

## Article

# On Modeling of Synthesis Process of Boron Carbide Based Nanocomposites

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**Abstract:** Nanocomposites based on boron carbide  $B_4C$  are hard materials with wide field of applications in modern technologies. A system of first-order ordinary differential equations that simulates the process of chemical synthesis of nanopowders of  $B_4C$ - $TiB_2$  compositions containing titanium diboride ( $TiB_2$ ) as an additional phase is suggested and resolved numerically for a typical ratio of reaction constants. Reagents and products concentrations are found as time-functions. In this way, the optimal route of production technology of boron carbide-based nanomaterials can be identified.

**Keywords:** modeling; chemical synthesis; liquid charge; nanocomposite; boron compounds



**Citation:** Chkhartishvili, L.; Antashvili, L.; Dalakishvili, L.; Chedia, R.; Tsagareishvili, O.; Mikeladze, A. On Modeling of Synthesis Process of Boron Carbide Based Nanocomposites. *Condens. Matter* **2021**, *6*, 3. <https://doi.org/10.3390/condmat6010003>

Received: 6 January 2021

Accepted: 15 January 2021

Published: 18 January 2021

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## 1. Introduction

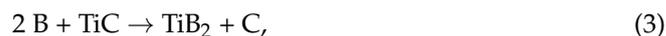
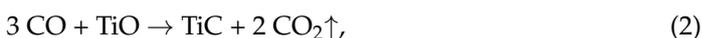
Because of complex properties useful for diverse industrial applications, hard nanocomposites based on boron carbide (with the approximate chemical formula  $B_4C$ ) serve for an important class of advanced materials. In previous works [1–6], we developed an effective method of their chemical synthesizing in nanopowdered form from corresponding liquid charges. As is known (e.g., see [7]), optimization of the parameters of chemical technologies is possible through their mathematical modeling. Here, we develop a set of ordinary differential equations describing evolution of concentrations of reactants (reagents, intermediate substances, and products) of chemical reactions, in which the boron carbide/titanium diboride  $B_4C$ - $TiB_2$  nanocomposites are formed.

In the original technology developed, for boron (B), sources include amorphous boron (a-B), boron oxide ( $B_2O_3$ ), or boric acid ( $H_3BO_3$ ). A carbon source is some liquid organic compound  $C_xH_yO_z$  containing carbon (C), hydrogen (H), and oxygen (O). As for the titanium (Ti) source, usually a titanium dioxide ( $TiO_2$ ) powder is used for this purpose. The reagents are obtained in the process of a multi-stage heat treatment of the aqueous suspension of these precursors.

The B-containing reagent is always a powder of amorphous boron. Thus, the boron source practically does not change when a-B serves as the precursor material. Organic solvent pyrolysis reduces the most part of carbon into carbon black with turbostratic graphite structure. Besides, carbon is emitted with carbon dioxide ( $CO_2$ ). At temperatures higher than  $\sim 700$  °C, C reacts with  $CO_2$  forming carbon monoxide (CO):  $CO_2 + C \rightarrow 2 CO$ . Note that the production of a carbide-based composite requires free carbon in excess. Under corresponding conditions, C-containing reagents are not  $CO_2$  and CO, but C and CO. As for carbon, during the heat pretreatment,  $TiO_2$  is retained in powdered form almost without changes.

## 2. Formally Simple Chemical Reactions Representing Technology

According to the standard mathematical modeling method [8] of the technological process, the corresponding physical-chemical transformation has to be imagined as a set of (formally) simple, irreversible, homogeneous, and isothermal chemical reactions conducted in a closed volume. Transformation of reagents B, C, CO, and TiO<sub>2</sub> into products B<sub>4</sub>C and TiB<sub>2</sub> seems to occur through the following reactions:



Hence, in addition to boron carbide (B<sub>4</sub>C) and titanium diboride (TiB<sub>2</sub>) the product is carbon dioxide (CO<sub>2</sub>) as well. Free carbon (C) being a reagent in Reactions (1) and (4) is an intermediate substance in Reaction (3). Similarly, carbon monoxide (CO) is a reagent in Reaction (2) and an intermediate substance in Reaction (1). Finally, titanium oxide (TiO)—according to Reactions (1) and (2)—and titanium carbide (TiC)—according to Reactions (2) and (3)—serve only as intermediate substances.

By definition, the order of a chemical reaction is the total number of particles—“molecules”—participating in an elementary collision act. Therefore, for Reactions (1)–(4), the orders are 2, 4, 3, and 5, respectively. As practice shows, the order of a simple chemical reaction cannot exceed 3 and, therefore, Reactions (2) and (4) seem to be complex. However, the establishment of real, i.e., effective, orders for these reactions requires more detailed consideration of their chemical mechanisms.

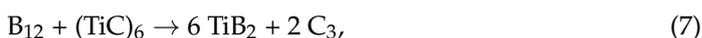
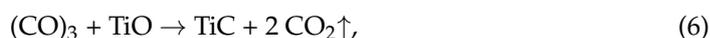
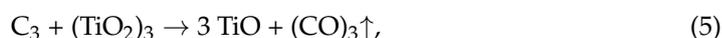
First, note that the icosahedral cluster B<sub>12</sub> is the main structural motif for any condensed phase of elemental boron (as well as boron-rich compounds), including amorphous boron [9]. It remains stable only in the material’s bulk and, upon (in our case, high-temperature) ablation from the powder particle surface, takes a quasiplanar form with broken bonds and, accordingly, greatly increased chemical activity [10]. For this reason, it is natural to think that, not four individual B atoms, but a B<sub>12</sub> quasiplanar cluster enter into the reaction. Clusters formation is also characteristic of carbon ablation process. One of the highest mass spectrometric peaks corresponds to C<sub>3</sub> clusters [11]. Therefore, the mechanism of Reaction (4) can be represented as the interaction of only two particles: clusters B<sub>12</sub> and C<sub>3</sub>.

Similarly, the mechanism of Reaction (3), in which elemental boron also acts as a reagent, seems to be the interaction of B<sub>12</sub> cluster with the (TiC)<sub>6</sub> fragment of the titanium carbide structure.

At high temperatures, in a medium containing both carbon and oxygen, various oxycarbon structures are formed. Among the small oxycarbon clusters [12], only (CO)<sub>3</sub> is metastable and, for this reason, hyperactive chemically. Therefore, the mechanism of Reaction (2) can be imaged as the interaction of a metastable cluster (CO)<sub>3</sub> with a fragment of the titanium oxide structure in the form of a diatomic TiO molecule.

In its original form, the order of Reaction (1) is already 2. However, it is most likely carried out not by the interaction between C atom and TiO<sub>2</sub> molecule [13], but some small carbon cluster, for example the same C<sub>3</sub> and the corresponding fragment (TiO<sub>2</sub>)<sub>3</sub> of the titanium dioxide structure.

Thus, the production of B<sub>4</sub>C–TiB<sub>2</sub> nanocomposite powder is (formally) represented by the following combination of simple chemical reactions:





Note that all of them are of second order, since reagents are represented by pairs of clusters.

Because all reactants (reagents, intermediates, and products) are in dispersive (nanopowdered or even free cluster) or gaseous forms, their mixing is assumed to be good enough to consider distribution of reactants concentrations in the reaction space, i.e., chamber volume, as almost homogeneous.

Now, we have to discuss another key assumption of the model used: chemical closeness of the reaction chamber or lack of exchange of matter with environment. Most reactants are in the solid phase and, consequently, remain in the chamber during whole technology process. There are only two reactants, CO and CO<sub>2</sub>, in the gas phase. In Reaction (2), gaseous CO produced from the precursor mixture serves for a reagent together with intermediate CO produced in Reaction (1). Thus, at the properly chosen charge composition, no presence of free (not reacted) CO is expected in the system. CO<sub>2</sub>, the final gaseous product, is carried away from the chamber by an inert gas (e.g., argon) flow. As mentioned above, in principle, carbon dioxide can react with carbon. However, at the properly chosen charge composition, no presence of free (not reacted) C is expected. It means that CO<sub>2</sub> left in the system would behave as an inert gas and then dispute the exchange of CO<sub>2</sub> gas with environment, the reaction chamber effectively remaining closed.

### 3. Reactions Rates

From the acting masses law, the rates  $V_1$ ,  $V_2$ ,  $V_3$ , and  $V_4$  of second-order chemical Reactions (5)–(8) are square functions of corresponding reagents or intermediates concentrations (number of formula unit “molecules” per unit volume) [B], [C], [CO], [TiO<sub>2</sub>], [TiO], and [TiC]:

$$V_1 = k_1[C][TiO_2], \quad (9)$$

$$V_2 = k_2[CO][TiO], \quad (10)$$

$$V_3 = k_3[B][TiC] \quad (11)$$

$$V_4 = k_4[B][C]. \quad (12)$$

By definition, the reaction constants  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are positive and not dependent on the reagent concentrations. However, their temperature-dependence (Arrhenius law) is quite significant, and, when the thermal treatment is not isothermal, reaction constants are also complex time-functions. In the technology under consideration, at the heating stage, reagents are formed from precursor charge, while the basic chemical Reactions (5)–(8) proceed too slowly. As for the cooling stage, it starts after all the reagents and products are completely consumed and formed, respectively. Therefore, the assumption that the technology is almost isothermal and the corresponding reaction rates are time-constants is acceptable. Such assumption significantly simplifies the system of chemical kinetics equations and, consequently, its solution.

The rate of change of a reagent concentration is opposite in sign to the reaction rate, i.e., negative. On the contrary, the rate of change of a product concentration should be positive. In both cases, the reaction rate magnitude is multiplied by the stoichiometric coefficients of corresponding reagents. Thus, the partial rates of changing of reactants concentrations with time  $t$  are:

$$\begin{aligned}
 \frac{d[C]_{(1)}}{dt} &= -V_1 = -k_1[C][TiO_2], \\
 \frac{d[TiO_2]_{(1)}}{dt} &= -V_1 = -k_1[C][TiO_2], \\
 \frac{d[TiO]_{(1)}}{dt} &= +V_1 = +k_1[C][TiO_2], \\
 \frac{d[CO]_{(1)}}{dt} &= +V_1 = +k_1[C][TiO_2], \\
 \frac{d[CO]_{(2)}}{dt} &= -3V_2 = -3k_2[CO][TiO], \\
 \frac{d[TiO]_{(2)}}{dt} &= -V_2 = -k_2[CO][TiO], \\
 \frac{d[TiC]_{(2)}}{dt} &= +V_2 = +k_2[CO][TiO], \\
 \frac{d[CO_2]_{(2)}}{dt} &= +2V_2 = +2k_2[CO][TiO], \\
 \frac{d[B]_{(3)}}{dt} &= -2V_3 = -2k_3[B][TiC], \\
 \frac{d[TiC]_{(3)}}{dt} &= -V_3 = -k_3[B][TiC], \\
 \frac{d[TiB_2]_{(3)}}{dt} &= +V_3 = +k_3[B][TiC], \\
 \frac{d[C]_{(3)}}{dt} &= +V_3 = +k_3[B][TiC], \\
 \frac{d[B]_{(4)}}{dt} &= -4V_4 = -4k_4[B][C], \\
 \frac{d[C]_{(4)}}{dt} &= -V_4 = -k_4[B][C], \\
 \frac{d[B_4C]_{(4)}}{dt} &= +V_4 = +k_4[B][C].
 \end{aligned}$$

Here  $[B_4C]$ ,  $[TiB_2]$ , and  $[CO_2]$  are the product concentrations. Summarizing these partial rates, we obtain the total rates of changing in concentrations of all the reactants:

$$\begin{aligned}
 \frac{d[B]}{dt} &= \frac{d[B]_{(3)}}{dt} + \frac{d[B]_{(4)}}{dt} = -2k_3[B][TiC] - 4k_4[B][C], \\
 \frac{d[C]}{dt} &= \frac{d[C]_{(1)}}{dt} + \frac{d[C]_{(3)}}{dt} + \frac{d[C]_{(4)}}{dt} = -k_1[C][TiO_2] + k_3[B][TiC] - k_4[B][C], \\
 \frac{d[TiO_2]}{dt} &= \frac{d[TiO_2]_{(1)}}{dt} = -k_1[C][TiO_2], \\
 \frac{d[CO]}{dt} &= \frac{d[CO]_{(1)}}{dt} + \frac{d[CO]_{(2)}}{dt} = +k_1[C][TiO_2] - 3k_2[CO][TiO], \\
 \frac{d[TiO]}{dt} &= \frac{d[TiO]_{(1)}}{dt} + \frac{d[TiO]_{(2)}}{dt} = k_1[C][TiO_2] - k_2[CO][TiO], \\
 \frac{d[TiC]}{dt} &= \frac{d[TiC]_{(2)}}{dt} + \frac{d[TiC]_{(3)}}{dt} = k_2[CO][TiO] - k_3[B][TiC], \\
 \frac{d[B_4C]}{dt} &= \frac{d[B_4C]_{(4)}}{dt} = +k_4[B][C], \\
 \frac{d[TiB_2]}{dt} &= \frac{d[TiB_2]_{(3)}}{dt} = +k_3[B][TiC], \\
 \frac{d[CO_2]}{dt} &= \frac{d[CO_2]_{(2)}}{dt} = +2k_2[CO][TiO].
 \end{aligned}$$

The numbers of “molecules” of intermediate substances reacted and produced per unit time, respectively, are equal each to other, so that the total rates of change in TiO and TiC concentrations are zero:

$$\frac{d[TiO]}{dt} = \frac{d[TiC]}{dt} = 0.$$

Consequently, the following conditions should be fulfilled:

$$k_1[C][TiO_2] = k_2[CO][TiO] = k_3[B][TiC].$$

#### 4. System of Chemical Kinetics Equations

Based on the above consideration, we obtain the system of chemical kinetic equations:

$$\frac{d[B]}{dt} = -2k_1[C][TiO_2] - 4k_4[B][C], \tag{13}$$

$$\frac{d[C]}{dt} = -k_4[B][C], \tag{14}$$

$$\frac{d[TiO_2]}{dt} = -k_1[C][TiO_2], \tag{15}$$

$$\frac{d[\text{CO}]}{dt} = -2k_1[\text{CO}][\text{TiO}_2], \quad (16)$$

$$\frac{d[\text{B}_4\text{C}]}{dt} = +k_4[\text{B}][\text{C}], \quad (17)$$

$$\frac{d[\text{TiB}_2]}{dt} = +k_1[\text{C}][\text{TiO}_2], \quad (18)$$

$$\frac{d[\text{CO}_2]}{dt} = +2k_1[\text{C}][\text{TiO}_2]. \quad (19)$$

If we denote  $[\text{B}] \equiv N_1(t)$ ,  $[\text{C}] \equiv N_2(t)$ ,  $[\text{TiO}_2] \equiv N_3(t)$ ,  $[\text{CO}] \equiv N_4(t)$ ,  $[\text{B}_4\text{C}] \equiv N_5(t)$ ,  $[\text{TiB}_2] \equiv N_6(t)$ , and  $[\text{CO}_2] \equiv N_7(t)$ , this system takes the new form:

$$\frac{dN_1(t)}{dt} = -4k_4N_1(t)N_2(t) - 2k_1N_2(t)N_3(t), \quad (20)$$

$$\frac{dN_2(t)}{dt} = -k_4N_1(t)N_2(t), \quad (21)$$

$$\frac{dN_3(t)}{dt} = -k_1N_2(t)N_3(t), \quad (22)$$

$$\frac{dN_4(t)}{dt} = -2k_1N_3(t)N_4(t), \quad (23)$$

$$\frac{dN_5(t)}{dt} = +k_4N_1(t)N_2(t), \quad (24)$$

$$\frac{dN_6(t)}{dt} = +k_1N_2(t)N_3(t), \quad (25)$$

$$\frac{dN_7(t)}{dt} = +2k_1N_2(t)N_3(t). \quad (26)$$

From these equations, it is clear that total rates of change in concentrations of reagents ( $N_1(t)$ ,  $N_2(t)$ ,  $N_3(t)$ , and  $N_4(t)$ ) and products ( $N_5(t)$ ,  $N_6(t)$ , and  $N_7(t)$ ) are definitely negative and positive, respectively. Thus, they are monotonously decreasing or increasing functions of time. Accordingly, at the relevant choice of charge composition at the final ( $t = \infty$ ) and initial ( $t = 0$ ) time moments, respectively, these concentrations are expected to equal zero:

$$N_1(\infty) = N_2(\infty) = N_3(\infty) = N_4(\infty) = N_5(0) = N_6(0) = N_7(0) = 0. \quad (27)$$

## 5. Initial Conditions

To solve the system of first-order ordinary differential equations describing the reagent and product concentration evolution with time, it is necessary to provide their concentrations at the initial ( $t = 0$ ) and final ( $t = \infty$ ) time moments, respectively:  $N_1(0)$ ,  $N_2(0)$ ,  $N_3(0)$ ,  $N_4(0)$ ,  $N_5(\infty)$ ,  $N_6(\infty)$ , and  $N_7(\infty)$ . Note that some of these values can be related to each other.

Let us introduce the stoichiometric coefficients  $1 - x$  and  $x$  for the product  $(\text{B}_4\text{C})_{1-x}(\text{TiB}_2)_x$  components, where  $x < 1$ . Thus,

$$\frac{N_5(\infty)}{N_6(\infty)} = \frac{1}{x} - 1.$$

Since boron carbide- (not titanium diboride-)based composites are considered, the inequality  $1 - x > x$  or  $x < 1/2$  must hold. Analogously, if  $1 - y$  and  $y$ , where  $y < 1$ , are the stoichiometric coefficients of the reagent components:  $\text{C}_{1-y}(\text{CO})_y$ , i.e.,  $\text{CO}_y$ , the following relation must hold:

$$\frac{N_2(0)}{N_4(0)} = \frac{1}{y} - 1.$$

If  $N$  denotes the final concentration of the product's basic component—boron carbide ( $B_4C$ )—then:

$$N_5(\infty) = N.$$

That of the product's other component—titanium diboride ( $TiB_2$ )—is:

$$N_6(\infty) = \frac{xN}{1-x}.$$

To find the rest of initial conditions, we need mass balance relations for all reagent and product constituents' chemical elements—B, C, Ti, and O. As  $[B]_0$  initial and  $[B]_\infty$  final concentrations of boron are equal:

$$N_1(0) = [B]_0 = [B]_\infty = 4N_5(\infty) + 2N_6(\infty) = \frac{2(2-x)N}{1-x}, N_1(0) = \frac{2(2-x)N}{1-x}.$$

As  $[C]_0$  initial and  $[C]_\infty$  final concentrations of carbon are equal:

$$N_2(0) + N_4(0) = [C]_0 = [C]_\infty = N + N_7(\infty), N_2(0) + N_4(0) - N_7(\infty) = N.$$

As  $[Ti]_0$  initial and  $[Ti]_\infty$  final concentrations of titanium are equal:

$$N_3(0) = [Ti]_0 = [Ti]_\infty = N_6(\infty), N_3(0) = N_6(\infty) = \frac{xN}{1-x}.$$

As  $[O]_0$  initial and  $[O]_\infty$  final concentrations of oxygen are equal:

$$\frac{2xN}{1-x} + N_4(0) = 2N_3(0) + N_4(0) = [O]_0 = [O]_\infty = 2N_7(\infty), 2N_7(\infty) - N_4(0) = \frac{2xN}{1-x}.$$

From the above-obtained system of three equations for three unknown quantities  $N_2(0)$ ,  $N_4(0)$ , and  $N_7(\infty)$ , we find their values:

$$N_2(0) = \frac{2yN}{(1-x)(1+y)}, N_4(0) = \frac{2(1-y)N}{(1-x)(1+y)}, N_7(\infty) = \frac{(1+x-(1-x)y)N}{(1-x)(1+y)}.$$

Finally, summarizing the results, we formulate the initial conditions to the system of Equations (20)–(26):

$$N_1(0) = \frac{2(2-x)N}{1-x}, \quad (28)$$

$$N_2(0) = \frac{2yN}{(1-x)(1+y)}, \quad (29)$$

$$N_3(0) = \frac{xN}{1-x}, \quad (30)$$

$$N_4(0) = \frac{2(1-y)N}{(1-x)(1+y)}, \quad (31)$$

$$N_5(\infty) = N, \quad (32)$$

$$N_6(\infty) = \frac{xN}{1-x}, \quad (33)$$

$$N_7(\infty) = \frac{(1+x-(1-x)y)N}{(1-x)(1+y)}. \quad (34)$$

### 6. Converting Problem into Dimensionless Form

It is expedient to analyze the problem in dimensionless form. Let us denote:

$$\kappa \equiv \frac{4k_4}{k_1}, \tag{35}$$

$$\tau \equiv \sqrt{k_1 k_4} N t, \tag{36}$$

$$n_i(\tau) \equiv \frac{N_i(t)}{N}. \tag{37}$$

In dimensionless kinetic-parameter  $\kappa$ , time-argument  $\tau$ , and unknown concentration-functions  $n_i(\tau)$ , the system of equations describing chemical kinetics takes the following form:

$$\frac{dn_1(\tau)}{d\tau} = -2\sqrt{\kappa}n_1(\tau)n_2(\tau) - \frac{4}{\sqrt{\kappa}}n_2(\tau)n_3(\tau), \tag{38}$$

$$\frac{dn_2(\tau)}{d\tau} = -\frac{\sqrt{\kappa}}{2}n_1(\tau)n_2(\tau), \tag{39}$$

$$\frac{dn_3(\tau)}{d\tau} = -\frac{2}{\sqrt{\kappa}}n_2(\tau)n_3(\tau), \tag{40}$$

$$\frac{dn_4(\tau)}{d\tau} = -\frac{4}{\sqrt{\kappa}}n_2(\tau)n_3(\tau), \tag{41}$$

$$\frac{dn_5(\tau)}{d\tau} = +\frac{\sqrt{\kappa}}{2}n_1(\tau)n_2(\tau), \tag{42}$$

$$\frac{dn_6(\tau)}{d\tau} = +\frac{2}{\sqrt{\kappa}}n_2(\tau)n_3(\tau), \tag{43}$$

$$\frac{dn_7(\tau)}{d\tau} = +\frac{4}{\sqrt{\kappa}}n_2(\tau)n_3(\tau). \tag{44}$$

The initial conditions for these dimensionless equations are:

$$n_{01} \equiv n_1(0) = \frac{2(2-x)}{1-x}, \tag{45}$$

$$n_{02} \equiv n_2(0) = \frac{2y}{(1-x)(1+y)}, \tag{46}$$

$$n_{03} \equiv n_3(0) = \frac{x}{1-x}, \tag{47}$$

$$n_{04} \equiv n_4(0) = \frac{2(1-y)}{(1-x)(1+y)}, \tag{48}$$

$$n_{\infty 5} \equiv n_5(\infty) = 1, \tag{49}$$

$$n_{\infty 6} \equiv n_6(\infty) = \frac{x}{1-x}, \tag{50}$$

$$n_{\infty 7} \equiv n_7(\infty) = \frac{(1+x-(1-x)y)}{(1-x)(1+y)}. \tag{51}$$

These conditions are formulated such that they guarantee the final concentrations of reagents  $n_{\infty 1} \equiv n_1(\infty)$ ,  $n_{\infty 2} \equiv n_2(\infty)$ ,  $n_{\infty 3} \equiv n_3(\infty)$ ,  $n_{\infty 4} \equiv n_4(\infty)$  and the initial concentrations of products  $n_{05} \equiv n_5(0)$ ,  $n_{06} \equiv n_6(0)$ ,  $n_{07} \equiv n_7(0)$  equal zero in the frames of numerical calculation errors:

$$n_{\infty 1} = n_{\infty 2} = n_{\infty 3} = n_{\infty 4} = n_{05} = n_{06} = n_{07} \approx 0. \tag{52}$$

Note that the subsystem of Equations (38), (39) and (40) can be resolved independently as they contain only three unknown functions  $n_1(\tau)$ ,  $n_2(\tau)$ , and  $n_3(\tau)$ . When these functions are found, the rest of the unknown functions are easily determinable from the rest of equations of full system. Excluding functions  $n_1(\tau)$  and  $n_2(\tau)$ , we obtain the equation determining the function  $n_3(\tau)$ :

$$\frac{dn_3(\tau)}{d\tau} + \frac{\sqrt{\kappa}n_3^2(\tau)}{1-\kappa} + \left(\frac{n_{01}}{2n_{03}^\kappa} - \frac{n_{03}^{1-\kappa}}{1-\kappa}\right) \frac{n_3^{1+\kappa}(\tau)}{\sqrt{\kappa}} = 0. \tag{53}$$

Its solution is:

$$\tau(n_3) = - \int_{n_{03}}^{n_3(\tau)} \frac{dn'}{\frac{\sqrt{\kappa}n'^2}{1-\kappa} + \left(\frac{n_{01}}{2n_{03}^\kappa} - \frac{n_{03}^{1-\kappa}}{1-\kappa}\right) \frac{n'^{1+\kappa}}{\sqrt{\kappa}}}. \tag{54}$$

In particular, for the parameter  $\kappa = 1/2$ , we can explicitly evaluate this integral:

$$\begin{aligned} \tau(n_3) &= -\frac{1}{\sqrt{2}} \int_{n_{03}}^{n_3(\tau)} \frac{dn'}{n'^2 + \left(\frac{n_{01}}{2\sqrt{n_{03}}} - 2\sqrt{n_{03}}\right) n'^{3/2}} = \\ &= \frac{2\sqrt{2}n_{03}}{n_{01}-4n_{03}} \left( \sqrt{\frac{n_{03}}{n_3}} - 1 + \frac{2n_{03}}{n_{01}-4n_{03}} \ln \frac{1 + \frac{2n_{03}}{n_{01}-4n_{03}}}{\sqrt{\frac{n_{03}}{n_3} + \frac{2n_{03}}{n_{01}-4n_{03}}}} \right). \end{aligned} \tag{55}$$

However, to obtain the explicit function  $n_3(\tau)$ , we need to invert the latter expression for  $\tau(n_3)$ , which is impossible.

Instead, below, we solve the system of ordinary differential Equations (38)–(44) with initial Conditions (45)–(51) numerically at  $\kappa = 1/2$  and; then, to check the correctness of the analytical Solution (55), we calculate that solution at discrete values of  $n_3$  obtained numerically. After that, we build an inverse plot, the discrete set of values calculated by Equation (55) vs. these discrete values of  $n_3$ , together with the numerical solution for  $n_3$ . If Solution (55) is correct, these two plots must coincide in the frames of numerical calculation errors.

### 7. Numerical Solution Code

To solve Equations (38)–(44) numerically, we first need to fix the dimensionless parameter  $\kappa$  contained in this set of equations. Formula (35) determines it by the ratio of reaction constants  $k_1$  and  $k_4$ .

On the one hand,  $k_1$  is the constant of Reaction (1), in which carbon C reacts with titanium dioxide  $TiO_2$ . The chain of Reactions (1)–(3) leads to the formation of one of the final products, namely titanium diboride  $TiB_2$ . A  $TiB_2$  molecule is formed per C atom. On the other hand,  $4k_4$  is the constant of Reaction (4), in which carbon C reacts with boron B. That reaction directly leads to the formation of other final product, namely boron carbide  $B_4C$ . Again, a  $B_4C$  molecule is formed per C atom.

Thus, obtaining  $B_4C$ – $TiB_2$  compositions means that above reaction rates meet the following condition:  $k_1 > 4k_4$  or  $0 < \kappa < 1$  (note that the integral in above-obtained Solution (54) is divergent at  $\kappa = 1$ ). For test-calculations, let us take this parameter at the interval midpoint:  $\kappa = 1/2$ .

We applied Python to solve Equations (38)–(44) numerically. More specifically, a Scipy Library was used to obtain the results and Matplotlib to draw the corresponding graphs. The methods were Odeint and Cumtrapz.

First, we created the function that describes the system and returns the  $1 \times 3$  matrix of derivatives of reduced concentrations  $n_1$ ,  $n_2$ , and  $n_3$  of reagents. Taking  $\kappa$  as the fixed number of 0.5, we used the relation

$$y = \frac{1-x}{1+x}$$

for loop to change the  $x$  parameter from 0 to 1. The  $y$  parameter that depends on  $x$  changed accordingly.

For each value of parameter  $x$ , we have different initial conditions and transmit our function to the Odeint solver as an argument that gives us the solutions written as three column matrices with rows of the same number as dimensionless time-steps. Each column corresponds to the concentration of reagents for the different time values. From these three concentrations, we find the change of the fourth reagent concentration  $n_4$  change in time with the help of Cumtrapz algorithm. We use the same scheme (Cumtrapz) to obtain the results for reduced concentrations  $n_5, n_6,$  and  $n_7$  of products. After that, we draw the corresponding graphs and then choose the ones that satisfy initial (final) conditions.

In addition, we compared the results to the analytical solution that we defined as another function, Tau, that depends on  $n_3$  and the initial concentrations of the first and third reagents:  $n_{01}$  and  $n_{03}$ . It was impossible for us to determine analytically the solutions of  $n_3$  from the equation that contained variable Tau. Thus, to check our results, we did the inverse operation and put the values of its arguments  $n_3, n_{01},$  and  $n_{03}$  into analytically obtained function Tau and compared it with the numerical solution of the same function. The results show that they matched perfectly.

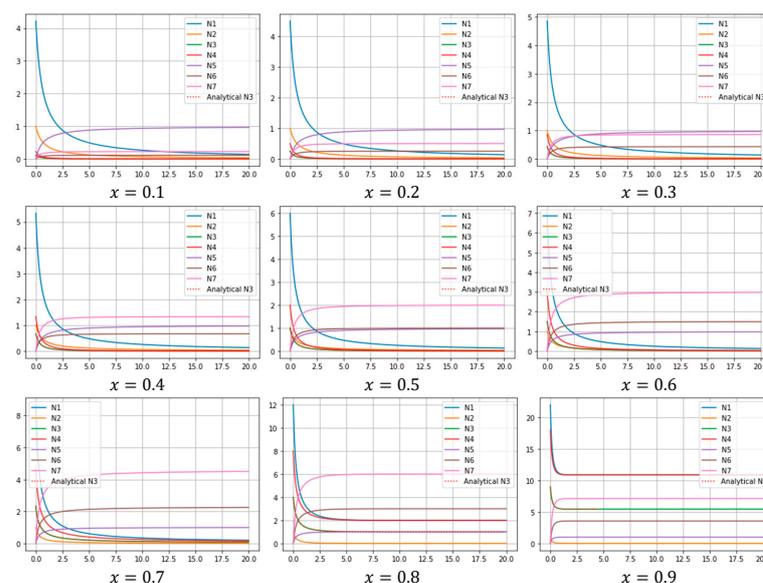
### 8. Test Solutions

Table 1 summarizes the initial conditions used in numerical solutions.

**Table 1.** Initial and final reduced concentrations of reagents  $n_{0i}$  and products  $n_{\infty i}$ , respectively, at different stoichiometric ratio  $x$  of synthesized  $(B_4C)_{1-x}(TiB_2)_x$  composite.

| $x$            | 0.1  | 0.2  | 0.3  | 0.4  | 0.5  | 0.6  | 0.7  | 0.8   | 0.9   |
|----------------|------|------|------|------|------|------|------|-------|-------|
| $n_{01}$       | 4.22 | 4.50 | 4.86 | 5.33 | 6.00 | 7.00 | 8.67 | 12.00 | 22.00 |
| $n_{02}$       | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00  | 1.00  |
| $n_{03}$       | 0.11 | 0.25 | 0.43 | 0.67 | 1.00 | 1.50 | 2.33 | 4.00  | 9.00  |
| $n_{04}$       | 0.22 | 0.50 | 0.86 | 1.33 | 2.00 | 3.00 | 4.67 | 8.00  | 18.00 |
| $n_{\infty 5}$ | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00  | 1.00  |
| $n_{\infty 6}$ | 0.11 | 0.25 | 0.43 | 0.67 | 1.00 | 1.50 | 2.33 | 4.00  | 9.00  |
| $n_{\infty 7}$ | 0.22 | 0.50 | 0.86 | 1.33 | 2.00 | 3.00 | 4.67 | 8.00  | 18.00 |

The corresponding curves are presented in Figure 1.



**Figure 1.** Calculated time-dependences of reagents and products concentrations at different stoichiometric ratio  $x$  of synthesized  $(B_4C)_{1-x}(TiB_2)_x$  composite.

As expected, the concentrations of reagents and products are monotonously increasing and decreasing functions of time, respectively. The initial concentrations of all products are zero. As for the final concentrations of reagents, in most cases, they vanish as well. However, at stoichiometric ratio  $x$  close to 1 ( $x \geq 0.8$ ), their saturation levels exceed 0. The explanation seems to be related with impossibility at too high  $x$  to meet mass balance relations for all chemical elements participating in the reactions, in particular carbon.

### 9. Possibility of Method Extending to Other Nanocomposites

To not be restricted only by boron carbide/titanium diboride nanocomposites, let us discuss the generalization possibilities of the developed method of mathematical modeling of the chemical reaction kinetics taking place during production of a nanopowder material. There seem to be two different directions of such analysis: separate production of boron carbide as basic component of this class of composites and simultaneous production of components of other biphasic nanocomposites.

A comprehensive review on boron carbide synthesis and consolidation methods given in [14] can serve for obtaining data explainable/interpretable within the model proposed here for the chemical synthesis of boron carbide-based nanocomposites. The main methods of boron carbide production are carbo- or magnesiothermic reductions, synthesis from elements or polymer precursors, and vapor phase reactions. However, commercially, boron carbide is produced only by the first two: carbothermic reduction of boric acid in electric furnace or its magnesiothermy in the presence of carbon. Our modeling method is applicable for carbothermic reduction, synthesis from elements, and synthesis from polymer precursors. Thus, it is expedient to characterize them briefly.

The yield of carbothermic reduction is relatively low due to losses of boron due to boron oxides formation. Despite this, carbothermic reduction is usually adopted as a commercial method because of the simple equipment and cheap raw material used. However, it is not suitable for the production of boron carbide enriched in boron isotopes because such a raw material is too expensive. The overall reaction,  $4 \text{H}_3\text{BO}_3 + 7 \text{C} \rightarrow \text{B}_4\text{C} + 6 \text{CO} + 6 \text{H}_2\text{O}$ , of carbothermic reduction of boric acid ( $\text{H}_3\text{BO}_3$  (and boron trioxide  $\text{B}_2\text{O}_3$ )) proceeds in three stages:  $4 \text{H}_3\text{BO}_3 \rightarrow 2 \text{B}_2\text{O}_3 + 6 \text{H}_2\text{O}\uparrow$ ,  $\text{B}_2\text{O}_3 + 3 \text{CO}\uparrow \rightarrow 2 \text{B} + 3 \text{CO}_2\uparrow$ , and  $4 \text{B} + \text{C} \rightarrow \text{B}_4\text{C}$ . On heating,  $\text{H}_3\text{BO}_3$  converts into  $\text{B}_2\text{O}_3$  (releasing water ( $\text{H}_2\text{O}$  vapor)), reduction of which with CO is thermodynamically feasible above 1400 °C. However, the temperature in the reaction area is usually maintained at higher temperatures, ~2000 °C, to enhance the reaction rate as the boron carbide formation is a highly endothermic process (needing 16,800 kJ/mol).

According to the thermodynamic studies of gas phase carbothermic reduction of boron anhydride,  $\text{B}_2\text{O}_2$  and BO are formed from  $\text{B}_2\text{O}_3$  in reactions  $\text{B}_2\text{O}_3 + \text{C} \rightarrow \text{B}_2\text{O}_2 + \text{CO}$  and  $\text{B}_2\text{O}_3 + \text{C} \rightarrow 2 \text{BO} + \text{CO}$  and then reduced to free boron or target product—boron carbide. In particular,  $\text{B}_4\text{C}$  nanopowders can be prepared by reduction of  $\text{B}_2\text{O}_3$  vapor by carbon black at 1350 °C.

Synthesis from elements is mostly considered as a non-commercial route of boron carbide production due to the high cost of elemental boron. It is preferred only for obtaining chemically very pure or enriched in B-isotopes boron carbides. In this technology, B and C powders are mixed to form an almost homogeneous mixture, pellets of which are then reacted at temperatures of >1500 °C in vacuum or inert atmosphere. There are some reported attempts of the preparation of nanostructure boron carbide in this way.

Synthesis of boron carbide from polymer precursors is an alternative to the above-described high temperature techniques. Some B-containing organic compounds such as carborane ( $\text{C}_2\text{B}_n\text{H}_{n+2}$ ), triphenylborane, polyvinyl pentaborane, borazine, etc. on pyrolysis in the temperature range 1000–1500 °C in vacuum or inert atmosphere yield  $\text{B}_4\text{C}$  powder. In addition, a free-flowing boron carbide powder can be obtained from boric acid and sugar mixture dissolved in ethylene glycol, dried in air at ~180 °C, and then heated in hydrogen at ~700 °C.

Reaction kinetics and, consequently, quality of  $B_4C$  product are strongly affected by the feed charge porosity/dispersity, chemical composition, type of carbon used, heating/cooling rates, and treatment temperature and duration in the reactor core. A comparative summary of details of various experimental data summarized in [14] can serve for refinement reaction constants needed for mathematical modeling of the chemical technologies for obtaining boron carbide powders.

As for the biphasic nanocomposites, below, we consider the case of functional compositions of strongly correlated electron oxides, materials with important potential applications in spintronics and energy devices.

Recently, a low-temperature (and thus also low-cost) and scalable sol-based synthesis route has been reported [15] for prototypical bimagnetic  $LaFeO_3-CoFe_2O_4$  (LFO-CFO) nanocomposites. In the corresponding reaction mechanism, both phases are formed simultaneously and the CFO heat of formation assists the LFO phase crystallization. Besides, a symbiotic phenomenon is observed: LFO matrix restricts the growth of CFO particles. In this technology, at first, two separate sols are prepared by dissolving at room temperature the precursors of LFO ( $La(NO_3)_3 \cdot 6H_2O$  and  $Fe(NO_3)_3 \cdot 9H_2O$ ) and CFO ( $Co(NO_3)_2 \cdot 6H_2O$  and  $Fe(NO_3)_3 \cdot 9H_2O$ ) in distilled water added with glycine acting as the chelating agent. These two solutions are mixed, and then the composite sol is heated to 80 °C. Next, the temperature is increased and maintained at 150 °C until the formation of a gel. Finally, the temperature is increased up to 250 °C, when a self-combustion reaction occurs and yields a powder product.

Multiferroic  $Pb(Zr,Ti)O_3-CoFe_2O_4$  (PZT-CFO) nanocomposites have been prepared [16] in a similar synthesis technique that maximizes the surface contact area and, hence, interfacial coupling between the ferroelectric (PZT) and ferrimagnetic (CFO) phases. First, sols of PZT and CFO are prepared separately. PZT precursor solution is prepared by dissolving at room temperature lead acetate ( $Pb(CH_3COO)_2 \cdot 3H_2O$ ), zirconium propoxide ( $Zr(CH_2CH_2CH_3O)$ ) and titanium isopropoxide ( $Ti(OCH(CH_3)_2)$ ) in 2-methoxyethanol and acetic acid, and then zirconium propoxide and titanium isopropoxide are added. Similarly, CFO precursor solution is prepared by dissolving at room temperature cobalt acetate tetrahydrate ( $(CH_3COO)_2Co \cdot 4H_2O$ ) and iron nitrate nonahydrate ( $Fe(NO_3)_3 \cdot 9H_2O$ ) in 2-methoxyethanol and acetic acid, and then ethanolamine and ethanolamine are added. The mixed precursor solution is first stirred at room temperature and then at 80 °C. Next, the temperature is increased and maintained at ~150 °C until the gel formation. Then, the temperature is increased to ~300 °C, when a self-combustion reaction occurs yielding a powder.

In such biphasic composite, PZT component can be replaced [17] by strontium hexaferrite ( $SrFe_{12}O_{19}$ ) (SFO) component, also prepared by the sol-gel combustion. First,  $Fe(NO_3)_3 \cdot 9H_2O$  and  $Sr(NO_3)_2 \cdot 6H_2O$  precursors are dissolved in deionized water. Then, a citric acid aqueous dispersion is added at room temperature.  $NH_3$  is added drop-wise. Next, sol is heated to 80 °C to form a gel. After the entire solution is converted into a gel, the temperature is increased to 300 °C inducing self-combustion and obtaining the dry powders. This sol-gel synthesis procedure can be directly adapted to simultaneously prepare the exchange-coupled hard/soft biphasic nanocomposite  $SrFe_{12}O_{19}-CoFe_2O_4$  (SFO-CFO).

Thus, sol-gel self-combustion synthesis is an efficient and reproducible approach to synthesize biphasic nanocomposites. Optimizing of the synthesis conditions decreases the thermal treatment temperature, allows controlling the nanocrystallites size, and, in this way, improves the product quality. These nanocomposites reveal synthesis conditions and charge composition effect on their magnetic properties.

Despite the radical differences in chemical compositions, the obtained technologies of two biphasic nanocomposite powders, such as boron carbide/titanium diboride and strongly correlated electron oxides, show similarities to each other: both materials are obtained as a result of multi-stage heat-treatments of sol charges—precursors solved in water and liquid organic compounds. Therefore, if we write down the kinetic equations for the chemical reactions occurring during the sol-gel synthesis of strongly correlated electron

oxides (LFO–CFO, PZT–CFO, SFO–CFO, etc.) [15–17], then the mathematical modeling of this technology can be carried out using the method developed by us for the synthesis of boron carbide/titanium diboride nanocomposite powders.

## 10. Concluding Remarks

In summary, based on the analysis of mechanisms of chemical reactions taking place during synthesis from liquid charge of the nanopowder composites of boron carbide and titanium diboride, a system of ordinary differential equations simulating kinetics of this technology is suggested. B, C, TiO<sub>2</sub>, and CO are considered as reagents, while the expected products are B<sub>4</sub>C, TiB<sub>2</sub>, and CO<sub>2</sub>.

This set of equations is resolved numerically for a typical ratio of reaction constants at different stoichiometric ratios  $x$  of components B<sub>4</sub>C and TiB<sub>2</sub> in target composites (B<sub>4</sub>C)<sub>1-x</sub>(TiB<sub>2</sub>)<sub>x</sub>. In this way, reagent and product concentrations are found as time-functions. As expected, the concentrations of reagents and products are monotonously increasing and decreasing functions of time, respectively. The correctness of the specially elaborated computing code is proved by perfect matching of an analytical solution with the corresponding numerical one.

This method of mathematical modeling will lead to the optimization of parameters of production technology of hard nanocomposites based on boron carbide. Besides, it can be extended to separate production of boron carbide as basic component of this class of composites, as well as synthesizing other biphasic nanocomposites.

**Author Contributions:** Conceptualization, L.C. and R.C.; methodology, L.C.; software, L.A. and L.D.; validation, L.A. and L.D.; formal analysis, L.C. and R.C.; investigation, O.T. and A.M.; resources, O.T.; data curation, A.M.; writing—original draft preparation, L.C., L.A. and L.D.; writing—review and editing, L.C.; visualization, L.A. and L.D.; supervision, L.C.; project administration, L.C. and O.T.; funding acquisition, L.C., O.T. and A.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Shota Rustaveli National Science Foundation of Georgia, grant number AR-18-1045: “Obtaining of boron carbide-based nanostructured heterophase ceramic materials and products with improved performance characteristics”.

**Conflicts of Interest:** The authors declare no conflict of interest.

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