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Thermodynamic modeling of plasma synthesis of zirconium carbide

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Abstract. Thermodynamic analysis of equilibrium and quasi-equilibrium compositions of multicomponent systems for various technological options of hydrocarbons pyrolysis and zirconium carbide synthesis is carried out. The objects of thermodynamic modeling were the systems C-H-N, Zr-C-H-N and Zr-O-C-H-N. The formation of ZrC is possible when the vapors of zirconium and cyanogen interact at a temperature below 4000K.

1. Introduction

To date, in the production of refractory materials two basic options for technological application of high-temperature heating have been formed: the long-term heat treatment of the compacted solid batch of the given chemical and granulometric composition by the directed plasma jet and rapid synthesis in the conditions of turbulent chemically active plasma flow (so-called plasma synthesis) [1-3]. The second option along with the intensification and the possibility of realizing the process in a continuous mode ensures the production of the target products in the nanodisperse state.

To assess the technological feasibility of plasma synthesis of zirconium carbide, its thermodynamic modeling was carried out. The plasma synthesis of high-temperature compounds has the following specific features that require compulsory methodological accounting when performing its thermodynamic modeling:

- extremely limited residence time of dispersed feedstock in the evaporation zone and reaction mixture in the zone of formation of the target product in the flow of gas-coolant with a temperature of 5500-2000K, which is several micro- or milliseconds, respectively, makes it possible to assume the dominant role of the temperature factor over time and, hence, the possibility of achieving equilibrium;
- high probability of formation of the target products in the analyzed conditions during interactions in the gas phase or with its participation;
- the need to implement plasma synthesis in the systems consisting of several chemical elements introduced with the processed raw materials and plasma forming gas and generating multiphase and multicomponent systems, predetermines the unconditional application of computer technologies for carrying out thermodynamic modeling;
- the special importance of the results of thermodynamic modeling of plasma synthesis processes in the absence of a real possibility to describe their kinetic regularities and mechanism with sufficient reliability;
- the predicted nature of thermodynamic modeling results of plasma synthesis processes, which makes it possible to consider them as technological guidelines requiring experimental confirmation.

2. The modeling technique

Thermodynamic modeling of synthesis processes was carried out to predict the optimal parameters for the production of zirconium carbide (the ratio of components and temperature), determine the equilibrium parameters of the process (the degree of conversion of the raw material into carbide, the composition of gaseous and condensed products), estimate the contribution to the carbide formation of gas-phase reactions providing an effective processing of dispersed raw materials in the conditions of plasma technologies.

The objects of thermodynamic modeling were the systems C-H-N, Zr-C-H-N and Zr-O-C-H-N due to the possibility of using hydrocarbon raw materials – methane, plasma forming gas – nitrogen as zirconium-containing raw materials of zirconium and its dioxide. The thermodynamic estimation of carbide formation processes in the Zr-C-N and Zr-O-C-H-N systems is carried out for the first time.

The compositions of gaseous and condensed products necessary for analysis were calculated by the "constant method". The "constant" method is based on the joint solution of the following equations.

- law of mass action

$$n_i = \left(\frac{P}{N}\right)^{\sum_{i=1}^{q} a_{ij}-1} \prod_{\gamma=1}^{q} n_j^{a_{ij}/K_i}, \quad 1 \le i \le m\text{-}q; \tag{1}$$

- material balance

$$\sum_{i-1}^{m} a_{ij} n_i + \sum_{i-1}^{f} n_{is} = C_j, \quad 1 \le j \le q; \tag{2}$$

- the total number of moles of the gas mixture

$$\sum_{i-1}^{m} n_i = N, \tag{3}$$

- existence of a condensed phase

$$K_i^S = \frac{P}{N} n_i, \tag{4}$$

- Dalton law

$$\sum_{j=1}^{m} P_j = P, \tag{5}$$

where n_i – the number of moles of the corresponding component in the gas phase; n_{is} – the number of moles of the corresponding component in the condensed phase; N – the total number of moles of all components in the gas phase; m – the number of components in the gas phase; K_i – equilibrium constants of the dissociation reactions of complex gaseous components into atoms; a_{ij} – matrix of stoichiometric coefficients of dissociation reactions of complex substances; j – the number of components that are present in the condensed phase; C_j – the number of atoms of the element j in the system, divided by the Avogadro number; K_i^s – partial saturation pressure over the corresponding condensed phase.

It should be noted that for plasma synthesis processes changes in the conditions for the existence of condensed phases can be expected due to their formation in the form of nano-sized particles, i.e. with a great curvature of the surface for which the partial pressure over the condensed phase exceeds the saturation pressure above the flat surface. However, at the present time there is no uniform opinion on

the size threshold (~ 1 or 2-10 nm) and the corresponding reference data. Earlier, the "constant" method was repeatedly successfully used by the scientific school of Professor G.V. Galevsky for thermodynamic modeling of high-temperature interactions in complex carbide and boride-forming systems Si-O-C-H-N, Si-C-H-N, Cr-O-C-B-H-N, Cr-B-H-N, etc., and therefore it was chosen as the main for thermodynamic study of carbide-forming systems in the production of zirconium carbide in the conditions of plasma flow.

The temperature dependence of interaction products compositions for the systems under study was calculated using the PLASMA computer simulation softawer, supplemented by the development of an embedded database required for analyzing the processes of obtaining oxygen-boron-nitrogen-carbon-containing compounds of refractory metals. The temperature range of 2000-6000 K was considered at a constant total pressure in the system equal to 0.1 MPa. The equilibrium constants of the reactions of elements compounds formation, borrowed from publications and reference books [4-8], were used as initial ones, in particular for ZrC – from [5], ZrN – from [6].

The components of the gas and condensed phases taken into account in the calculations are presented in table 1, and their ratios in table 2. The ratios of the initial components were determined in accordance with the stoichiometry of reactions of the target products formation and the parameters of the technological equipment (flow of the plasma-forming gas).

Table 1. Compositions of the gas and condensed phases of the systems under study.

System	Phase composition	
	Gas	Condensed
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, CH_2, CH_3, CH_4, C_2H, C_3H, C_4H, C_2H_2, C_2H_3, C_2H_4, CN, CN^{-1}, NCN, NCC, C_2N_2, C_4N_2, HCN, HCCN, C_3HN	C
Zr–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, CH_2, CH_3, CH_4, C_2H, C_3H, C_4H, C_2H_2, C_2H_3, C_2H_4, CN, CN^{-1}, NCN, NCC, C_2N_2, C_4N_2, HCN, HCCN, C_3HN, Zr, ZrH	C, Zr, ZrC, ZrN
Zr–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, CH_2, CH_3, CH_4, C_2H, C_3H, C_4H, C_2H_2, C_2H_3, C_2H_4, CN, CN^{-1}, NCN, NCC, C_2N_2, C_4N_2, HCN, HCCN, C_3HN, O, O_2, NO, NO_2, H_2O, CO, CO_2, Zr, ZrO, ZrO_2	C, Zr, ZrC, ZrN, ZrO, ZrO_2

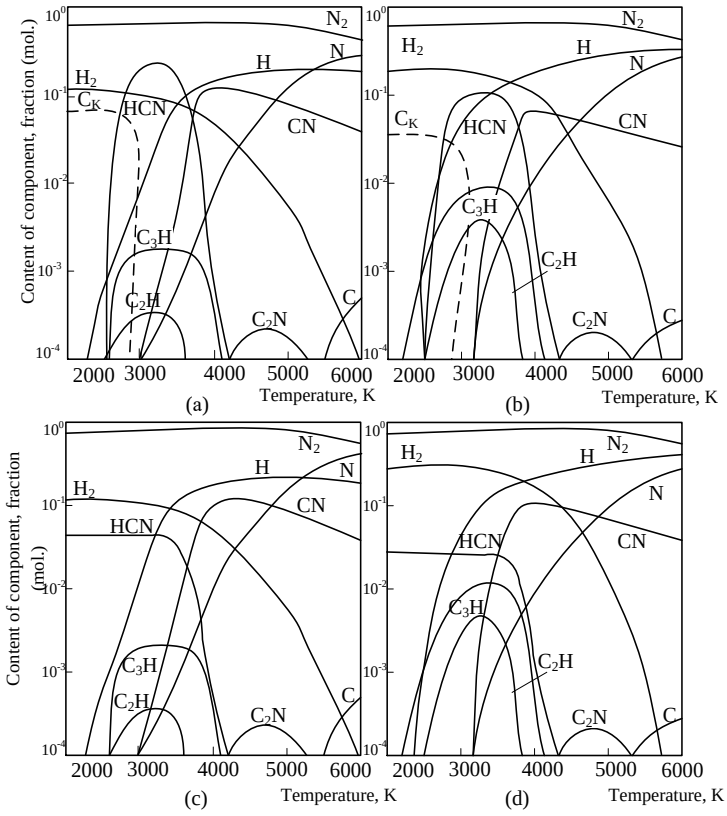
Table 2. Specified ratio of components in the systems under study.

Ratio of components, mole	Note
C:H:N=0.75:3:20	By stoichiometry for the reaction $CH4 = C + 2H2$ (6)
C:H:N=0.75:6:20	A 2-fold excess of hydrogen compared with the stoichiometry for reaction (6)
Zr:C:H:N = 0.25:0.25:1:20	By stoichiometry according to the reaction $Zr + CH_4 = ZrC + 2H_2$ (7)
Zr:C:H:N = 0.25:0.375:1.5:20	A 150% carbon amount compared to the stoichiometry for reaction (7)
ZrO:C:H:N = 0.25:0.50:0.75:3:20	According to the stoichiometry for the reaction $ZrO_2 + 3CH_4 = ZrC + 2CO + 6H_2$ (8)
Zr:O:C:H:N= 0.25:0.50:0.20:0.75:20	75% shortage of carbon compared with the stoichiometry for reaction (8)
Zr:O:C:H:N= 0.25:0.50:0.375:1.5:20	50% shortage of carbon compared with the stoichiometry for reaction (8)

Zr:O:C:H:N = 0.25:0.50:0.47:1.88:20	37.5% lack of carbon compared with the stoichiometry for reaction (8)
Zr:O:C:H:N = 0.25:0.50:0.56:2.25:20	25% shortage of carbon compared with the stoichiometry for reaction (8)
Zr:O:C:H:N = 0.25:0.50:0.66:2.63:20	12.5% shortage of carbon compared with the stoichiometry for reaction (8)

3. The results of modeling and their analysis

The thermodynamic analysis of the C-H-N system was performed to obtain predictive information about the possible composition of the gas phase formed as a result of methane pyrolysis and its interaction with the heat-carrier gas. The temperature dependence of equilibrium and quasi-equilibrium compositions is shown in figure 1.



The results of calculating the equilibrium compositions of the system (figure 1 a, b) revealed the presence of HCN, CN, C_3H, C^2H in the gas phase at a temperature of 2800-4200 K, with about 98% of the carbon being bound to the hydrogen cyanide. The decomposition of the hydrogen cyanide occurs at temperatures below 2800 K and leads to the formation of free carbon in the condensed state.

a – C:H:N=0.75:3:20; b – C:H:N=0.75:6:20
c – C:H:N=0.75:3:20; d– C:H:N=0.75:6:20

Figure 1. Equilibrium (a, b) and quasi-equilibrium (c, d) composition of the system C-H-N, depending on the ratio of components and temperature.

The calculation results of quasi-equilibrium compositions (figure 1 c, d), which differ significantly in the temperature range of the hydrogen cyanide stability (2000-2800 K), make it possible to obtain the composition of the final products and the main process indices corresponding to the experimental data [8].

The results of the thermodynamic calculations of the Zr-C-H-N system are shown in figure 2. In this system the formation of ZrC is possible by the reaction

$$Zrg+CNg=ZrCk+0.5N2t \quad (9)$$

A 100% ZrC yield is achieved with the stoichiometric ratio of components Zr:C in the temperature range 2300-4000 K. With an excess of carbidizer (ratio Zr:C=0.25:0.375) in the conditions of equilibrium, the product of the synthesis is a carbide-carbon composition containing 2.8% of free carbon. In the conditions of quasiequilibrium with an excess of carbide, cyanide is stable in the temperature range 2300-3800 K, which makes it possible to obtain carbide not contaminated with

pyrolytic carbon. At a temperature below 2300 K, the interaction of carbide with nitrogen is thermodynamically possible according to reaction

$$ZrCk + N2 = ZrNk + 0.5N2g \quad (10)$$

The results of the thermodynamic calculations of the Zr-C-O-H-N system are shown in figure 3. As the ratio of Zr:O:C changes from 0.25:0.50:0.19 to 0.25:0.50:0.75 the degree of conversion of zirconium to carbide varies from 0.25 to 1. Zirconium carbide is stable in the temperature range 2300-4000 K. The formation of ZrC is possible by reactions (9) – up to 98.5% and (11) – up to 1.5%

$$ZrOg + 2CNg = ZrCk + COg + 0.5N2g \quad (11)$$

At a temperature below 2300 K, the reaction (10) becomes thermodynamically possible leading to the formation of a ZrN nitride.

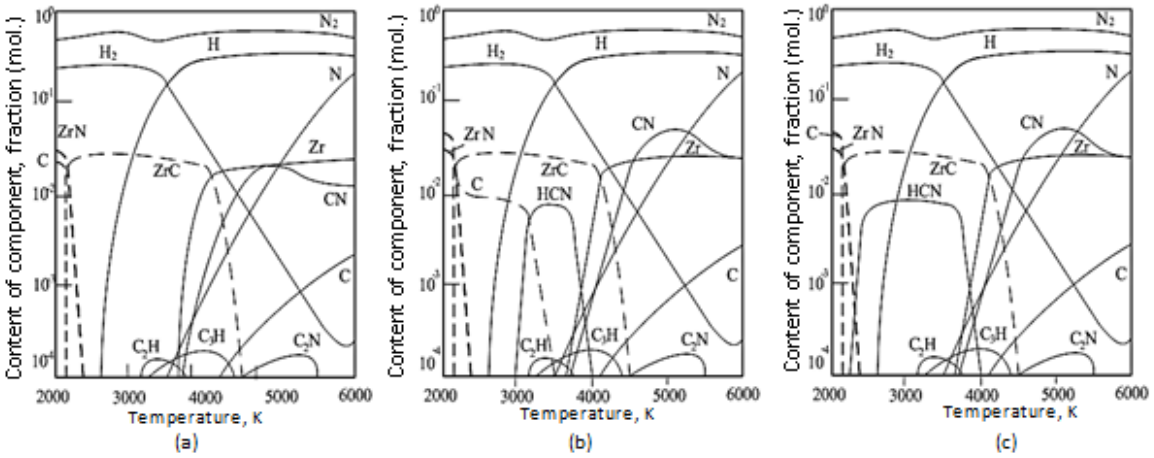


Figure 2. Results of thermodynamic calculations of the Zr-C-H-N system: a) the equilibrium compositions of the gas and condensed phases depending on the temperature at a ratio of Zr:C:H:N=0.25:0.25:1:20; b) the equilibrium compositions of the gas and condensed phases depending on the temperature at the ratio Zr:C:H:N=0.25:0.375:1.5:20; c) quasi-equilibrium compositions of the gas and condensed phases depending on the temperature at a ratio of Zr:C:H:N=0.25:0.375:1:20.

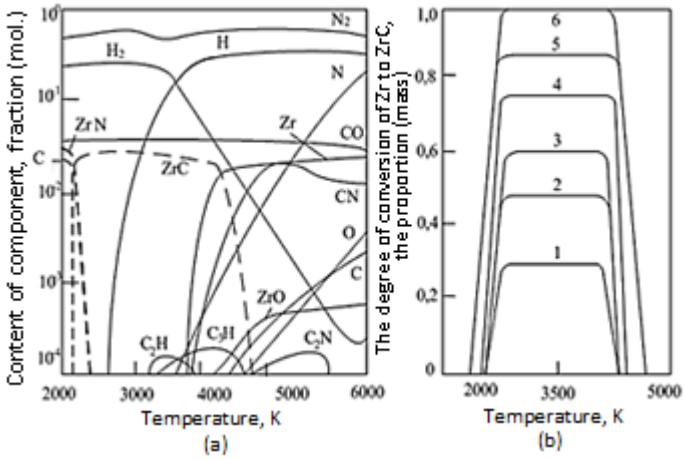


Figure 3. Results of thermodynamic calculations of the Zr-C-O-H-N system: a) equilibrium compositions of the gas and condensed phases depending on the temperature at a ratio of Zr:C:O:H:N=0.25:0.75:0.50:3:20; b) the dependence of the degree of conversion of Zr to ZrC on the ratio Zr:C=0.25:0.20 (1); 0.25:0.375 (2): 0.25:0.47 (3): 0.25:0.56 (4); 0.25:0.66 (5); 0.25:0.75 (6).

4. Conclusion

Thermodynamic study of equilibrium and quasi-equilibrium compositions of multicomponent systems for the pyrolysis of hydrocarbons and various technological options for the production of zirconium carbide has been carried out.

It is established that:

- in the C-H-N system under equilibrium conditions, 100% gasification of carbon is achieved in the temperature range of 2800-3800 K due to the formation of hydrogen cyanide and hydrocarbon radicals. Up to 98% of carbon is present in the gas phase as HCN. Quasi-equilibrium conditions that exclude the formation of condensed carbon make it possible to expand the temperature range of the thermodynamic stability of hydrogen cyanide to 2300 K;
- in the Zr-C-H-N system, the formation of zirconium carbide is possible at temperatures below 4000 K in equilibrium and quasi-equilibrium conditions with stoichiometric and excessive amounts of carbon; with an excess of carbon at a ratio Zr:C=0.25÷0.375 in the conditions of equilibrium a carbide-carbon composition containing 2.8% carbon is formed, in the conditions of quasi-equilibrium – zirconium carbide;
- in the system Zr-C-O-H-N is also stable in the temperature range 2300-4000 K; when the ratio of Zr:O:C is changed from 0.25:0.50:0.19 to 0.25:0.50:0.75, the degree of conversion of zirconium to carbide will change from 0.25 to 1;
- in both systems, the formation of zirconium carbide is thermodynamically possible through gas-phase reactions involving zirconium and cyanide vapors, i. e. according to the “steam-crystal” scheme, which allows the achievement of its high yield in the real conditions of plasmosynthesis to be predicted.

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