

Phase formation in Ti-CuO system under reactive sintering conditions

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Abstract. The present work presents a model of reactive sintering and some experimental data for the Ti-CuO system. This is a typical metallothermal mixture in which reactions are accompanied by high heat release. A non-equilibrium phase composition including intermetallide and oxide phases was obtained in the experiment. The kinetic model is based on formal kinetics and heat balance equation. A number of approximate semi-empirical approaches have been used to estimate the formal kinetic parameters. The results of calculations illustrate the dynamics of the process. The model allows the study of product composition under varying heating conditions and initial composition of the press.

Keywords: reaction sintering, composition, intermetallics.

1. Introduction

To date, combustion synthesis technologies as well as in the reactive sintering regime have become widespread due to fundamental research. In particular, it is shown that if the physicochemical parameters of the medium, as well as the instantaneous spatial distributions of temperature and concentration are known, it is possible to calculate the reaction rate in the entire reacting mixture. Because of this, such processes are controllable and allow the synthesis of materials with desired structure and properties. It is known that if the rate of heat release due to a reaction is lower than the rate of heat loss (e.g., due to conduction, convection), a self-sustaining process cannot be realized. This phenomenon is also key in bulk synthesis, as a self-propagating reaction (in the mode of combustion or thermal explosion) can lead to inhomogeneities in the microstructure of the material, which is tried to avoid. The process should be made controllable. Liquid-phase sintering is one of the most promising methods of material synthesis today [1]. About 90% of sintered materials are produced by this method.

Metal matrix composites are widely used in various fields, including mechanical engineering, aviation industry, and radio engineering. For example, metal composites can be used to manufacture structural elements of GTE (gas turbine engines) operating at low and high temperatures; also in electrical engineering there is an increased interest in copper compounds with strengthening particles as materials for high-current break contacts [2, 3]; polycrystalline diamond compacts are used for geological drilling, oil and gas exploration [4]. One of the interesting systems that can be used to produce a composite with strengthening oxide particles is a mixture of Ti and CuO powders. Copper has high ductility and electrical conductivity, while titanium is light, strong and corrosion resistant. In this case, the oxide is the most easily fusible component. Its interaction with titanium leads to chemical substitution reactions, which release energy, due to which the strengthening phase is evenly distributed in the matrix. When the melting point of one of the components in the system is reached, viscous flow occurs in which the liquid phase fills all voids, thus increasing the strength of the product by reducing porosity. In multicomponent systems, in addition to shrinkage, the process is accompanied by the formation of alloys and new compounds produced by chemical reaction. In this case, volumetric changes of the body, generally speaking, can have any sign, and sintering can be called reaction sintering [5]. Since with the formation of new compounds, the enthalpy of formation can be much higher than the melting point of the original components, due to which the pores can expand, sometimes this can lead to the destruction of the body.

The aim of the study was to analyze possible chemical transformations in powder mixtures and numerically implement a process model sintering taking into account the chemical stages.

2. Modeling the sintering process

The simplest model of reaction sintering includes the heat balance equation.

$$Vc\rho\frac{dT}{dt} = VW_{ch} + \sigma\varepsilon S(T_W^4 - T^4) - \alpha_p S(T - T_e) \quad (1)$$

where T_W – is the temperature of the vacuum chamber walls changing by a linear law

$$T_W = T_0 + at, \quad T < T_s,$$

$$T_W = T_s, \quad T \geq T_s,$$

σ – Stefan-Boltzmann constant; ε – degree of blackness; α_p – heat transfer coefficient in Newton's law; W_{ch} – total heat release due to possible chemical reactions. In conditions of vacuum sintering heat losses by convection can be neglected.

We assume that melting takes place in the temperature range T_{min} – T_{max} where the fraction of the liquid phase η_L varies from zero to one:

$$\eta_L = 0, T \leq T_{min}$$

$$\eta_L = \left(\frac{T - T_{min}}{T_{max} - T_{min}} \right)^2, T_{min} < T \leq T_{max} \quad (2)$$

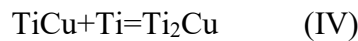
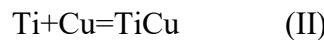
$$\eta_L = 1, T > T_{max}$$

In our case T_{min} – corresponds to the melting point of copper oxide, T_{max} – to the melting point of titanium. The appearance of liquid phase is taken into account in the change of heat capacity:

$$c = \left[c_s + \frac{Q_{eff}}{m} \frac{\partial \eta}{\partial T} \right] (1 - \eta_L) + c_L \eta_L \quad (3)$$

where c_s – heat capacity of the mixture in the solid phase, c_L – heat capacity of the mixture in the liquid phase; Q_{eff} – effective latent melting heat (J/mol).

The change in the composition of the press due to chemical reactions follows from the system of kinetic equations. Assuming, in accordance with [6], that the main chemical reactions in the system are the following



leading to the formation of hardening particles TiO_2 and a mixture of intermetallides TiCu , TiCu_2 , Ti_2Cu , the change in composition will be described by solving the system of kinetic equations

$$\frac{dC_k}{dt} = \sum_{i=1}^r \nu_{ki} \frac{m_k}{m_{sum}} \Phi_i \quad (4)$$

where

$$\Phi_I = z_1(T)C_1C_7^2; \quad \Phi_{II} = z_2(T)C_1C_2; \quad \Phi_{III} = z_3(T)C_4C_2; \quad \Phi_{IV} = z_4(T)C_4C_1,$$

$$Z_i(T) = z_{i0} \exp\left(-\frac{E_{ai}}{RT}\right),$$

where E_{ai} – activation energy, J/mol; z_{i0} – pre-exponential factors (dimensionality for the first reaction is $(\text{m}^3/\text{mol})^2/\text{sec.}$; for the other three – $(\text{m}^3/\text{mol})/\text{sec.}$, R – universal gas constant. Hence,

$$W_{ch} = Q_I \Phi_I + Q_{II} \Phi_{II} + Q_{III} \Phi_{III} + Q_{IV} \Phi_{IV},$$

where Q_i – heats of reactions, $i = \text{I, II, III, IV}$.

Since the law of conservation of mass is satisfied, then

$$\sum_{k=1}^7 C_k = 1$$

At the initial moment of time there is a mixture, the composition of which is given by:

$$T = T_0; C_k = C_{k0}; k = 1 \div 7; T_W = T_0. \quad (8)$$

For mass concentrations of components Ti, Cu, TiO₂, TiCu, TiCu₂, Ti₂Cu and CuO notations are taken $C_1 \dots C_7$.

3. Modeling results

No data for reactions (I) through (IV) have been found in the literature. Therefore, approximate semiempirical methods were used to estimate the parameters [7–9]. The data used in the calculations are presented in Table 1. Other parameters:

$$\begin{aligned} T_{min} &= 1720 \text{ }^\circ\text{K}; T_{max} = 1943 \text{ }^\circ\text{K}; c_S = 646 \text{ J}/(\text{kg}\cdot\text{K}); c_L = 446 \text{ J}/(\text{kg}\cdot\text{K}); \\ \rho &= 5287 \text{ kg}/\text{m}^3; V = 7 \cdot 10^{-7} \text{ m}^3; S = 4 \cdot 10^{-4} \text{ m}^2; Q_{eff} = 482055 \text{ J}/(\text{kg}\cdot\text{K}); \\ \alpha_p &= 10^{-6} \text{ J}/(\text{kg}^2\cdot\text{K}). \end{aligned}$$

It is assumed $T_s = 1173 \text{ }^\circ\text{K}$; $a = 1 \text{ K}/\text{sec}$.

Table 1. Parameters of chemical reactions.

reaction	z_{i0} , 1/sec.	$E_{a,i}$, J/mol	ΔH , kJ/mol
I	$8.67 \cdot 10^{14}$	80000	-633.039
II	$1.41 \cdot 10^{15}$	52000	-19.196
III	$2.29 \cdot 10^{17}$	124000	-24.9 25
IV	$1.57 \cdot 10^{12}$	72000	-36.393

Note. ΔH – reaction enthalpies, $E_{a,i}$ – activation energies. $Q = -\Delta H$;

The problem was solved numerically. Since the maximum order difference in the pre-exponential multipliers is 5, the ODE system is rigid. The reaction rates at 1173 °K: 0.2, 6.9, 0.7 and 10^{-4} 1/sec. for 1, 2, 3 and 4 reactions respectively. Explicit methods, when solving such problems, lead to instabilities, so an implicit Euler method of 1st order accuracy was used in this work. As a “check” of the method, the law of conservation of mass and the laws of conservation of the number of atoms in a closed system were analyzed. Since the system is isolated and there are no additional sources and sinks of mass, throughout the process, the sum of all concentrations should yield unity (or 100%). The computational error was 0.05%, i.e., the conservation laws were satisfied to the 5th decimal place, which is an acceptable result for a first-order precision method.

As an example, fig. 1 shows the dynamics of temperature and composition of composites when varying the initial composition of the press under sintering conditions. The composition of the

products appears to be non-equilibrium, i.e. not all possible transformations are completed by the end of the sintering process, as evidenced by the “unsteady” character of most kinetic curves. In order to observe the differences between the curves, fast and slow variables (rapidly and slowly changing concentrations) are presented on different scales. Obviously, the initial composition affects both the composition of the products and the behavior of the pressing temperature. So at $C_{10} = 0.6$, $C_{70} = 0.4$ products contain 20% TiCu and 17% TiCu₂ (curves 1); at $C_{10} = 0.5$, $C_{20} = 0.05$, $C_{30} = 0.05$, $C_{70} = 0.4$ we have a composite containing 29% and 23% of the same intermetallides (among other substances, curves 3). The presence of titanium oxide and intermetallides in the initial pressing can be related to the way the samples were prepared for sintering (as a result of partial mechanoactivation during mixing and pressing). This is confirmed by the experimental data presented below.

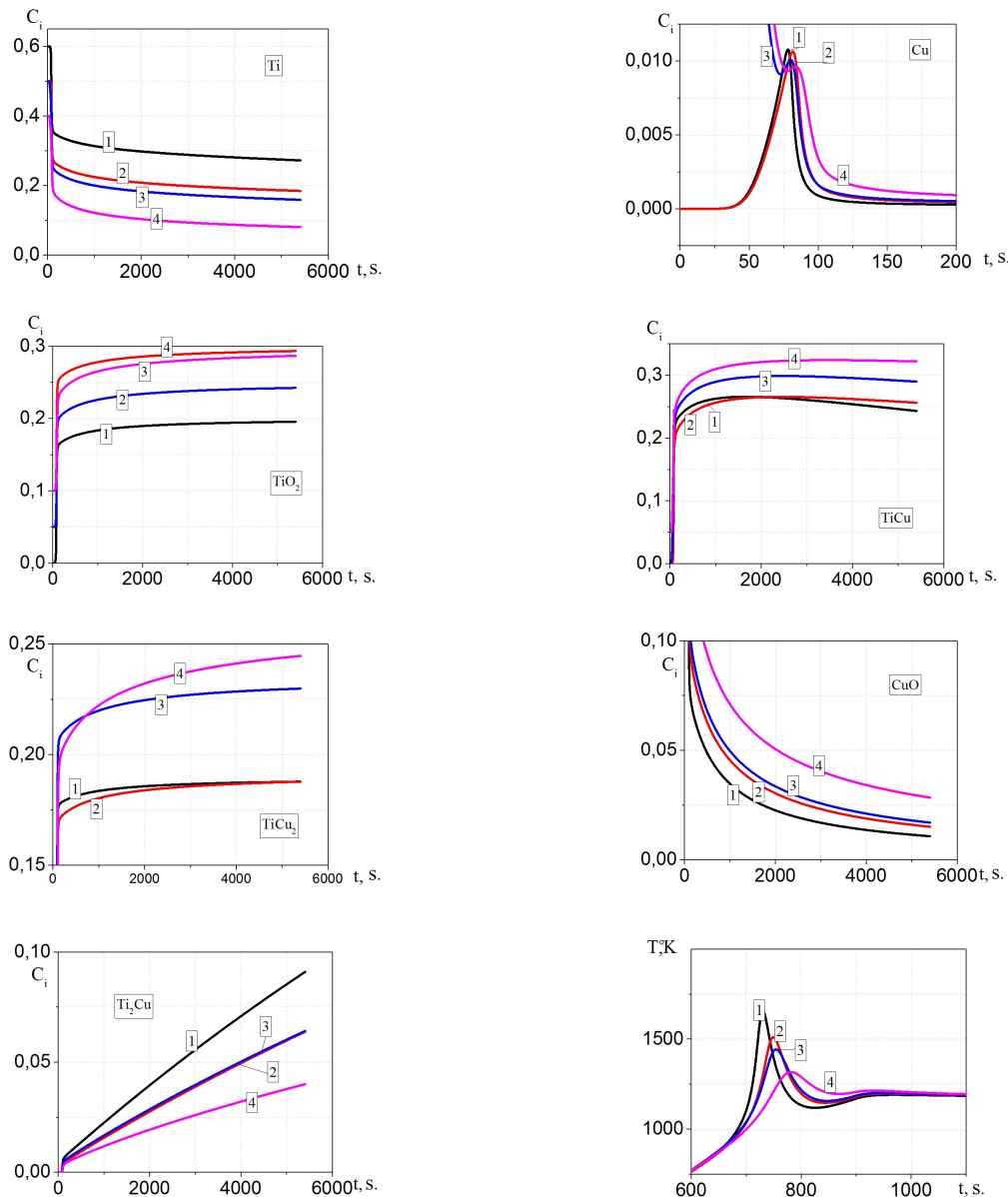


Fig. 1. Dynamics of change of composition and temperature at different initial press composition:

1 – $C_{10} = 0.6$ [Ti], $C_{70} = 0.4$ [CuO]; 2 – $C_{10} = 0.5$ [Ti], $C_{30} = 0.1$ [TiO₂], $C_{70} = 0.4$ [CuO];

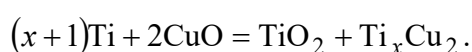
3 – $C_{10} = 0.5$ [Ti], $C_{20} = 0.05$ [Cu], $C_{30} = 0.05$ [TiO₂], $C_{70} = 0.4$ [CuO];

4 – [Ti] = 0.4, [TiO₂] = 0.1, [Cu] = 0.05; [TiCu] = 0.05, [CuO] = 0.4.

The main exothermic reactions occur within a short period of time, resulting in a temperature rise typical of a thermal explosion. In order to see the differences in the dynamics at different initial press composition, the temperature curves are not presented in full. There is no melting of the body at this set of parameters. After about 17 minutes from the beginning of the process, the temperature stops changing, the transformations in the system further proceed at a fixed temperature, below the melting temperature interval. At other sintering temperatures, a liquid phase appears, accelerating the process.

4. Experiment

Metal matrix composites with oxide inclusions were synthesized from TPP-8 grade titanium powders (coarse-grained, fractions <160 μm and <125 μm) and copper oxide (PMO, <120 μm). The ratio of components in the mixture was chosen from the condition of completion of total reactions of the following type



The mixing operation of metal and oxide powders was carried out using an 8000MMixer/Mill, as a result of which the powders could be partially mechanically activated and/or oxidized, but no special mechanoactivation was carried out. Pressing was used to obtain the samples: molding of the samples took place on the MS-500. Powder compacts (pressings) were prepared as cylindrical samples with a diameter of 10 mm and a height of 10–15 mm. Pressing was carried out using a mold with movable upper and lower punches. The porosity of the initial (raw, before sintering) compacts ranged from 35 to 38% depending on the type of composition. After molding the samples, the samples were sintered in the electric furnace SNVE-1.3.1/16 with the residual gas pressure not higher than 10^{-2} Pa.

The analysis showed that the samples of the composition (60 weight.% Ti+40 weight.% CuO) undergo volume growth to a greater or lesser extent. It can be argued that already at a temperature of 650 °C begin to realize some diffusion-reaction processes that lead to an increase in volume with compensation of solid-phase sintering of powder compositions. The temperature of 650 °C was sufficient for the initial copper oxide CuO to decompose into Cu, Cu₂O and Cu₄O₃. However, the expected formation of titanium oxide did not occur, nor did it combine with copper, although some free copper (up to 20 wt.%) was recorded by PCA. The volumetric growth can be associated with the release of impurity gases and with the formation of gaseous oxygen during the decomposition of copper according to the total reaction $4\text{CuO} = 2\text{Cu}_2\text{O} + \text{O}_2$.

At increase of heating temperature up to 800 °C, thermal explosion with destruction of the sample due to high exoeffect is already realized in the mixture. In this case, the products contain a mixture of oxides TiO, Cu₂O, TiO₂, Ti₂O₃, pure copper Cu and intermetallide Cu₃Ti₂, and the composition of the preserved samples is extremely heterogeneous. The percentage content of different phases is problematic to establish.

It should be noted that the mode with increasing sample temperature due to exothermic reactions in experimental conditions is not always realized. As in theory, it depends on the heating rate and the initial composition of the press. The resulting nonequilibrium phase composition suggests that for more correct prediction of the phase composition, the model should take into account a wider set of chemical stages, as well as volumetric changes.

5. Conclusion

Thus, the paper proposes a model of sintering that takes into account the stages of chemical reactions, as well as the changes in heat capacity and the appearance of the liquid phase fraction in the melting temperature range. An example of calculation of the process dynamics at different

initial composition of the press is presented. It is shown that the initial composition both quantitatively and qualitatively affects the character of kinetic curves, which indicates that it is possible to select the initial composition so as to obtain the final product of the desired composition. It is noted that the initial composition may include oxide, pure copper and intermetallide that could potentially be present in the press prior to sintering, which explains the excess atomic concentrations of oxygen and titanium from the experiment. To more accurately predict the phase composition, the model should account for a broader set of chemical steps as well as volumetric changes.

Acknowledgement

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