Kinetic and thermophysical phenomena in the synthesis of porous composites from (Ti+Si) and (Ti+Al+Si) powder mixtures in the reaction sintering mode

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Abstract. Theoretical and experimental study of the synthesis of porous composites from powder mixtures for Ti-Si and Ti-Al-Si systems in the reaction sintering mode is carried out in the present work. The thermokinetic model of reaction sintering is formulated taking into account competing physicochemical stages. The model includes the heat balance equation, the kinetic equations for the components involved in the reactions, the kinetic equation for porosity changing during heating, reaction sintering, and cooling. The melting is assumed to occur within the temperature range of liquidity and solidus. These processes lead to the appearance of local stresses and volumetric changes. The results of experimental studies show good agreement with the numerical calculations.

1. Introduction
Titanium-based composites are of particular interest among the most popular materials from the point of view of its interaction with a number of technologically important components: C, Si, B, Al, etc. [1–3]. In particular, titanium-matrix composite materials combine high wear, corrosion and heat resistance, chemical inertness, high hardness and strength. Among them, there are refractory titanium compounds. They are related to silicides and aluminides, have a good combination of physico-mechanical, thermophysical, and chemical properties, and can be successfully used in aggressive environments and at elevated temperatures [4-6]. As is known, there are five compounds in the Ti – Si system: Ti₅Si, Ti₅Si₃, Ti₃Si₄, TiSi and TiSi₂ [7]. The Ti₅Si₃ compound has a maximum melting point among the remaining compounds (T_{melt} = 2130 °C). This silicide has a noticeable region of homogeneity, which can reach 4 at. % in the concentration range from 35.5 to 39.5 at. % Si. The Ti – Al system also has a large set of intermetallic phases (TiAl₃, TiAl, TiAl₂, and Ti₃Al) [7]. The use of the titanium exothermic interaction with another component (for example, silicon or aluminum) in the reaction sintering process is one of the options for obtaining a titanium-matrix composite. The formation of various combinations of silicide and aluminide phases is possible depending on the quantitative ratio of the components in the powder mixture. Titanium silicide Ti₅Si₃ is of most interest among them, since it has a high melting point and low density. Also, this silicide is characterized by high oxidation resistance, thermal and electrical conductivity, and thermodynamic stability [8-10]. Sintering of titanium in the presence of other components has been widely studied in recent decades. Nevertheless, a number of observed regularities (volume changes, precipitation of nonequilibrium phases, sintering under conditions of secondary thermal impacts, etc.) remain unexplored.
In the present work, a theoretical and experimental study of the porous composites synthesis from powder mixtures for Ti-Si and Ti-Al-Si systems in the reaction sintering mode is carried out. Two-and-three-component powder compositions Ti-Si, Ti-Ti3Si3 and Ti-Al-Si are examined and materials based on them and obtained by vacuum reaction sintering of compacts are studied.

2. Procedure
In the case of two-component mixtures (Ti + Si), at least 60 vol. % Ti3Si3 silicide should be synthesized while maintaining up to 40 vol. % Ti in free (unreacted) state. When considering a three-component composition (Ti+Al+Si) a ratio of titanium, silicon and aluminum in the mixture calculation was chosen to ensure guaranteed phase synthesis in an equivalent volume of TiAl3 and Ti3Si3 in the first option, and Ti3Al and Ti3Si3 in the second option. For a mixture of elementary titanium and silicon powders, the components ratio was 75.4 wt. % Ti and 24.6 wt. % Si to ensure the synthesis of at least 60 vol. % Ti3Si3. For the composition (Ti+Al+Si) from a mixture of titanium, aluminum and silicon powders the ratios were chosen in two versions. The first option for the possible synthesis of a two-phase composite TiAl3 + Ti3Si3 is: titanium – 63.5 wt.%; aluminum -17.9 wt.%; and silicon – 18.6 wt.%. The second option for the possible synthesis of the composition Ti3Al+Ti3Si3 is: titanium – 77.5 wt.%; aluminum -5.4 wt.%; and silicon – 17.1 wt.%. Powder compacts from the calculated mixtures were prepared in the form of cylindrical samples with a diameter of 10 mm and a height of 10-15 mm. The porosity of the initial (green) compacts ranged from 25 to 35%, depending on the composition. Sintering was carried out in a vacuum furnace at temperatures from 1200 to 1350 °C with a holding time of 180 minutes. Volumetric and structural changes were analyzed by measuring the volume of the compacts, their integral density and porosity before and after sintering. Structural studies of the synthesis products were carried out in the Shared Use Center “NANOTECH” ISPMS SB RAS using optical metallography methods (AXIOVERT-200MAT, Zeiss, Germany) and X-ray diffraction analysis (DRON-7, Russia). For interpretation of X-ray results, the ASTM database was used.

3. Model
The mathematical model of the reaction sintering process of the composite in a vacuum chamber is generally similar to the model [11], but in contrast to it, it takes into account various options for melting the initial powder compositions in the temperature range from Ts to Tg. The model generally takes into account from 5 to 9 reactions in the Ti–Al system; 3–12 reactions in the Ti–Si system [12], as well as the possible formation of ternary compounds Ti2Al3Si12 and Ti2Al3Si12. The formal kinetic equations for the components are:

\[ \rho \frac{dy_k}{dt} = \omega_k, \]

where \( \omega_k \) is the sum of the sources and sinks of the k component in the reactions,

\[ \omega_k = \sum_{i=1}^{r} m_k v_{ki} \phi_i, \]

where \( \phi_i \) are the reaction rates, mol/(m³ s), \( m_k \) is the molar mass of the k component, kg/mol, \( v_{ki} \) is the stoichiometric coefficient of the k component in the i-reaction, \( i = 1, \ldots, r \); and \( y_k \) are the components concentrations defined as:

\[ y_k = \frac{\rho_k}{\rho}; \quad \sum_{k=1}^{n} y_k = 1 \]

Reaction features at the micro level are taken into account when writing kinetic functions in reaction rates. The reaction rates depend on temperature according to the Arrhenius law. The law of conservation of mass in reactions is represented by stoichiometric ratios:
The temperature distribution in the sample is neglected due to its small size in comparison with the heating zone size that can form during the observation time. The temperature change follows from the balance equation:

\[ Vc_0^p \frac{dT}{dt} = -\varepsilon \sigma (T^4 - T_e^4) S_n + V \sum_{i=1}^{r} W_i \]  

(2)

where \( S_n \) is the area of the entire surface of the sample, \( V \) is its volume, and \( W_i \) is the heat generation in chemical reactions per unit volume.

The initial conditions are determined by the initial composition of the mixture. Different physical and chemical processes are activated in the mixture, depending on the composition of the powders (Ti+Si, Ti+Ti_5Si_3, Ti+Al+Si; Ti+Al+Ti_5Si_3 and Ti+TiAl+Ti_5Si_3). In the temperature range from \( T_S \) to \( T_L \), the liquid phase accumulates and the heat capacity increases, similar to [13]. This affects the dynamics of the process. The temperature \( T_e \) varies according to a defined law.

Volumetric changes associated with the composite synthesis were evaluated by the formula [14]

\[ \omega = \sum_{i=1}^{r} \alpha_k y_k \]

where \( \alpha_k \) are the coefficients of the components concentration expansion.

The problems (1), (2) with initial conditions corresponding to the used powder composition are solved numerically. The final phase composition depends on all control parameters (components ratios of the mixture, heating rates and sintering temperatures). The product composition corresponds qualitatively to experimental data (Table 1). However, the role of sintering conditions in the phase ratio requires further study.

| Initial mixture | Preferential phase composition of sintered products |
|-----------------|---------------------------------------------------|
| Ti+Si           | Ti + Ti_5Si_3 + Ti_5Si_4 + TiSi                  |
| Ti + Ti_5Si_3   | Ti + Ti_5Si_3                                    |
| Ti + Si +Al     | Ti_3Al, TiAl, TiAl_1, Ti_2Al_1Si_2, Ti_1Al_3Si_5, Ti_8Si_12, Ti_5Si_4 + Ti_5Si_3 |
| Ti + Al+ Ti_5Si_3 | Ti_3Al, TiAl, TiAl_1+ Ti_5Si_3                  |

4. Experiment

Figure 1 shows the comparative results of changes in the porosity of the Ti-Si composition compacts with various combinations of components: from a conventional mixture of titanium and silicon powders, with using silicide in mixture; and from their synthesized powder analog. Obviously, the sintering of a simple mixture of elementary titanium and silicon powders leads to a significant volume growth of compacts and an increase in residual porosity (Fig. 1, column A). In this case, the main reason for volumetric changes is the inhibition of the adjacent titanium particles fusion as a result of the Ti_5Si_3 silicide streaks formation between them by reactive diffusion of silicon into titanium.

When elementary silicon is replaced in a powder mixture by its Ti_5Si_3 compound, the sintering process occurs more intensively, since silicide particles no longer form a barrier zone for adjacent titanium particles. This leads to a noticeable decrease in porosity. The most intensive compaction and decrease in porosity occurred during the third usage option of this composition, when metal matrix powders with the same volume content of silicide were firstly obtained by the SHS method, and then they were sintered (Fig. 2). The microstructure presented in Fig. 2 shows that the most nonequilibrium state with incomplete homogenization processes manifests itself during the reaction sintering of pure titanium and silicon components.
Figure 1. Change in porosity of pressed compacts made of powder materials of composition Ti + 60 vol.% (Ti5Si3) sintered at 1250 °C: (A) – a mixture of titanium and silicon powders; (B) a mixture of powders of titanium and silicide Ti5Si3; C – powder metal matrix material synthesized in the SHS process (wave combustion mode of a billet from a mixture of titanium and silicon).

Figure 2. Microstructure of sintered Ti + 60 vol% (Ti5Si3) compacts from mixture titanium and silicon powders (a); from a mixture of titanium powder and Ti5Si3 silicide powder (b); from SHS composite powders (c). Sintering temperature is 1250°C.

When a simple mixture of silicon and titanium is sintered, extended isolated sections of the formed silicide are observed to surround many particles of unreacted titanium (Fig. 2, a). The composites microstructure sintered from Ti + (Ti5Si3) powder mixtures (Fig. 2b) differs radically from the above microstructure of sintered titanium-silicon compositions. In this case, silicide is present as inclusions of various shapes and sizes in the titanium matrix, the microstructure of which is much more dispersed than the microstructure of titanium particles in sintered composites (Fig. 2, a). A more dispersed and dense structure is formed during sintering of synthesized powders of the same composition. An additional preliminary SHS operation allowed forming a finely dispersed structure with an almost uniform phase distribution with low pore content (Fig. 2, c). X-ray diffraction analysis of the sintered Ti + Si compositions has shown that after sintering α-Ti lines are practically absent, and the lines of Ti3Si3 and Ti5Si4 silicides mainly dominate (Table 2). The Ti5Si4 phase is metastable and turns into a stable Ti3Si3 silicide with increasing isothermal exposure. During the sintering of the Ti + (Ti5Si3) mixture, no changes in the phase composition occur. Radiographs contain only reflections from α-Ti and Ti5Si3. A similar phase composition is observed after sintering the synthesized composite powders with the same integral silicon content.

Sintering temperature significantly affects the compacts structure from the synthesized powder of the Ti+ Ti5Si3 composition. By the example of the composition Ti+60 vol.% (Ti5Si3) (Fig. 3), secondary recrystallization processes can be observed that lead to the silicide grains coarsening. Not the least role in this can be played by the eutectic influence that exists in this system at 1330 °C. Accordingly, such structural transformations lead to noticeable volumetric changes with compaction and a decrease in residual porosity.
Table 2. Phase composition of Ti + 60 vol.% (Ti$_5$Si$_3$) powder materials after synthesis and sintering

| Material                        | $T_{\text{sintering}}$ | Phases, wt.% | Possibly $\text{TiO/}(\text{TiH}_{0.71})$ |
|--------------------------------|------------------------|--------------|------------------------------------------|
| SHS powder before sintering    | -                      | 61.7         | 30.7                                     | 7.6                       |
| SHS powder after sintering     | 1200 °C                | 66.1         | 14.7                                     | 11.7                      |
|                                | 1350 °C                | 81.4-75.7    | 7.6-13.3                                 | 10.9                      |

Figure 3. Microstructure of the SHS powder Ti + 60 vol.% (Ti$_5$Si$_3$) (a) and sintered compacts from it: (b) – 1200°C; (c) – 1350°C.

In the analysis of the ternary Ti-Al-Si compositions, we focused on two types of powder compositions containing titanium aluminide Ti$_3$Al and TiAl$_3$. The second phase was assumed to be Ti$_5$Si$_3$ silicide as the most stable compound: TiAl$_3$ + Ti$_5$Si$_3$ and Ti$_3$Al + Ti$_5$Si$_3$. Pressings from these mixtures were sintered only at 1000 °C, since this temperature was sufficient to provoke intense reaction sintering with the formation of a large amount of liquid phase. As a result, the compacts not only lost their geometric shapes, but actually melted, which prevented from correct assessment of the volumetric changes. Moreover, their structure was characterized by a dense matrix with inclusions of almost perfectly round pores. Obviously, these pores were secondary in nature, and were formed as a result of liquid-phase sintering (Fig. 4). Therefore, it is impossible to correctly assess the change in the porosity of sintered compacts in ternary mixtures of the compositions TiAl$_3$ + Ti$_5$Si$_3$ and Ti$_3$Al + Ti$_5$Si$_3$, since the nature of the pores before and after sintering is of a different nature.

Figure 4. Microstructure of samples sintered at 1000 °C: a – TiAl$_3$+Ti$_5$Si$_3$; b – Ti$_3$Al+Ti$_5$Si$_3$.

The X-ray diffraction analysis has shown that the selected ratio of the components in the ternary system of titanium-aluminum-silicon provides the synthesis of the planned phases (Table 3), although in a different proportion.
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Conclusions

Presented thermokinetic model of reaction sintering takes into account the competing physicochemical stages. By the example of sintering a simple mixture of elementary titanium and silicon powders, one can see a significant volume growth of samples with an increase in residual porosity due to the predominant formation of silicides Ti₅Si₃ and Ti₃Si₂. Replacing silicon with its Ti₅Si₃ compound in the mixture stimulates the sintering process and reduces porosity, but no changes in the phase composition occur. Sintering a pre-synthesized powder of the same composition further reduces the residual porosity, while maintaining a high-quality phase composition. For the Ti-Si system, the model takes into account the reactions, resulting in the formation of titanium silicides, which are possible in accordance with the equilibrium state diagram: TiSi, Ti₅Si₃, Ti₅Si₅, Ti₃Si₅, and Ti₃Si₆. With an excess of titanium, its presence in the matrix is possible. When aluminum is added to the system, the situation becomes more complicated. Titanium is spent both on the formation of particles and on the formation of an intermetallic matrix. That is, in addition to the 9 equations for the formation of silicides, the reactions leading to the formation of intermetallic compounds are also taken into account: TiAl, Ti₃Al, and TiAl₃. However, a simplified version of the model can be reduced to two equations for parallel reactions — particle and matrix formation. In the analysis of sintering of ternary Ti-Al-Si compositions based on two variants of the powder compositions, Ti₃Al + Ti₅Si₃ and Ti₅Al + Ti₃Si₅, intense reaction sintering, which led to the fusion of the samples, has been detected. In this case, the qualitative phase composition corresponded to the planned one, but Ti₅Si₃ silicide was the dominant phase in each composition.

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