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Reactive diffusion and stresses in local volumes during the sintering of powder mixture Ti-Al-Fe-Fe_2O_3

M.A. Anisimova[1,2], A.G. Knyazeva[1,2], E.N. Korosteleva[1,2,], I.O. Nikolaev[1]*

[1]*Institute of Strength Physics and Materials Science SB RAS, Tomsk, Russia*
[2]*Tomsk Polytechnic University, Tomsk, Russia*
[*]*elenak@ispms.ru*

Abstract. In this study, the role of interphase boundaries in the reaction-diffusion interaction of powder components is assessed using the example of the Ti-Al-Fe-Fe_2O_3 system. Taking this into account, phase formation in multicomponent powder systems during sintering is analyzed. An example of the formulation of the phase formation problem in the form of a reactive diffusion task for the Al-Fe_2O_3 system is considered, where a possible summary reaction scheme can presumably lead to the formation of Al_2O_3 particles and Fe_XAl_Y intermetallic compounds. An analytical solution based on the quasi-stationary approximation is shown. An estimate of stresses for a local volume in a reaction-diffusion medium is given, which is performed from the problem of mechanical equilibrium.
Keywords: sintering, reactive diffusion, mechanical stresses.

1. Introduction

Phase formation during sintering in multicomponent powder systems depends largely on the mutual arrangement of powders of different types, their shape, surface properties, temperature, etc. [1]. Depending on the percentage ratio of components, homogeneity of mixing and the nature of heating, different sequences of reactions and accompanying phenomena can be distinguished, which can lead to different phase composition in local volumes. Possible situations of meeting and interaction of particles with each other, as a rule, are reduced to models of reactive diffusion in different coordinate systems. Reactive diffusion in the literature means the formation of one or several new phases (products) between two old (parent) phases as a result of diffusion [2]. These are problems with moving interfaces, the number of which can be different depending on component pairs and temperature [3]. Reactive diffusion problems are often met in different applications. These include processes in thin films [4], hydrogenation [5], oxidation in an oxygen-containing environment [6], crack nucleation under diffusion stresses [7], synthesis of new materials in powder technologies [8], and others. In modelling the formation of non-stoichiometric intermediate phases as a result of diffusion-controlled reactions, the authors [9] show that the composition of compounds can be quite different depending on whether bulk or grain-boundary diffusion predominates. The change of composition due to diffusion and the appearance of new phases is always accompanied by stresses and strains, which, in turn, can affect phase formation through different channels. In [10], a model of reactive diffusion in nanorods (nanowires) was developed, and the vacancy distribution and accompanying elastic stresses were calculated. The authors of the article [11], while studying the mechanism of mechanical degradation of spherical gradient electrodes, showed that the reversible electrochemical reaction has a different effect on the stress values in electrodes with a composition gradient depending on the rates of competing processes. The interaction between diffusion and stresses in spherical geometry is also analyzed in [12]. A model of the behaviour of a bilayer electrode under the action of an external load, taking into account the dependence of the elastic modulus on the concentration, is presented in [13]. The authors found that positive external load accelerates the diffusion process of Li ions, while negative external load hinders the diffusion of Li ions. In [14], in the framework of the micropolar theory of elasticity, it was shown that inhomogeneous stress and strain fields lead to inhomogeneous concentration distribution. Among the variety of powder systems with interacting components, there are a number of the most in-demand in modern production technologies. Such multicomponent powder materials include composites based on the Ti-Al-Fe-Fe_2O_3 system. In this

regard, the analysis of the reaction-diffusion interaction of components under sintering conditions, taking into account the boundaries of the phase interface, is of scientific and practical interest.

In the present work, different situations of particle interactions in the Ti-Al-Fe-Fe_2O_3 system under sintering conditions are analyzed. The stresses and strains are evaluated depending on the position of the interface and the distribution of concentrations in the phases on the example of the interaction between Al and Fe_2O_3.

2. The problems on phase formation

The pre-oxidized and crushed metal chips used in [15] can be considered as a flat object. Then, depending on the sintering temperature and the meeting of particles with each other, different situations are possible (Fig. 1), in which some phases are formed locally, the growth of which is accompanied by the appearance of local mechanical stresses. For example, at a temperature higher than the melting point of Al, aluminium will interact with iron oxide with the release of a large amount of heat. This will produce aluminium oxide, which is refractory. The released iron will enter the aluminium melt, which can lead to the formation of Al-Fe intermetallides.

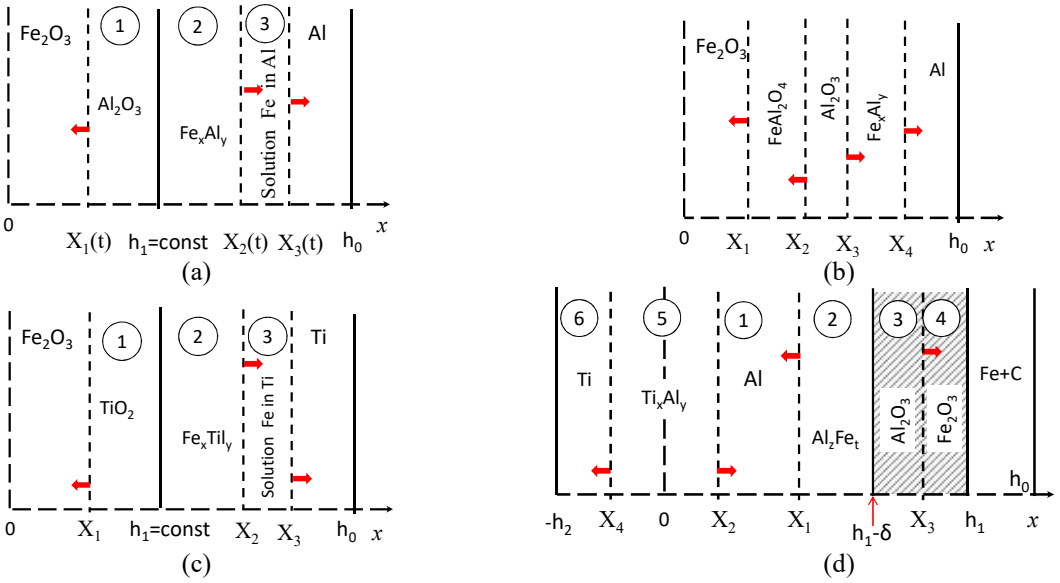

Fig. 1. Illustration of the formulations of private tasks.

This situation is conventionally depicted in Fig. 1a. It corresponds to the total reactions

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe;\ XFe+YAl \rightarrow Fe_XAl_Y.$$

If there was an oxide film on aluminium (due to improper storage or method of preparation of samples for sintering), there is a high probability of appearance of $FeAlO_4$ phase (Fig. 1b). The intermetallide will begin to form when "the aluminium oxide on the right is finished. In favour of such a development of events, for example, the results of the experiment [16]. The mechanism of double oxide formation corresponds, for example, to the reactions of

$$3Fe_2O_3 + 2Al = 5FeO + FeAl_2O_4$$

or

$$2Fe_2O_3 \rightarrow 4FeO + O_2;\ FeO + Al_2O_3 \rightarrow FeAl_2O_4.$$

When the melting point of iron oxide adjacent to titanium is reached, a thermite-type reaction is possible

$$2Fe_2O_3 + 3Ti \rightarrow 4Fe + 3TiO_2$$

with following formation of Ti-Fe intermetallides (Fig. 1c).

However, the presence of nearby molten aluminium oxide can significantly complicate the situation (Fig. 1d): aluminium will draw a part of titanium to itself with the formation of intermetallides of a different group.

In any case, problems on phase formation are reduced to typical problems of reactive diffusion. For example, for the situation shown in Fig. 1a, the mathematical formulation of the problem includes the diffusion equation in phases and conditions at moving interphases:

$$\frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x}\left(D_k \frac{\partial C_k}{\partial x} \right),\ k = \mathrm{Fe_2O_3}, \mathrm{Al_2O_3}, \mathrm{Fe_XAl_Y}, \mathrm{Fe(Al)},$$

$$x = X_1(t):\ C_{\mathrm{Fe_2O_3}} = 0,\ C_{\mathrm{Al_2O_3}} = C_1,$$

$$\left(C_{\mathrm{Fe_2O_3}} - C_{\mathrm{Al_2O_3}}\right)\frac{dX_1}{dt} = -D_{\mathrm{Fe_2O_3}} \frac{\partial C_{\mathrm{Fe_2O_3}}}{\partial x} + D_{\mathrm{Al_2O_3}} \frac{\partial C_{\mathrm{Al_2O_3}}}{\partial x},$$

$$x = X_2(t):\ C_{\mathrm{Fe_XAl_Y}} = C_2,\ C_{\mathrm{Al}} = 1,$$

$$\left(C_{\mathrm{Fe_XAl_Y}} - C_{\mathrm{Fe(Al)}}\right)\frac{dX_2}{dt} = -D_{\mathrm{Fe_XAl_Y}} \frac{\partial C_{\mathrm{Fe_XAl_Y}}}{\partial x} + D_{\mathrm{Fe(Al)}} \frac{\partial C_{\mathrm{Fe(Al)}}}{\partial x},$$

$$x = X_3(t):\ C_{\mathrm{Fe(Al)}} = C_4,\ C_{\mathrm{Al}} = 1,$$

$$\left(C_{\mathrm{Fe(Al)}} - C_{\mathrm{Al}}\right)\frac{dX_3}{dt} = -D_{\mathrm{Fe(Al)}} \frac{\partial C_{\mathrm{Fe(Al)}}}{\partial r} + D_{\mathrm{Al}} \frac{\partial C_{\mathrm{Al}}}{\partial r},$$

The symmetry condition is true at $x = 0$, and ideal contact takes a place at $x = h_1 = const$. For initial time we have only Fe_2O_3 and Al.

Here C_k – is Al-concentration in phases, h_1 – the size of the total oxide particle (including iron oxide and aluminium oxide), which is assumed not to change, D_k – diffusion coefficient, $D_k = \underline{D_{k,0}} exp(-E_k/RT)$, D_{k0} – pre-exponential factor, E_k – activation energy of aluminium diffusion in phases; T – temperature; R – universal gas constant; C_1, C_2, C'_3, C_3 – solubility limits, which are known from the diagram of state ($C_1 = 0.01$; $C_2 = 0.72$; $C_3 = 0.73$; $C_4 = 0.98$).

This problem, similarly to those presented in [3, 15], is solved in the quasi-stationary approximation, according to which the problem is divided into two: finding the concentration distribution in the region with boundaries, the position of which corresponds to some moment of time t, and determining the new position of the interface.

The distribution of aluminium concentration in the phases satisfies the equations

$$C_k(x) = A_k x + B_k,\ k = 1\ (Al_2O_3),\ 2\ (Fe_XAl_Y),\ 3\ (Fe(Al));\ C_{\mathrm{Fe_2O_3}}(x) = 0;\ C_{\mathrm{Al_2O_3}}(x) = 1,$$

where the integration constants are obtained from the system of linear equations, which is obtained by using the boundary conditions for the concentration at the boundaries. The final expressions for the integration constants are as follows:

$$B_1 = C_1 - A_1 X_1;\ A_2 = \Theta A_1;\ B_2 = C_2 - A_2 X_2;\ B_3 = C_3 - A_3 X_2;\ B_3 = C_4 - A_3 X_3;$$

$$A_1 = \frac{(\gamma C_2 - C_1)}{(h_1 - X_1) - \gamma\Theta(h_1 - X_2)},\ A_3 = \frac{(C_4 - C_3)}{X_3 - X_2},\ \text{where } \Theta(T) = \frac{D_{\mathrm{Al_2O_3}}}{D_{\mathrm{Fe_XAl_Y}}}.$$

Using these formulas and boundary equations for diffusion flows, we arrive to a system of three ordinary differential equations for the interfaces X_1, X_2, X_3, which we solve numerically by the Euler method.

An example of time dependence of the interface position and phase fractions (which were calculated from the given dimensions of the "particle" and the calculation area and the current position of the interface) is given in Fig. 2. The parameters of diffusion coefficient accepted in calculations are presented in Table 1. Temperature $T = 1100$ K is set.

Table 1. Diffusion parameters of aluminium in phases.

	Al_2O_3	Fe_zAl_t	Fe(Al)
D_0, m^2/s	$5 \cdot 10^4$	$1.46 \cdot 10^{-5}$	$1.71 \cdot 10^{-4}$
E, kJ/mol	380	223	142.4

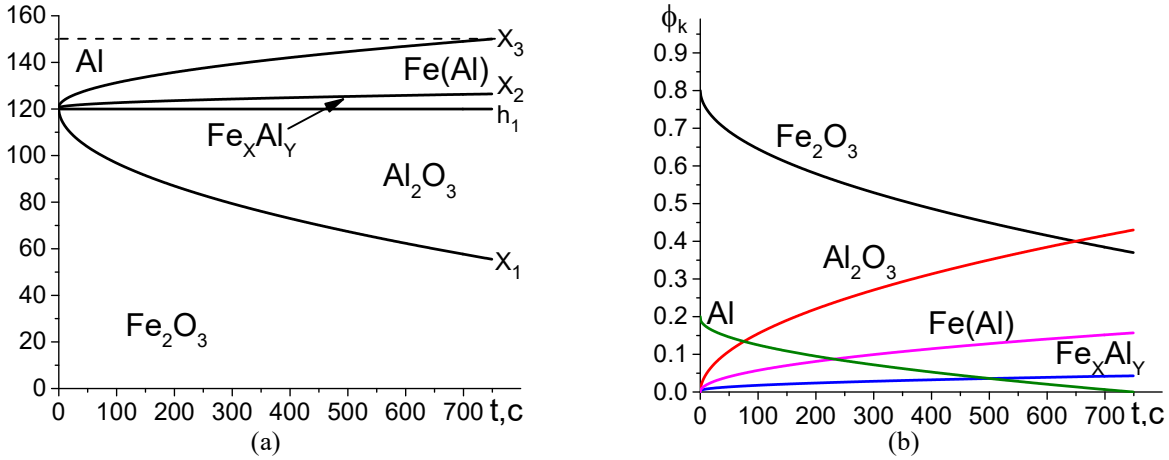

Fig. 2. Time dependence of interface position (a) and phase fractions (b).

Other private tasks are formulated and solved in a similar way.

3. Evaluation of mechanical stresses

To estimate the mechanical stresses associated with the evolution of the phase composition, we solve the problem of mechanical equilibrium of the selected local volume. Since the chip is a flat object, the surrounding phases are also considered flat in the first approximation, which allows us to use the known analytical solution for a free unfastened plate [17], for which the equal force along the contour and the equal moment of forces are equal to zero and

$$\sigma_{xx} = \sigma_{xy} = \sigma_{xz} = \sigma_{yz} = 0, \ \sigma_{zz} = \sigma_{yy} = \sigma(x).$$

The general expression for the stresses in the plane of the plate for our case has the form

$$\sigma = \frac{E}{1-\nu}\left(\varepsilon - \frac{\omega}{3}\right) = -\frac{\omega}{3}\frac{E}{1-\nu} + \frac{E}{1-\nu}(Nx + M)$$

where ω is a piecewise continuous function of aluminium concentration in phases,

$$N = \frac{J_1 \cdot I_3 - I_1 \cdot I_2}{J_2 \cdot I_3 - I_2^2} \quad M = \frac{J_1 \cdot I_2 - I_1 \cdot J_2}{J_2 \cdot I_3 - I_2^2},$$

and *Ij*, *Jl* are determined by the conditions of the phase formation problem and the properties of the phases. For example,

$$I_1 = \int_0^{h_0} \frac{\omega(x,t)}{3} \frac{E}{1-\nu} dx = (\alpha_{Al} - \alpha_{ph1})(A_1 S_1 + B_1(h_1 - X_1)) \frac{E_{Al_2O_3}}{1-\nu_{Al_2O_3}} +$$

$$+ (\alpha_{Al} - \alpha_{ph2})(A_2 S_2 + B_2(X_2 - h_1)) \frac{E_{FexAly}}{1-\nu_{FexAly}} + (\alpha_{Al} - \alpha_{ph3})(A_3 S_3 + B_3(X_3 - X_2)) \frac{E_{Fe(Al)}}{1-\nu_{Fe(Al)}},$$

$$I_2 = \int_0^{h_0} \frac{E}{1-\nu} x dx = \frac{E_{Fe_2O_3}}{1-\nu_{Fe_2O_3}} \frac{X_1^2}{2} + \frac{E_{Al_2O_3}}{1-\nu_{Al_2O_3}} S_1 + \frac{E_{FexAly}}{1-\nu_{FexAly}} S_2 + \frac{E_{Fe(Al)}}{1-\nu_{Fe(Al)}} S_3 + \frac{E_{Al}}{1-\nu_{Al}} \left(\frac{h_0^2}{2} - \frac{X_3^2}{2} \right),$$

where $S_1 = (h_1^2 - X_1^2)$, $S_2 = (X_2^2 - h_1^2)$, $S_3 = (X_3^2 - X_2^2)$.

The concentration expansion coefficients included in the solution of the equilibrium problem were estimated from the individual properties of substances (by molar volumes of phases). The result is presented in Table 2. Table 3 presents the mechanical properties of the phases used in the calculations.

Strains in the direction of the OX axis (in the direction of diffusion and phase growth) are continuous. However, strains and stresses in the plane of the plate (perpendicular to the OX axis) are discontinuous (Fig. 3). If the strains can be considered small, the stresses are very high, which, on the one hand, is justified by the approximation used, and on the other hand, is consistent with the known data of sintering experiments indicating high residual stresses. More realistic estimates are probably possible when using more appropriate models for inelastic media.

Table 2. Coefficients of concentration expansion of phases.

	Al	Fe_2O_3	Al_2O_3	Fe_zAl_t	Fe(Al)
w_k, m^3/mol	$10 \cdot 10^{-6}$	$30.47 \cdot 10^{-6}$	$36.4 \cdot 10^{-6}$	$14.89 \cdot 10^{-6}$	$14.89 \cdot 10^{-6}$
α_k	0.029	0.088	0.105	0.042	0.068

Table 3. Mechanical properties of phases.

	Al	Fe_2O_3	Al_2O_3	Fe_zAl_t	Fe(Al)
E, GPa	70	210	380	296	87
ν	0.34	0.31	0.25	0.236	0.33

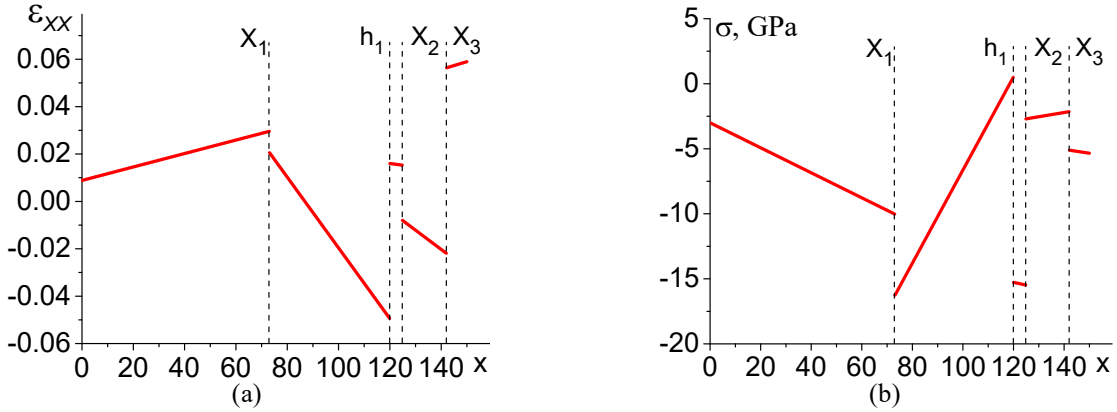

Fig. 3. Strains (a) and stresses (b) in the plane perpendicular to the phase growth direction.

4. Conclusion

Thus, reactive diffusion problems arising at modelling of phase formation in local volumes of multicomponent powder pressings under sintering conditions are presented. An example of the problem solution for the Al-Fe_2O_3 system is given. It is found that stresses in the vicinity of

interfaces are very large and depend significantly on diffusion-kinetic parameters. Note that in some situations it is possible to construct approximate solutions of fully coupled problems taking into account the influence of stresses on diffusion, because time is a parameter for the problem of mechanical equilibrium, and the diffusion and mechanical equilibrium problems are solved "independently". When there are at most three moving boundaries in the problem, analytical solutions are not very cumbersome.

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