

## Basic models of phase formation at the mesolevel under reactive sintering of Ti-Al-Fe<sub>2</sub>O<sub>3</sub> powder mixture

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**Abstract.** In this work, based on the analysis of literature data, the main physicochemical stages that can be expected under the conditions of reaction sintering of the Ti-Al-Fe<sub>2</sub>O<sub>3</sub> system are established. Particular physical models of phase formation are analyzed under various temperature conditions, which can take place in local volumes of a heterogeneous mixture. As a reactive diffusion model example, a variant of the model for the interaction of titanium particles with an aluminum melt is presented.

**Keywords:** meso-volume, reaction cell, intermetallic, reactive diffusion, oxides.

### 1. Introduction

Titanium-based composites are used in various industries due to their relatively low density, high strength and corrosion resistance. The possibility of using a large number of additional components in the form of both simple elements and compounds that significantly increase its functional and physicomachanical characteristics is widely used. One of the possible options for the creation of composites based on titanium is the use of reaction sintering, in the course of which the strengthening phase in the form of oxides is directly synthesized. If for relatively simple binary systems like Ti+Al the situation with the limiting physical and chemical stages is relatively clear, then when adding third-grade powders to the mixture, options that are not obvious at first glance are possible. Thus, in the system Ti+Al+Fe<sub>2</sub>O<sub>3</sub>, depending on the percentage of powders, homogeneity of mixing and nature of heating, different variants of meso-volumes can be distinguished, in which the sequence of reactions and accompanying phenomena can lead to different phase composition. As a result, the composition of the entire composite will be very heterogeneous [1].

To analyze possible variants of events in reaction sintering conditions based on literature data, the particular phase-formation models are analyzed under varying temperature conditions (Fig.1): Ti+Al (reactions proceed in the melt); Ti+Al (interrelation happens in solid phase in diffusion couple at constant temperature); three variants of interphase interaction: Ti (melt)+Fe<sub>2</sub>O<sub>3</sub> (solid); Al (melt)+Fe<sub>2</sub>O<sub>3</sub> (solid); (Ti+Al) (melt)+Fe<sub>2</sub>O<sub>3</sub> (solid).

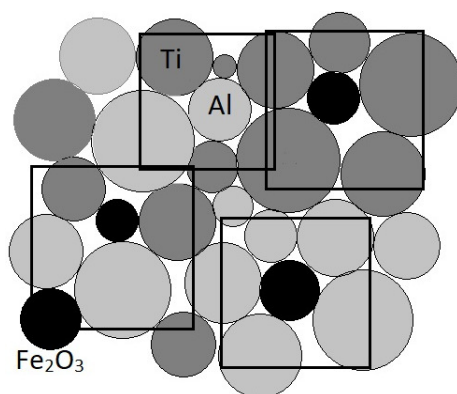


Fig.1. Problem illustration.

### 2. Background

In the equilibrium synthesis of materials from binary powder mixtures, a so-called diffusion zone is formed at the interface between the interacting components, which, as a rule, is multilayer

[2]. The features of structure formation processes in this case are determined by the structure of the equilibrium state diagram. On the one hand, the products layer is absorbed by the liquid particle (or the eutectic formed on its surface), and on the other hand, it continuously grows. Thus, in the general case, reactive diffusion processes and dissolution occur simultaneously. With the appearance of a liquid phase, the dissolution of a refractory component in a low-melting component at the initial stage of synthesis is hardly possible. Reactive diffusion of low-melting component atoms into the refractory component lattice is a more probable process [3]. The well-known physical models for selected subsystems are analyzed below.

### 2.1. *Система Ti+Al*

The Ti – Al system is one of the representatives of the systems class in which the interaction occurs by the reactive diffusion mechanism.

According to the Ti-Al state diagram [4], the interaction of aluminum with titanium can give rise to intermetallic phases  $\text{TiAl}_3$ ,  $\text{TiAl}_2$ ,  $\text{TiAl}$ ,  $\text{Ti}_3\text{Al}$ . In addition, solid solutions of variable composition will be formed, existing in a limited range of concentrations. Among the given intermetallic compounds, only the  $\text{TiAl}$  and  $\text{TiAl}_3$  phases have a wide concentration range of homogeneity.

The results of experiments [5, 6] show that during sintering, when the temperature is above the melting point of aluminum, high-temperature synthesis reactions take place between Ti and Al, as a result, various phases of solid solutions based on Ti, phases  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$ ,  $\text{TiAl}_2$ , and  $\text{TiAl}_3$  are formed. As the heat treatment time increases, the  $\text{TiAl}_3$  phase disappears, and the amount of Ti, as well as the Ti-based solid solution, becomes smaller. At the same time, the amounts of the  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$ , and  $\text{TiAl}_2$  phases increase. Over time, only  $\text{Ti}_3\text{Al}$  and  $\text{TiAl}$  remain as a result of sintering.

The following sequence of reactions is supposed. First,  $\text{TiAl}_3$  is formed, and then, due to diffusion-controlled solid-phase reactions,  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$  and  $\text{TiAl}_2$  appear in the Ti- $\text{TiAl}_3$  pair. After all the liquid Al is consumed, there is a competitive diffusion of elements between the layers of the Ti/ $\text{Ti}_3\text{Al}$ / $\text{TiAl}$ / $\text{TiAl}_2$ / $\text{TiAl}_3$  phases, and the thickness of the  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$ , and  $\text{TiAl}_2$  layers increases with the gradual disappearance of  $\text{TiAl}_3$ . When  $\text{TiAl}_3$  is depleted the areas occupied by Ti, Ti-based solution, and  $\text{TiAl}_2$  begin to decrease while the  $\text{Ti}_3\text{Al}$  and  $\text{TiAl}$  phases continue to grow [5].

The reaction diffusion process in the “solid-solid” system can be described as follows: the diffusion of Al atoms in  $\text{TiAl}_3$  and into the Ti layer leads to the transformation of the Ti layer into a Ti-based solid solution layer and a  $\text{Ti}_3\text{Al}$  layer [7]. Meanwhile, the diffusion of Ti atoms into the  $\text{TiAl}_3$  layer leads to the transformation of a part of the  $\text{TiAl}_3$  phase near the initial Ti layer into a  $\text{TiAl}$  layer. Then, in the presence of  $\text{TiAl}$ ,  $\text{TiAl}_2$  is formed between  $\text{TiAl}$  and the  $\text{TiAl}_3$  layer. However, the amount of the  $\text{TiAl}_2$  layer first increases, and then the layer becomes thinner, and all  $\text{TiAl}_3$  layer disappears.

In the thermal explosion mode, the reaction in the Ti-Al system proceeds according to the equilibrium mechanism in the case of smaller Ti particles and according to the non-equilibrium mechanism in the case of larger Ti particles [8]. In the latter case, the product contains  $\text{TiAl}_3$ ,  $\text{TiAl}$ ,  $\text{Ti}_3\text{Al}$  phases, a Ti-based solid solution, and unreacted Al is absent.

### 2.2. *Al + Fe<sub>2</sub>O<sub>3</sub>*

The Al- $\text{Fe}_2\text{O}_3$  thermite combustion products contain at least one hard metal phase (reduced metallic iron, intermetallic compounds) and a light ceramic phase ( $\text{Al}_2\text{O}_3$ ). Because these phases are mutually insoluble and have very different densities, some phase separation occurs on cooling [9]. This step affects the structure of the final products. Experimental study of the reaction mechanism and the formation of structures upon cooling is difficult due to the presence of extreme conditions, namely high temperature, high reaction rate, high heating and cooling rates, as well as the

occurrence of interacting physical and chemical phenomena, such as phase transitions and diffusion of reactants and products, nucleation and grain growth, dissolution in the solid phase, radiative heat transfer, and others.

In the experimental work [10], the authors treated by-products of the steel industry, mainly mixtures of iron oxides, by adding aluminum in a stoichiometric amount to accelerate the thermite reaction. They identified the following products:  $\text{Al}_2\text{O}_3$ ,  $\text{FeAl}_2\text{O}_4$ , Fe,  $\text{Fe}_3\text{O}_4$ . Regardless of the ratio of iron oxides, under the conditions of this work, the same phases were formed from the initial mixture.

According to [9–14], the following sequence of stages is possible:

- 1)  $2\text{Al} + \text{Fe}_2\text{O}_3 = \text{Al}_2\text{O}_3 + 2\text{Fe}$ ;
- 2)  $2\text{Fe}_2\text{O}_3 \rightarrow 4\text{FeO} + \text{O}_2$ ;
- 3)  $\text{FeO} + \text{Al}_2\text{O}_3 = \text{FeAl}_2\text{O}_4$ ;
- 4)  $9\text{Fe}_2\text{O}_3 + 2\text{Al} = 6\text{Fe}_3\text{O}_4 + \text{Al}_2\text{O}_3$ ;
- 5)  $3\text{Fe} + \text{Al} = \text{Fe}_3\text{Al}$ .

The presence of  $\text{FeAl}_2\text{O}_4$  and  $\text{Fe}_3\text{Al}$  in the products clearly depends on the ratio  $\text{Fe}_2\text{O}_3:\text{Al}$ . It is assumed that the  $\text{FeAl}_2\text{O}_4$  compound is formed in areas where  $\text{Fe}_2\text{O}_3$  was in excess. The presence of intermetallic compounds is explained by the contact of the Fe and Al melt in the regions of the samples with an excess of Al [9, 13].

### 2.3. $\text{Ti} + \text{Fe}_2\text{O}_3$

The thermite reaction  $\text{Ti}-\text{Fe}_2\text{O}_3$  includes several stages, such as the reduction of  $\text{Fe}_2\text{O}_3$  with titanium to form Fe and  $\text{TiO}_2$  phases, followed by the formation of an intermetallic metastable phase  $\text{Ti}_2\text{Fe}$  [15]:

- 1)  $2\text{Fe}_2\text{O}_3 + 3\text{Ti} = 4\text{Fe} + 3\text{TiO}_2$
- 2)  $(z+2x)\text{Ti} + x\text{Fe} \rightarrow z\text{Ti} + x\text{Ti}_2\text{Fe}$

At the same time, the data obtained are in the temperature range of 1300–1500 K, which is lower than the melting point of the phases ( $\text{Ti}$ : 1993 K;  $\text{Fe}_2\text{O}_3$ : 1650 K;  $\text{TiO}$ : 2024 K;  $\text{Fe}_2\text{Ti}$ : 1600 K). This means that only solid phase reactions take place in the process.  $\text{TiO}_2$  and  $\text{Ti}_2\text{Fe}$  phases are not equilibrium. Reaction (2) proceeds under nonequilibrium conditions of rapid temperature change after reaction (1). This effect and the possible presence of oxygen near the reacted region lead to the formation of an unstable phase  $\text{Ti}_2\text{Fe}$ .

### 2.4. $(\text{Ti} + \text{Al}) + \text{Fe}_2\text{O}_3$

According to [16], in the  $\text{Ti}-\text{Al}-\text{Fe}_2\text{O}_3$  system, a solid-phase substitution reaction first proceeds in a powder mixture of  $\text{Fe}_2\text{O}_3$  with Al with the formation of Fe and  $\text{Al}_2\text{O}_3$  phases, which is as follows:

- 1)  $2\text{Al} + \text{Fe}_2\text{O}_3 = 2\text{Fe} + \text{Al}_2\text{O}_3$ .

Further, Al reacts with  $\text{Fe}_2\text{O}_3$  with the formation of an ordered intermetallic compound  $(\text{Fe},\text{Ti})_3\text{Al}$  and a crystalline phase of  $\text{Al}_2\text{O}_3$  according to the following reaction:

- 2)  $3\text{Al} + \text{Ti} + \text{Fe}_2\text{O}_3 = (\text{Fe}; \text{Ti})_3\text{Al} + \text{Al}_2\text{O}_3$ .

The reaction between Al and  $\text{Fe}_2\text{O}_3$  proceeds in a self-sustaining regime; the heat released during this process accelerates the formation of  $(\text{Fe},\text{Ti})_3\text{Al}$ . Hence it follows that the formation of  $(\text{Fe},\text{Ti})_3\text{Al}$  and  $\text{Al}_2\text{O}_3$  includes two successive stages:

- 2')  $2\text{Al} + \text{Fe}_2\text{O}_3 = 2\text{Fe} + \text{Al}_2\text{O}_3$  and 2'')  $2\text{Fe} + \text{Al} + \text{Ti} = (\text{Fe}; \text{Ti})_3\text{Al}$ .

In self-propagating high-temperature synthesis [17], the phase composition of the reaction products is more complex. In addition to aluminum oxide, as a result of the reactions of titanium with iron, aluminum, and oxygen, phases  $\text{Ti}_3\text{Al}$ ,  $\text{TiFe}$ ,  $\text{Ti}_3\text{FeO}_2$  form. It follows from this that only a part of aluminum is spent on the reduction of iron from aluminum oxide, and unused aluminum,

iron oxide and titanium in excess react with the formation of double intermetallic compounds and a complex oxide.

### 3. Process simulation

The problem of the new phases growth in powder systems can be formulated in terms of reactive diffusion theory [18] for different pairs of components. As an example, the Ti-Al system is considered here. The analysis of the phase formation process in this system is the subject of many publications by the authors [2, 8]. It is assumed that the synthesis of the composite is carried out at given temperatures (above the melting point of Al), so we can assume that a spherical titanium particle is surrounded by an aluminum melt. As described in section 2.1, the following phases can form between the particle and the matrix: Ti-based solid solution,  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$ ,  $\text{TiAl}_2$  и  $\text{TiAl}_3$ .

In the general case, the problem includes the diffusion equation for each phase in a spherical coordinate system. The symmetry condition is satisfied in the center; the conditions at the boundaries between the phases take into account the presence of solubility limits and a discontinuity in diffusion fluxes associated with the movement of interphase boundaries. On the outer boundary, the impermeability condition for the boundary of the selected mesocell is used.

Assuming that the distribution of concentrations is quasi-stationary at the mesocell level, as in [19], we can divide the diffusion problem into two: a subproblem of finding the concentration distribution in regions of given sizes and a subproblem of determining the position of the phase boundaries. The first problem is solved by simple integration. The resulting system of ordinary differential equations for the interfaces is solved numerically by the Euler method. The results of the numerical solution are presented in the Figs. 2–3.

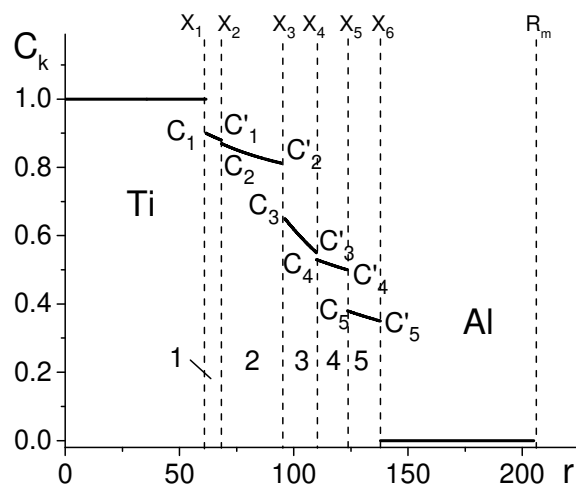


Fig.2. Distribution of particle material concentration in phases: 1 – Ti(Al); 2 –  $\text{Ti}_3\text{Al}$ , 3 –  $\text{TiAl}$ , 4 –  $\text{TiAl}_2$ ; 5 –  $\text{TiAl}_3$ .

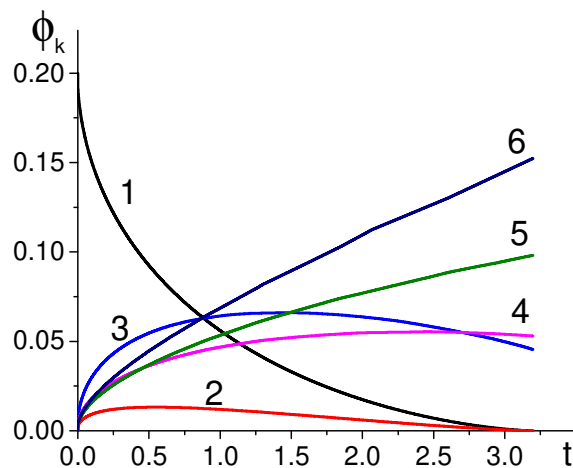


Fig.3. Change in the volume fraction of phases with time. 1 – Ti; 2 – Ti(Al); 3 –  $\text{TiAl}_3$ ; 4 –  $\text{TiAl}_2$ ; 5 –  $\text{TiAl}$ ; 6 –  $\text{Ti}_3\text{Al}$ .

### 4. Conclusion

Thus, based on the literature data, the paper proposes options for the stages of phase formation in the Ti-Al- $\text{Fe}_2\text{O}_3$  system for special cases that can be realized during particle contact. Several particular options for the interaction of Ti-Al; Ti - $\text{Fe}_2\text{O}_3$ ; Al - $\text{Fe}_2\text{O}_3$ ; (Ti+Al) - $\text{Fe}_2\text{O}_3$  are considered. An analysis of the literature showed that important role in the phase formation processes of is played by the proportion of interparticle contacts formed at the stage of mixing, which ensure the interaction of the components at the mesolevel. This suggests that, when constructing a model of the synthesis process, special attention should be paid to the choice of the reaction cell and the way it is represented. The proposed version of the diffusion model agrees qualitatively with the

experimental data for simple systems in which materials in the initial composition have significantly different melting temperatures. For more complex systems, another approach is required to describe transformations at the mesolevel, taking into account the features of both chemical stages and accompanying processes.

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