THERMODYNAMIC ANALYSIS OF THE Ti-O-C SYSTEM

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Complete thermodynamic analysis of the system Ti-O-C both under pressure and vacuum resulted the following reaction: $TiO_2 + 3C = TiC + 2CO$. The basic results for all structures are presented in the form of diagrams (dependence of the contents of components on temperature range 1000-2300 K).

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INTRODUCTION

Production of composite and nanostructural materials in most cases is realized through the reactions connected with reduction of oxides. Study of the processes of this type is one of the main tasks of theoretical and applied metallurgy.

Recent years are marked with intensive development of research of chemical and phase equilibrium in multicomponent and multiphase systems with the use of computer simulation technique (full thermodynamic analysis – FTA).[1,2] In particular great is the interest toward applying this approach[1] to studying the processes of producing composite and nanostructured materials.

It should be noted that the proposed method (FTA) gives an opportunity to control not only equilibrium conditions of the proceeding processes in the system, but also the mechanism of interaction of components in complicated systems and therefore, to correct structure of a final product.

FTA of interaction of titanium oxide (TiO_2) with carbon (C) was carried out at atmospheric pressure as well as in vacuum by the reaction:

$$TiO_2 + 3C = TiC + 2CO$$

Data on FTA of the considered system have not been found. Therefore results of the research of this specified system are of a great interest.

RESULTS AND DISCUSSIONS

Among the possible condensed components were considered: C, Ti, TiO, Ti_2O_3, TiO_2, Ti_3O_5, Ti_4O_7, TiC, $TiCO_{0,04}$, $TiC_{0.1}$, $TiC_{0.4}O_{0.6}$, $TiC_{0.75}O_{0.25}$; gaseous: O, O_2, O_3, C, C_2, C_3, C_4, C_5, CO, CO_2, C_2O, C_3O_2, Ti, TiO, TiO_2.

For research of balance of the specified reaction it is necessary to have a set of reliable data on thermodynamic properties of the elements and compounds, participating in the processes. However in the available reference books some data on thermodynamic properties (ΔH_{298}, T_m, C_p, C_{pl}) of those oxycarbides are absent.

With regard to the above mentioned there were estimated values of thermodynamic constants of oxycarbides and they were brought in the databank in ASTRA-4 program; estimation methods of the program were developed and described in Ref.[3] Main results of the provided FTA are presented in the form of charts.

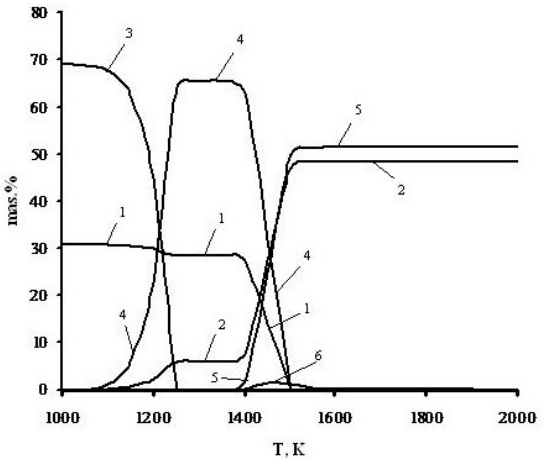

Figure 1. Temperature dependence of the comprised components at atmospheric pressure for reaction 1: 1-C; 2-CO; 3-TiO_2; 4-Ti_4O_7; 5-TiC; 6-$TiC_{0.75}O_{0.25}$

Fig. 1 presents a thermodynamic model of the carbothermal reduction process of TiO_2 (c) in the temperature range of 1000-2000 K at atmospheric pressure. Recovery of titanium starts at 1100 K with the formation of Ti_4O_7 (c) and CO in gaseous phase; content of TiO_2 (c) in the system starting from 1100 K sharply decreases and at ~ 1250 K completely disappears; in parallel, Ti_4O_7 (c) sharply increases to ~ 1250 K and further above 1350 K goes down to disappear at 1500 K. Carbothermal reduction of Ti_4O_7 (c) with the formation of TiC starts above ~ 1350 K and at 1550 K reaches maximum (~ 51.5 wt. %). Lower than 1500 K the condensed carbon disappears.

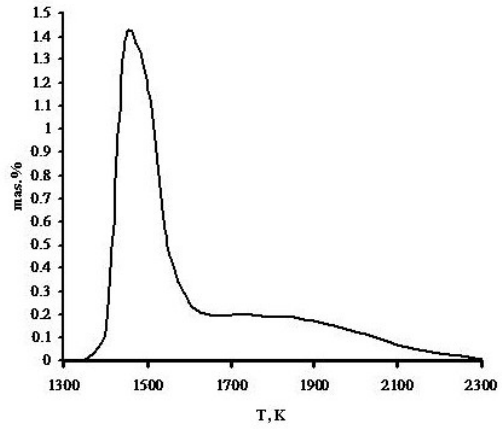

Figure 2. Temperature dependence of the content of oxycarbide ($TiC_{0.75}O_{0.25}$) at atmospheric pressure for reaction 1: 1-$TiC_{0.75}O_{0.25}$

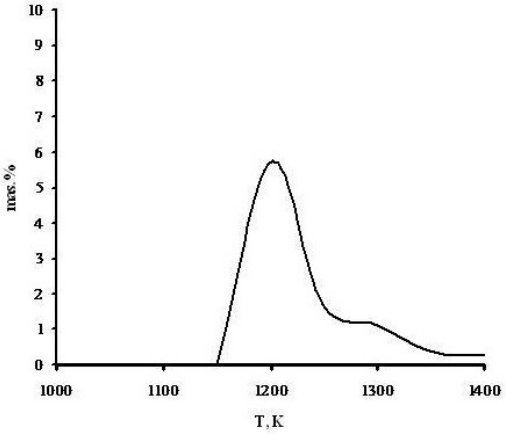

Figure 4. Temperature dependence of the content of oxycarbide ($TiC_{0.75}$ $O_{0.25}$) in vacuum (0.01atm) for reaction 1.

Fig. 2 presents a separate chart of temperature dependent changes of the content of titanium oxycarbide. It is seen that starting from 1400 K oxycarbides release $TiC_{0.75}O_{0.25}$ in the system, reaching the maximum at 1450 K (~ 1.4 wt. %); above this temperature content of $TiC_{0.75}O_{0.25}$ sharply drops down to ~ 1600 K, and further smoothly decreases to ~ 2300 K (reaching 0.01 wt. %). Above 2300 K content of oxycarbide is of an order of 10^{-4} - 10^{-5} wt. %.

Fig. 4 presents a separate chart of temperature dependent changes of the content of titanium oxycarbide. It is seen that starting from 1150 K oxycarbides release $TiC_{0.75}O_{0.25}$ in the system, reaching the maximum at 1200 K (~ 5.7 wt. %); above this temperature content of $TiC_{0.75}O_{0.25}$ sharply decreases to ~ 1250 K, and further smoothly goes down to ~ 1400 K.

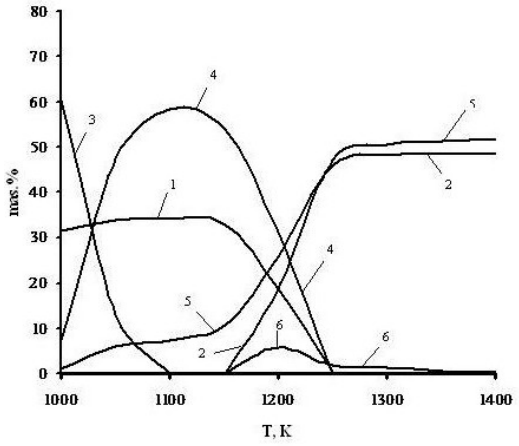

Figure 3. Temperature dependence of the content of components in vacuum (0.01atm) for reaction 1: 1-C; 2-CO; 3-TiO_2; 4-Ti_4O_7; 5-TiC; 6-$TiC_{0.75}O_{0.25}$

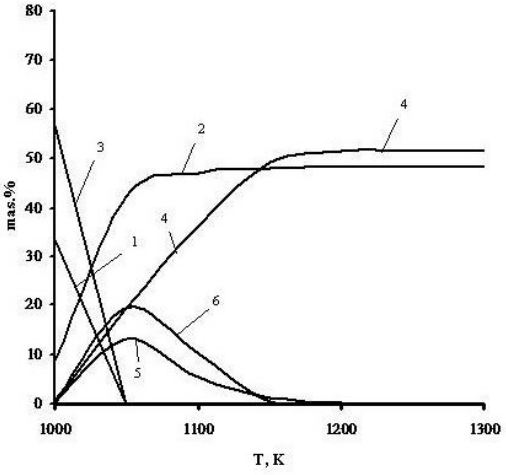

Figure 5. Temperature dependence of the content of components for reaction 1 in vacuum (0.01 atm): 1-C; 2-CO; 3-Ti_4O_7; 4-TiC; 5-$TiC_{0.75}O_{0.25}$; 6. $TiCO_{0.04}$

Fig. 3 presents a thermodynamic model of carbothermal reduction process of TiO_2 (c) in the temperature range 1000-1400 K in vacuum (0.01 atm). Recovery of the titanium starts at 1000 K with the formation of Ti_4O_7 (c) and CO in gaseous phase; content of TiO_2 (c) in the system sharply decreases and at ~ 1100 K completely disappears; in parallel, content of Ti_4O_7 (c) sharply increases to ~ 1100 K, further goes down and at 1200 K disappears. Carbothermal reduction of Ti_4O_7 (c) with the formation of TiC starts at 1200K and at 1350 K reaches maximum (~ 51.0 wt. %). Approximately above ~ 1250 K the condensed carbon disappears.

Fig. 5 presents a thermodynamic model of the carbothermal reduction process of TiO_2 (c) in the temperature range 1000-2300 K in vacuum (0.0001 atm).

Recovery of the titanium starts at temperature lower than 1000 K with the formation of Ti_4O_7 (c) and CO in gaseous phase; content of TiO_2 (c) in the system sharply decreases and at ~ 1050 K completely disappears; Carbothermal reduction of Ti_4O_7 (c) with the formation of TiC starts below~ 1050 K and at 1250 K reaches maximum (~ 51.5 wt. %). Below 1100 K the condensed carbon disappears.

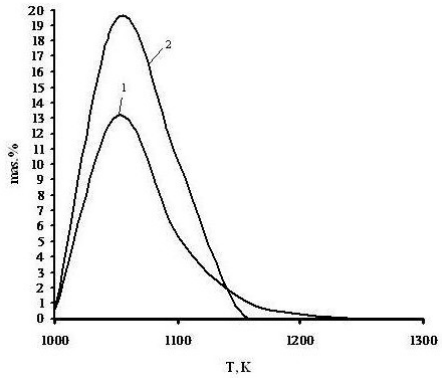

Figure 6. Temperature dependence of the content of oxycarbide in vacuum (0.0001 atm) for reaction 1: 1-$TiC_{0.75}O_{0.25}$; 2-$TiCO_{0.04}$

Fig. 6 presents a separate chart of temperature dependent changes of the content of titanium oxycarbide. It is seen that starting from 1000 K oxycarbides release $TiC_{0.75}O_{0.25}$ in the system, reaching the maximum at 1050 K (~ 13 and 19 wt. %, respectively); above this temperature the content of $TiC_{0.75}O_{0.25}$ sharply decreases to ~ 1200 K.

Issued from the thermodynamic analysis it is better to provide experiments in vacuum (< 0.0001 atm) as the process proceeds at lower temperatures.

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