

Basic Models of Volume Synthesis of Ti-Based Composites

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Abstract

The paper demonstrates the capability of the volume synthesis models for the prognosis of final composition. The simplest models for the titanium-based composites synthesis are presented. The melting with the gradual formation of liquid phase in the given temperature interval is taken into account. The controlling for the process is carried out at the expense of the heating rate change, variation of the initial composition of the mixture. The models were realized numerically. It was demonstrated that the irreversible final phase composition was obtained for all situations.

Keywords

Composite synthesis; numerical modeling; detailed kinetics; irreversible composition.

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Introduction

SHS-methods can be used in composite synthesis [1–5]. The volume synthesis or the synthesis in the explosion mode obeys some preference in comparison with the mode of layerwise combustion, since, for this mode, the best homogenization of synthesized product is observed and it is possible to control the process of changing the conditions of the thermal contact between the reacting system and the environment and between the reacting system and the heater. This process can be controllable also when the initial mixture composition is varied, the inert particles are used as admixtures; the heating rate and the heating method are changed; the external mechanical loading is applied [6–10]. In various synthesis methods, when thermal explosion mode is realized, the reactions can proceed in various ways depending on the equipment and are accompanied by the high heat release that can decrease due to inert admixtures or non-stoichiometric initial composition. The final composition of the synthesis product turns out irreversible and depends on numerous factors. The qualitative physical regularities were described on the basis of the known classical models [11]. The models of thermal explosion based on the reactive cell concept are very popular [12, 13]. However, the irreversible conditions typical for thermal explosion do

not agree with the suggested sequence of chemical stages. To develop the models to predict the irreversible composition of the product, various synthesis conditions were analyzed and a series of models was suggested taking into account the staging of the conversion.

Methods and materials

The titanium-based composites synthesized from non-stoichiometric mixtures $\text{Ti} + \text{C}$, B , Si and $(\text{Ti} + \text{Al}) + \text{C}$, B , Si with titanium excess were chosen for the investigation. For example, in the first case, it is expected that the composites $\text{Ti} + \text{TiC}$; $\text{Ti} + \text{TiB}_2$ and $\text{Ti} + \text{Ti}_5\text{Si}_3$ will be obtained. The ideal summary reaction schemes for first of them

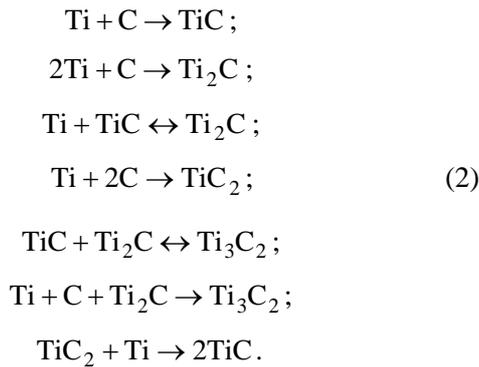


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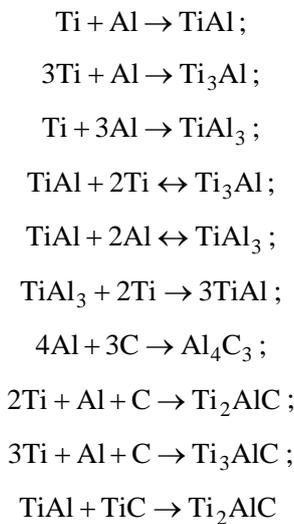


can be complicated at the cost of taking into account the solid solution $\text{Ti} + \text{C}$ and non-stoichiometric carbide Ti_aC_b formation that corresponds to broad homogeneity area on the state diagram $\text{Ti}-\text{C}$.

A more complex reaction scheme will include the reactions with irreversible products [14]:



Aluminum addition complicates the reaction scheme. We should add the reactions



to the previous scheme. The reaction rates depend on concentrations correspondingly to the mass action law. However, it is known that for the reactions with solid substances participation, the diffusion is the limiting stage determining the reaction rates. Because the spatial scale where the diffusion occurs (it is the level of individual grains, particles and interfaces between them) is much smaller than the heat scale, the simplifications are inevitable. We believe that micro scale processes are taken into account in the activation energies evaluation and in kinetic functions. The reaction retardation by a solid product gets the reflection in a special multiplier for each reaction rate

$$f = \exp(-s\eta_s)(\eta_0 + \eta_s)^{-p},$$

where η_s is the part of solid products; s, p are retardation parameters. The part of solid products has been determined in the melting temperature interval for the reacting mixture. The modification of kinetic functions is based on the results [15]. Formal-kinetic parameters have been found based on chemical thermodynamics. Activation energies have been proved

using the known data for diffusion coefficients. The qualitative behavior of kinetic equation's system depends on the dynamics of the temperature change determined by the experimental conditions. When the temperature distribution along the specimen, the thickness of chamber walls, and mechanical loading conditions were taken into account, we came to more complex mathematical models. As a result, we obtained the different models of solid-phase reactors [16–21]. All models were realized numerically.

Examples

The simplest model [16] corresponds to the pressing of small size when the temperature distribution can be neglected. In this approximation, only one reaction (1) takes place that corresponds to the summary reaction scheme. We believe that the melting is observed in some temperature interval between the solidus and liquidus temperatures, where the liquid phase part changes with some kinetic law. The pressing was heated by radiant heat from vacuum chamber walls (from the heater). The heating rate was controlled by heater temperature T_W that changes corresponding to given law. For illustration linear law is taken $T_W = T_0 + at$. The heating is switched when wall temperature achieves to given value Activation energy and chemical heat release is $E_a = 2.1 \cdot 10^5$ J/mol; $Q_0 = 1.73 \cdot 10^4$ J/cm³. Strong retardation of the reaction by reaction product is assumed for $s_0 = 10$. The numerical experiment showed the reaction does not complete during given time that connects with the heat losses by various physical mechanisms and with reaction retardation. The thermal explosion mode is feasible additionally to slow down the conversion. Fig. 1 illustrates the dynamics of the synthesis process. Critical wall temperature T_W^* exists, after which the thermal explosion realizes. For example, for volume part of carbon in the initial powder mixture $\xi = 0.2$, when wall temperature grows to 2480 K, one can see the specimen temperature behavior similar to thermal explosion (Fig. 1a) with conversion level near to 0.6 (Fig. 1b). Reaction goes basically in liquid phase that exists during long time (Fig. 1c). If the wall temperature grows to 2475 K (Fig. 2), the reaction goes slowly without temperature excursion. The part of liquid phase is less than in previous case. For $T_W = 2400$ the reaction proceeds very slowly in solid phase (this is not shown in pictures).

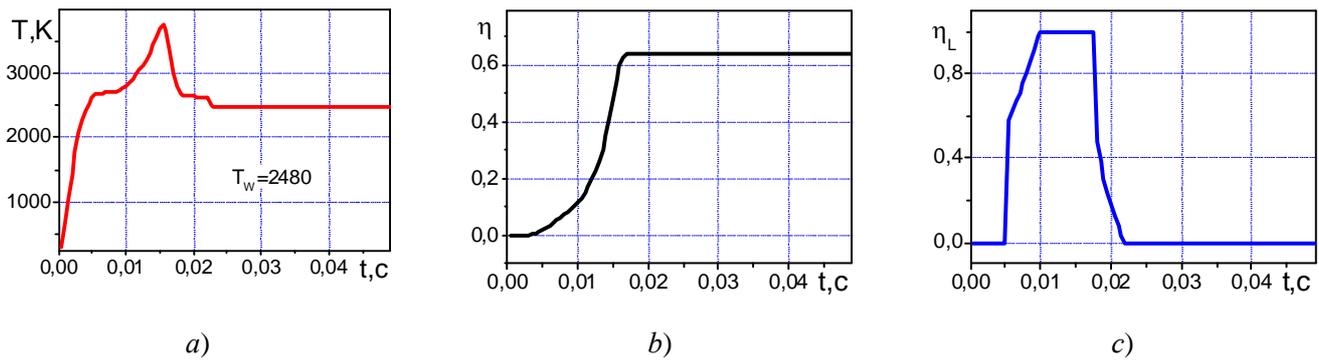


Fig. 1. Dynamics of composite T-TiC synthesis:

a – temperature; *b* – conversion level; *c* – part of liquid phase versus the time, $T_w = 2480$

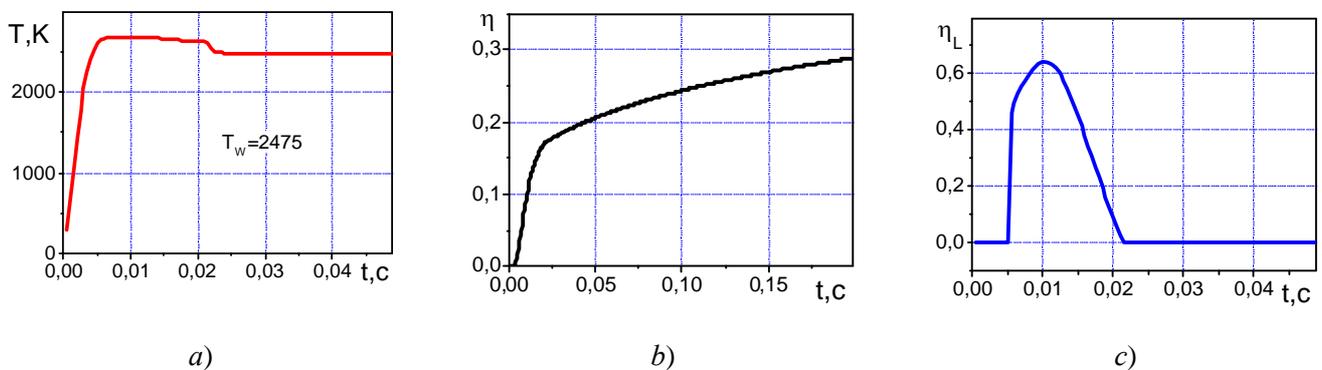


Fig. 2. Dynamics of composite T-TiC synthesis:

a – temperature; *b* – conversion level; *c* – part of liquid phase versus the time, $T_w = 2475$

The final composition varies depending on temperature T_w .

The second example illustrates the capability of the model with detailed reaction scheme (2). In this case we have the heat balance equation in the form similar to [6]. However, the overall chemical heat release includes the heats from nine reactions. The reaction retardation depends on the overall concentration of phases. To find the mass concentrations the kinetic equations are necessary

$$\rho \frac{dy_k}{dt} = \omega_k,$$

where source terms, $\text{kg}/(\text{m}^3\text{s})$, takes the worm

$$\omega_k = \sum_{i=1}^9 v_{ki} m_k \varphi_i.$$

Here v_{ki} are stoichiometric coefficient of k species in the reaction i ; $y_k = \rho_k / \rho_s$ are mass concentrations, $\rho_k = \eta_k m_k$, $\rho_s = \sum_{(i)} \rho_i m_i$, η_k are molar

concentrations. If porosity evolution is taken into account, some kinetic equation should be added to the

model [16, 21]. At the initial time moment, we have the initial irreversible composition and initial porosity.

The problem is solved numerically. The Euler's method is used. The result depends on the stages that are taken into account, heating and cooling rates, and on the composition of initial mixture.

Fig. 3 illustrates the dynamics typical for the thermal explosion. Only three reactions are included in calculations: $\text{Ti} + \text{C} \rightarrow \text{TiC}$; $\text{Ti} + \text{TiC} \rightarrow \text{Ti}_2\text{C}$; $\text{Ti} + \text{C} + \text{Ti}_2\text{C} \rightarrow \text{Ti}_3\text{C}_2$. It is assumed that external heating is ceased, when chemical reactions accelerate, and then the Newton heat exchange continues with the environment with temperature $T_e = T_w$ reached to this time. The initial composition is $y_{\text{Ti}} = 0.8$ and $y_{\text{C}} = 0.2$ that corresponds to equal molar concentrations. It was found, the higher the wall temperature rate, the more the temperature near explosion time. The Liquid phase exists for a short time when the reaction rates are maximal. The final composition is the same for different heating rate. We see the presence in the product TiC , Ti_2C , Ti_3C_2 . The last phase concentration is very small. All carbides can be identified in experiment as non-stoichiometric carbides.

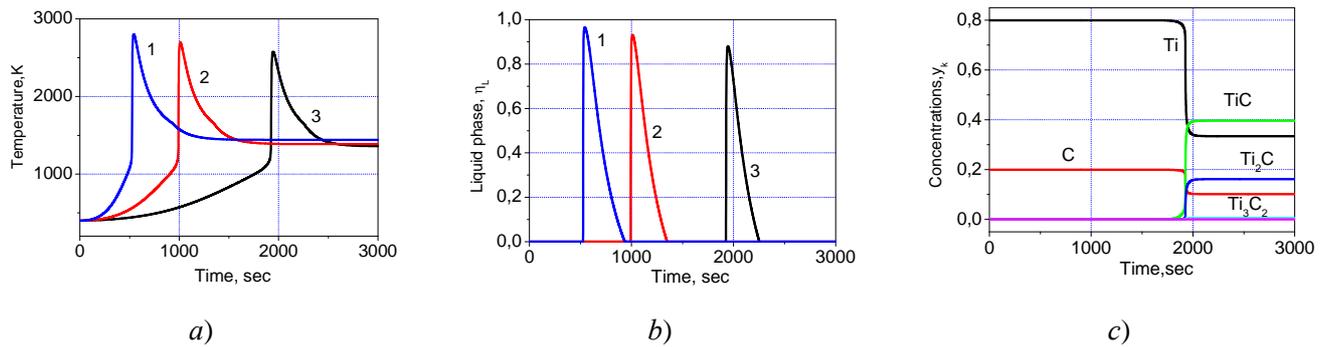


Fig. 3. Dynamics of composite synthesis.

a – temperature; *b* – part of liquid phase for different rise rate of wall temperature: 1 – 0.5; 2 – 1.0; 3 – 2.0 K/s; *c* – dynamics of phase composition change during volume synthesis for the case 1

If we take the initial composition with large titanium excess, thermal explosion mode is not observed. Reactions start without sharp temperature growths. If then the external heating continues we come to different final irreversible composition for different temperatures. This agrees qualitatively with the regularities observed experimentally.

Conclusions

The simplest models of volume synthesis of composites are presented. A similar approach taking into account the detailed reaction scheme is applicable for more complex situations. For example, composite synthesis can be carried out in a closed volume or in the container with walls of finite thickness. On the one hand, the walls demand the additional heat for heating to given temperature; on the other hand, the walls store the heat supporting the synthesis when the external heating is ceased or chemical heat release is not enough for reaction accomplishment. In this case, closed reactor walls exchange the heat with the heater immediately. The kinetic part of the problem is similar to the previous one. However, a thermal problem is more complex. The dynamics of this process was illustrated in [17] for the Al, Fe_2O_3 ; Fe; Cr; Ni system. The explicit accounting of the inert admixtures in the reacting composition leads to the specific degenerate mode [18]. For example, a combination of heating and mechanical loading, at the conditions of HIP (Hot Isostatic Pressing) or SPS (Spark Plasma Sintering), makes it possible to obtain a high density product with special properties. In this case, the dynamics of the synthesis depends on a bigger number of parameters. A mathematical model takes into account different methods of heating, including the Joule heating in the volume, the plunger heating, the heating through reactor walls, and symmetrical and non symmetrical

conditions of the loading. The synthesis mode depends additionally on geometrical parameters of the reactor. Various modifications of the model were described in [19–21]. Similar conditions can also lead to the irreversible composition of the product. From a mathematical point of view, the suggested model is a stiff set of ordinary equations that need accurate selection of the solution method. After that, the model could be used for the prognosis of the phase composition evolution with the variation of sintering conditions.

Acknowledgments

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