional ones have some specific features [1, 2]:

- transience of the carbide formation processes which makes it possible to question the possibility of achieving equilibrium;
- high-temperature flow conditions for fairly rapid achievement of equilibrium;
- achieving a high yield of carbides exclusively in the conditions that ensure the gas-phase character of the reactions of carbide formation;
- the production of carbides in the systems consisting of several chemical elements, that form multiphase multicomponent mixtures, necessitates the performance of their thermodynamic analysis on a computer;
- change in the conditions for the existence of condensed phases due to their formation in the form of nano-sized particles (with a large surface curvature) for which the partial pressure above the condensed phase exceeds the saturation pressure above the flat surface. However, at present there are no unified opinion on the size threshold (1 or 2-10 nm) and the corresponding reference data;
- unconditional expediency of performing thermodynamic calculations of equilibrium compositions of carbide-forming systems at various parameters in connection with insufficient information to describe with the necessary accuracy and reliability the kinetics and mechanism of the carbides formation.

Taking into account these features, the results of thermodynamic modeling of carbide formation can be considered as predictive, requiring experimental confirmation and as technological benchmarks, perfection indicators of the reactor, as well as the level of organization in it of heat and mass exchange processes.



The purpose of thermodynamic modeling of synthesis processes is to predict the optimal parameters for the production of titanium carbide (the ratio of components and temperature), to determine the equilibrium parameters of the process (the degree of conversion of raw materials to carbide, the composition of gaseous and condensed products), to evaluate the contribution to the carbide formation of gas-phase reactions that ensure the efficient processing of dispersed raw materials in the conditions of plasma-metallurgical technology.

2. Results and discussion

The objects of the study were Ti–O–C–H–N and Ti–C–H–N systems, since the raw materials used in the synthesis processes were: fine powder of titanium and titanium dioxide TiO₂, methane and plasma-forming gas – nitrogen.

The calculation of the equilibrium compositions of gaseous and condensed products was carried out by the “const method” based on the joint solution of the following equations: the law of acting masses, the material balance, the total number of moles of the gas mixture, the existence of a condensed phase and the Dalton law [1].

The calculations were carried out using the computer simulation of high-temperature complex chemical equilibria PLASMA (Institute of Chemistry of Solids and Mechanical Chemistry of the RAS Siberian branch), which has a built-in database of interaction products for oxide, boride, carbide, and nitride-forming systems. In the calculations, the temperature range 1000-6000 K was considered at a total pressure in the system of 0.1 MPa. The initial data were the equilibrium constants of the reactions of compounds formation from the elements given in [3-9].

The compositions of the gas and condensed phases of the systems under study are given in table 1.

Table 1. Compositions of gas and condensed phases.

System	The composition of the gas phase	Composition of the condensed phase
Ti-O-C-H-N	H, H ⁺ , H ₂ , N, N ₂ , NH, NH ₂ , NH ₃ , C, C ⁺ , C ₂ , C ₃ , C ₄ , C ₅ , CH ₂ , CH ₃ , CH ₄ , C ₂ H, C ₃ H, C ₄ H, C ₂ H ₂ , C ₂ H ₃ , C ₂ H ₄ , CN, CN ⁻¹ , NCN, NCC, C ₂ N ₂ , C ₄ N ₂ , HCN, HCCN, C ₃ HN, O, O ₂ , NO, NO ₂ , H ₂ O, CO, CO ₂ , Ti, TiO, TiO ₂ , TiOH	Ti, TiC, TiN, TiO, Ti ₂ O ₃ , Ti ₃ O ₅ , Ti ₄ O ₇ , TiO ₂
Ti-C-H-N	H, H ⁺ , H ₂ , N, N ₂ , NH, NH ₂ , NH ₃ , C, C ⁺ , C ₂ , C ₃ , C ₄ , C ₅ , CH ₂ , CH ₃ , CH ₄ , C ₂ H, C ₃ H, C ₄ H, C ₂ H ₂ , C ₂ H ₃ , C ₂ H ₄ , CN, CN ⁻¹ , NCN, NCC, C ₂ N ₂ , C ₄ N ₂ , HCN, HCCN, C ₃ HN, Ti	Ti, TiC, TiN

The choice of the ratios of the initial components in the investigated systems was determined by the stoichiometry of the reactions of the target products formation and the parameters of the technological equipment. The ratios chosen for the calculations are shown in table 2.

Table 2. The ratio of components in the studied systems.

Ratio of components, mole	Note
Ti:O:C:H:N=0.25:0.5:0.75:3:20	According to the stoichiometry for the reaction $\text{TiO}_2 + 3\text{CH}_4 = \text{TiC} + 2\text{CO} + 6\text{H}_2 \quad (1)$
Ti:O:C:H:N=0.25:0.5:0.78:3.12:20	104% of carbon content compared with the stoichiometry for reaction (1)
Ti:O:C:H:N=0.25:0.5:0.81:3.24:20	108% of carbon content compared with the stoichiometry for reaction (1)
Ti:O:C:H:N=0.25:0.5:0.84:3.36:20	112% of carbon content compared with the stoichiometry for reaction (1)
Ti:O:C:H:N=0.25:0.5:0.875:3.5:20	116% of carbon content compared with the stoichiometry for reaction (1)

Ti:O:C:H:N=0.25:0.5:0.91:3.64:20	120% of carbon content compared to the stoichiometry for reaction (1)
Ti:O:C:H:N=0.25:0.5:0.94:3.76:20	124% of carbon content amount compared to the stoichiometry for reaction (1)
Ti:C:H:N=0.25:0.25:1.0:20	According to the stoichiometry for the reaction $\text{Ti} + \text{CH}_4 = \text{TiC} + 2\text{H}_2$ (2)
Ti:C:H:N=0.25:0.375:1.0:20	150% of carbon content compared with the stoichiometry for reaction (2)

The results of thermodynamic calculations of equilibrium compositions of Ti–O–C–H–N system are shown in figure 1.

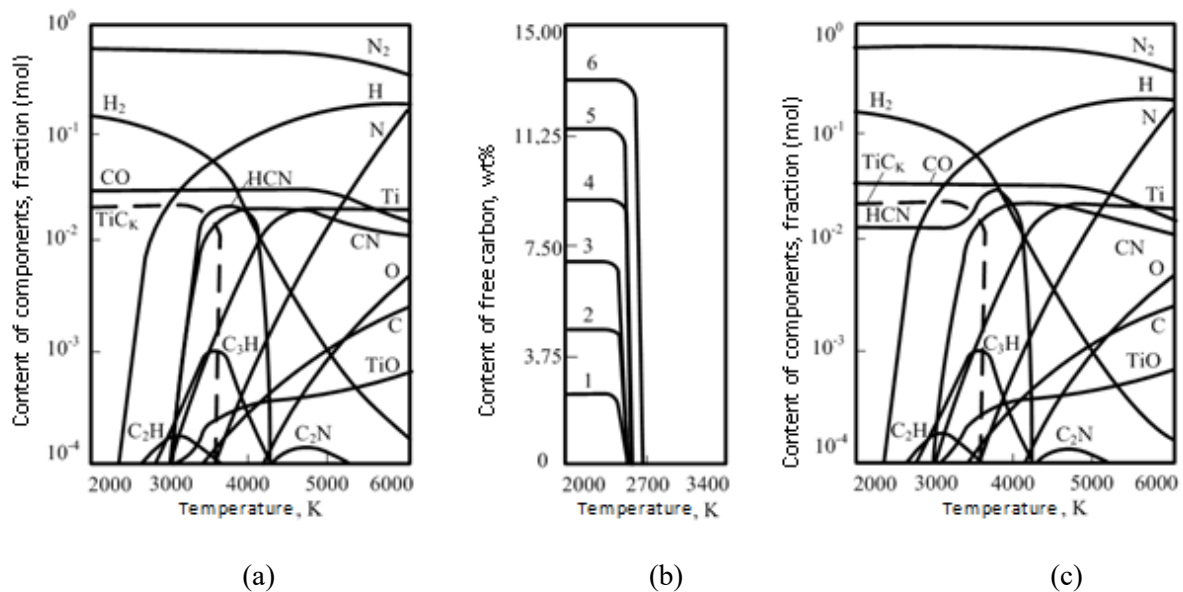
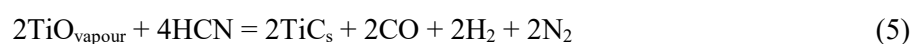


Figure 1. Results of thermodynamic calculations of Ti–O–C–H–N system: a – equilibrium compositions of the gas and condensed phases depending on the temperature with ratio Ti:O:C:H:N=0.25: 0.50: 0.75: 3: 20; b – dependence of the equilibrium concentration of free carbon in the condensed phase on the ratio TiC = 0.25:0.28 (1); 0.25:0.31 (2); 0.25:0.34 (3); 0.25:0.375 (4); 0.25:0.41 (5); 0.25:0.44 (6); c – quasi-equilibrium compositions of the gas and condensed phases of the Ti–O–C–H–N system with components ratio Ti:O:C:H:N=0.25:0.50:0.875:3.5:20.

In the system under consideration, the production of titanium carbide is possible at temperatures below 3500 K with all the component ratios considered in the calculations. The following gas-phase reactions of titanium carbide formation are thermodynamically possible:



Of the reactions 3 and 6, the most probable from a thermodynamics point of view is reaction 3: the degree of conversion of Ti to TiC in this reaction is 0.94. The complete conversion of titanium to carbide is achieved in the temperature range 3200-3500 K at a stoichiometric ratio Ti:C (figure 1a) and carbon excess in the system (figure 1b). However, in this case the condensed products contain free carbon, the equilibrium concentration of which varies from 2.55 to 12.75 wt% when the Ti:C ratio is changed within 0.25:(0.28÷0.44).

In the conditions of quasiequilibrium with an excess of the carbidizer at the ratio Ti:C=0.25:0.375 (figure 1c), the cyanide is stable in a wider temperature range – (2000-3800) K, which makes it possible to obtain carbide with no free carbon.

In the Ti–C–H–N system, the formation of titanium carbide is possible in the conditions of equilibrium (a) and quasi-equilibrium conditions (b) (figure 2). In the first case, when the ratio Ti:C = 0.25:(0.0625-0.25) is changed, the degree of conversion of titanium to carbide varies from 0.25 to 1. And at the ratio Ti:C = 0.25:0.375 (excess carbide), the synthesis product is a carbide – carbon composition, containing 9.1 wt% free carbon. In the second case, no condensation of carbon occurs. In both cases, the formation of carbide is thermodynamically possible according to the gas-phase reaction.

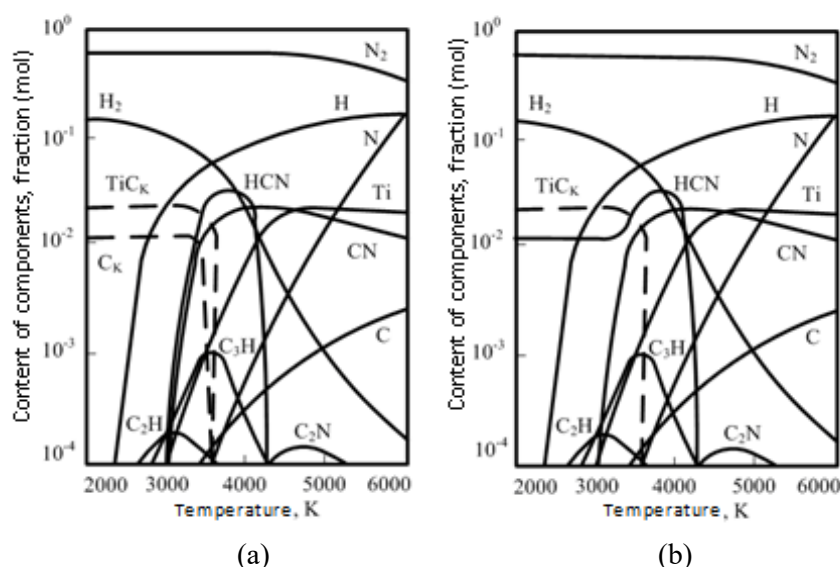


Figure 2. Equilibrium (a) and quasi-equilibrium (b) compositions of the gas and condensed phases of the Ti–C–H–N system with the ration of components Ti:C:H:N = 0.25:0.375:1.5:20.

The closeness of temperatures of titanium condensation (3533 K) and melting of the carbide formation (3530 K) does not allow an unambiguous assumption to be made about the possible mechanism of carbide formation, although the formation of carbide by the mechanism “vapour – crystal” is more likely.

3. Conclusion

Thermodynamic modeling of processes in carbide-forming systems Ti–C–H–N and Ti–O–C–H–N showed that in the Ti–O–C–H–N system titanium carbide formation is possible at a temperature below 3500 K with stoichiometric and excess amount of carbon. With an excess of carbon in the condensed products there is a free carbon, the equilibrium concentration of which varies from 2.55 to 12.75% by weight when the ratio Ti:C changes within 0.25:(0.28÷0.44). In the conditions of quasiequilibrium

with an excess of antigraphitizer the carbide cyanide is stable in a wider temperature range – (2000-3800) K, which makes it possible to obtain carbide that does not contain free carbon.

In the Ti–C–H–N system the formation of titanium carbide is also possible in equilibrium and quasi-equilibrium conditions. In the condition of equilibrium, when the ratio Ti:C = 0.25:(0.0625-0.25) varies, the degree of conversion of titanium to carbide varies from 0.25 to 1, and at 1.5 times excess of the antigraphitizer, carbide contains 9.1 wt% free carbon. In the conditions of quasi-equilibrium no condensation of carbon occurs.

For each case the formation of titanium carbide according to the gas-phase reaction involving titanium and cyanide vapours is typical, that is, according to the “vapour – crystal” scheme, which makes it possible to predict the possibility of achieving its high yield in the real synthesis conditions.

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