THERMODYNAMIC ANALYSIS OF INTERACTION OF CARBON WITH TiO_2, ZrO_2, AND B_2O_3 AND OBTAINING OF MIXTURE OF BORIDES AND CARBIDES OF TITANIUM AND ZIRCONIUM

J. I. Bagdavadze,[a] Z. N. Tsikaridze,[a] and K. Z. Ukleba[a]

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Metal borides and carbides, TiB_2/TiC and ZrB_2/ZrC are widely used nanostructured composite materials. A detailed thermodynamic analysis was performed to determine the formation conditions of titanium and zirconium borides and carbides in the Ti–B–O–C and Zr–B–O–C systems. The complete thermodynamic analysis was carried out in vacuum for the reactions $2TiO_2 + B_2O_3 + 8C = TiB_2 + TiC + 7CO$ and $2ZrO_2 + B_2O_3 + 8C = ZrB_2 + ZrC + 7CO$. On the basis of the theoretically found results, experimental synthetic routes were developed to prepare TiB_2/TiC and ZrB_2/ZrC composite materials.

* Corresponding Authors
E-Mail: ketino.ukleba@gmail.com
[a] Ferdinand Tavadze Metallurgy & Materials Science Institute, Laboratory of Boron & Composite Materials, 10 Elizbar Mindeli Street, Tbilisi, 0160 Georgia

INTRODUCTION

The nanostructured composite materials, including metal borides and carbides containing ones like TiB_2/TiC and ZrB_2/ZrChave a unique set of physical and chemical properties (high hardness, heat resistance, high-temperature strength, electrical and thermal conductivities, and resistance to the molten metals in combination with low specific weight, corrosion-, radiation- and wear-resistance).

There are some known methods to obtain of these composites,[1–7] but a complete thermodynamical analysis[8] of the system to optimize their synthesis conditions have not been performed yet. In this work, the comprehensive thermodynamical analysis has been conducted to find optimal conditions for preparation of carbides and borides of zirconium and titanium.

EXPERIMENTALS

Computer calculations were carried out with the ASTRA–4 program described in [8]in the temperature range 500–2000K with the step of 50K for vacuum conditions. The mixture of ZrB_2–ZrC was prepared by mixing the powders of ZrO_2, B_2O_3 and C followed by 30h grinding in a high power (1000rpm) mill. The mill was a piece of special equipment designed and built in our laboratory. After briquetting, the obtained powder was sintered in a high vacuum oven under an argon atmosphere at ~1400°C for 5 h.

RESULTS AND DISCUSSION

System Ti–B–O–C

The thermodynamical analysis of Ti–B–O–C system in vacuum is carried out for the reaction:

$$2TiO_2+B_2O_3+8C=TiB_2+TiC+7CO \qquad (1)$$

The following species were considered as possible condensed and gaseous components: C, Ti, TiO, Ti_2O_3, TiO_2, Ti_3O_5, Ti_4O_7, TiC, $TiCO_{0.04}$, $TiC_{0.10}O$, $TiC_{0.40}O_{0.60}$, $TiC_{0.75}O_{0.25}$, B, B_2O_3, B_4C, TiB, TiB_2, and Ar, 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, B, B_2, BO, BO_2, B_2O, B_2O_2, $B_2O_3$and TiB,.

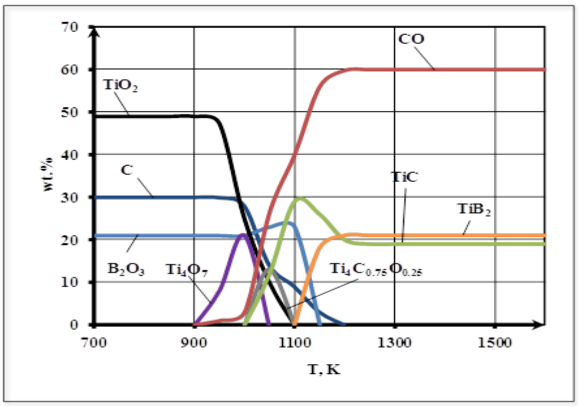

Figure 1. Dependence of components content on temperature for reaction (1) in vacuum (0.0001 atm) in temperature interval 700–1600 K.

The knowledge of reliable thermodynamic data of the reactive system components is necessary. Since some thermodynamic characteristics (ΔH_{298}, $T_{m.}$, $\Delta H_{m.}$, C_p, and

$C_{p(L)}$) of the abovementioned oxycarbides cannot be obtained from the literature, the corresponding thermodynamic constants of oxycarbides were calculated.[9]

The main results of the thermodynamic calculations for the Ti–B–O–C system are presented in Figure 1. It is evident that the reduction of TiO_2 begins above 900 K, and Ti_2O_3, Ti_3O_5 and Ti_4O_7 are allocated in the condensed phase. Their amounts increase to ~1000 K, but raising the temperature their amount started to decrease, and at~1100 K all of the titanium oxides disappear entirely. It appears some amount of condensed carbon and simultaneous allocation of CO in the gas phase begin at temperatures higher than 900K. At ~1200 K, the condensed carbon disappears and the amount of CO reaches its maximum which does not change further. At ~1000 K appears the allocation of TiC which amount sharply increases to ~1100 K and reaches its maximum (~29 wt. %). Increasing the temperature, its amount decreases to ~1200 K and its amount (~18 wt.%) does not change until 1600 K.

The thermodynamic analysis showed that the experiments have to be conducted in vacuum at temperatures higher than 1200K to obtain the requested TiB_2–TiC mixtures.

The system Zr–B–O–C

The detailed thermodynamic analysis of the Zr–B–O–C system in vacuum was carried out for the reaction:

$$2ZrO_2+B_2O_3+8C=ZrB_2+ZrC+7CO. \quad (2)$$

As possible condensed and gaseous components the following ones were considered: C, B, B_2O_3, B_4C, Zr, ZrO_2, ZrC, ZrB_2, and Ar, O, O_2, O_3, B, B_2, BO, BO_2, B_2O, B_2O_3, C, C_2, C_3, C_4, C_5, CO, CO_2, C_2O, C_3O_2, Zr, Zr_2, ZrO, ZrO_2, respectively.

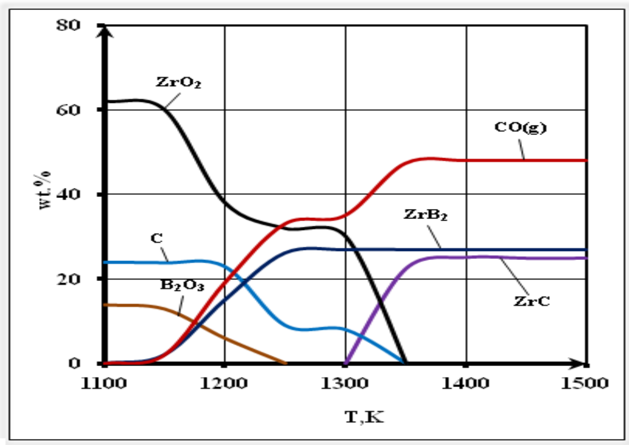

Figure 2. Dependence of components content on temperature for reaction (2) in vacuum (0.0001 atm) in temperature interval 1100–1500 K.

The results of the thermodynamical analysis performed on the Zr–B–O–C system are presented in Figure 2. A reduction process occurs above ~1100 K with the formation of zirconium diboride ZrB_2. Its amount increases up to ~1250K where reaches its maximum (~27 wt.%) and above this temperature does not change further. The amounts of condensed B_2O_3 and ZrO_2 were sharply decreased above~1100 K and completely disappeared at ~1250 and ~1350 K, respectively.

The condensed carbon amount smoothly changes around ~1100 K, but above this temperature its amount sharply decreases and completely disappears at ~1350 K.The condensed zirconium carbide ZrC is allocated above 1300 K, its amount drastically increases up to ~1350K reaching 25 wt.%, but above this temperature there are no further changes in its amount. Thermodynamic analysis of reaction 2 showed that the experiments should do above 1350 K.in vacuum to obtain the expected ZrB_2 and ZrC,

RESULTS

Based on the results of thermodynamic calculations, some tests have been done to prepare TiB_2–TiC mixtures from the mixture of TiO_2 and B_2O_3 with C (graphite) or with ZrO_2-B_2O_3/graphite mixtures in a high-temperature furnace in the argon atmosphere at ~1400°C for 3h.The X-ray diffraction patterns of the prepared powder are given in Figure 3.

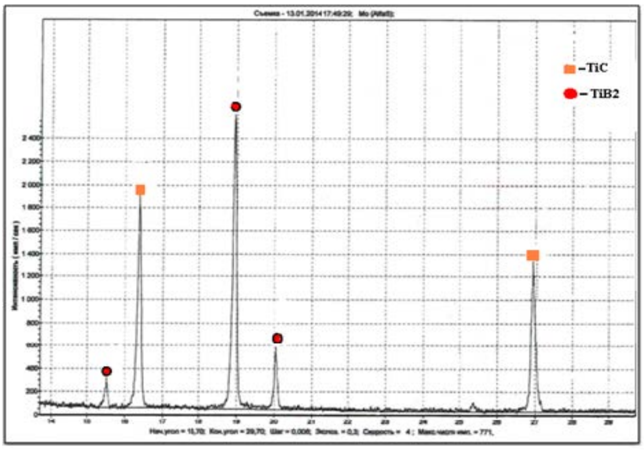

Figure 3. The X-ray diffraction pattern of a mixture of TiB_2 and TiC prepared from TiO_2-B_2O_3/graphite mixture at 1400 °C in 3 h

As can be seen, the product is ca. 1:1 mixture of TiB_2 and TiC.

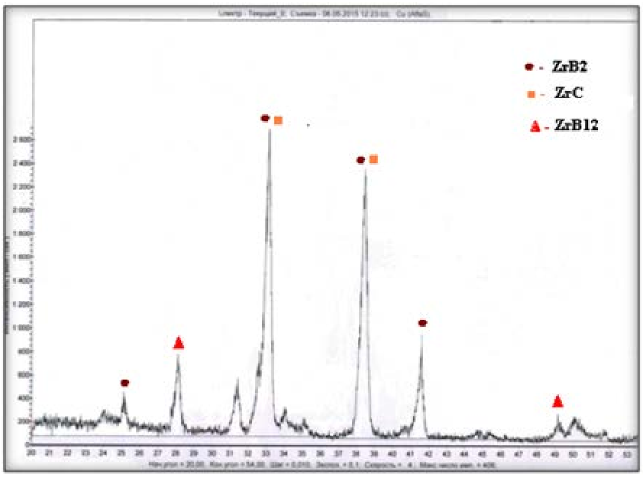

Figure 4. The x-ray diffraction pattern of a mixture of ZrB_2 and ZrC prepared from ZrO_2-B_2O_3/graphite mixture at 1400 °C in 3 h

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