Intermediate Layer Formation between Inclusion and Matrix during Synthesis of Unidirectional Fibrous Composite

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Abstract. The problem of transient layer formation in given composition between inclusions and matrix can be solved using mathematical modeling. This paper suggests a suitable model taking into account multi staging of chemical conversion. Numerical realization of this model allows studying the dynamics of transient layer formation at varying temperature and pressure. As a result, the phase structure and thickness of a transient zone depending on synthesis conditions are obtained.

Keywords: fiber composite, transient layer, mathematical modeling, diffusion, chemical reactions, given pressure and temperature

INTRODUCTION

Titanium aluminides and titanium-aluminum-alloys belong to heatproof light materials application-oriented for high temperature conditions. These alloys can serve as a basis for advanced heatproof composite materials [1]. However, it is necessary to solve certain problems related to materials science. To obtain intermetallic composite based on the carbide fibers reinforced by silicon and having optimal properties, the manufacturers try to restrain the chemical interrelation between matrix and fiber. If a chemical reactions touch only a thin layer between the matrix and the fiber, a bond hardening takes place. However, undesirable chemical compounds can form and lead to a fracture.

The effective properties of synthesized composite depend on matrix and fiber properties and on the thickness of transient layer composition that is formed during the composite synthesis [2–4]. It is important that a there is a capability of manipulating the interphase layer between the matrix and the fiber of the intermetallide reinforced by silicon carbide-based fibers for the purpose of ensuring the structural and chemical stability of the composite. On the other hand, the structure and the width of interphase layer significantly influence the residual stresses of composite materials, defining the strength characteristic of such composites, as well as their mechanical and dynamical properties [2–4]. So, the considered problem is very important for applications.

There is a series of experimental data about composition of transient layer generated under synthesis conditions [5], and thermodynamical calculations of the parameters of chemical reactions that are feasible in the diffusion zone

[6]. Though, the dynamics of transient layer formation, synthesis stages, the dependence of reaction course on technology or labor conditions, and the influence of initial concentrations of substances on final composition remain unstudied.

In this paper, a diffusion-kinetic model is suggested taking into account the dependence of diffusion coefficients and reaction rates on temperature and pressure. As a result the proposed model allows investigating the evolution of transient zone composition in the varying technological synthesis conditions.

PROBLEM FORMULATION

The diffusion-kinetic model of transient layer formation at the given temperature and pressure includes diffusion equations for mobile components and kinetic equations for conditionally immobile chemical compounds:

$$\rho \frac{\partial y_k}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r D_k \rho \frac{\partial y_k}{\partial r} \right) + \omega_k, \tag{1}$$

$$\rho \frac{dy_k}{dt} = \omega_k, \tag{2}$$

where y_k is the mass concentration of components (mass fraction, $y_k = \rho_k/\rho$, where ρ_k is partial density); t is time, s; r is space coordinate, meters; D_k is the effective diffusion coefficient depending on pressure and temperature:

$$\omega_k = \sum_{i=1}^{n_r} \nu_{ki} m_k \phi_i \tag{3}$$

are the sources and sinks for components due to chemical reactions, kg/(m^{3}s); n_r is the number of reactions; ν_{ki} is the stoichiometric coefficient of the k-th component in the i-th reaction, m_k is the molar mass of k-th component, kg/mol; ϕ_i is the rate of i-th reaction that depends on temperature and pressure, mol/(m^{3}s). These equations are correct for the fiber, where $\rho = \rho_f$, and for the matrix, where $\rho = \rho_m$.

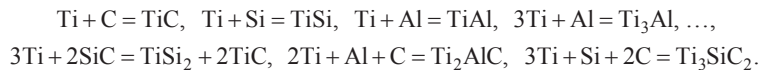We should add the stoichiometric relations and mass balance condition to the presented equations:

$$\sum_{k=1}^{n} \nu_{ki} m_k = 0, \ \ i = 1, 2, ..., n_r \ \text{ and } \ \sum_{k-1}^{n} y_k = 1.$$

Let us assume that the composite is formed from Ti$_2$AlNb intermetallic matrix with carbide undirected fibers (SiC).

We use the following designations: $k = 1, 2, ...$ for elements Ti, Al, Si, C, Nb (and other); $k = 21, 22, 23, ...$ for chemical compounds: TiC, SiC, TiSi, TiAl, …, Ti$_2$AlC, Ti$_3$SiC$_2$ that can form during the composite synthesis according to phase diagrams.

At the initial time moment only silicon, carbon and, possible, silicon carbide present in the region $r \leq R_0$, where R_0 is fiber radius. Intermetallide Ti$_2$AlNb and some alloying elements are contained in the region $r > R_0$. Symmetry conditions take place in the point $r = 0$ for $t > 0$. Ideal contact between fiber and matrix is assumed for mobile components, i.e. for $r = R_0$. Species fluxes are absent at $r = R_1$.

The problem was solved numerically. An implicit difference scheme, double-sweep method and Euler method were used. The chemical compounds can appear due to the following chemical reactions:

$$\text{Ti} + \text{C} = \text{TiC}, \ \ \text{Ti} + \text{Si} = \text{TiSi}, \ \ \text{Ti} + \text{Al} = \text{TiAl}, \ \ 3\text{Ti} + \text{Al} = \text{Ti}_3\text{Al}, \ \ldots,$$
$$3\text{Ti} + 2\text{SiC} = \text{TiSi}_2 + 2\text{TiC}, \ \ 2\text{Ti} + \text{Al} + \text{C} = \text{Ti}_2\text{AlC}, \ \ 3\text{Ti} + \text{Si} + 2\text{C} = \text{Ti}_3\text{SiC}_2.$$

It is assumed, that the reaction rates depend on concentrations in accordance with the mass action law, as well as on temperature in compliance with Arrhenius law. Kinetic parameters are found from literature or calculated on the basis of thermodynamical data.

For diffusion coefficients, the following formula was used

$$D_k = z_D D_{k0} \exp\left(-\frac{E_k - k_D V_k P}{RT} \right)(1 + y_k).$$

The coefficient z_D accounts for the presence of enhanced diffusion canals; V_k is activation volume (proportional to atomic ones); k_D is the coefficient accounting for the sensitivity of a reaction rate to applied load.
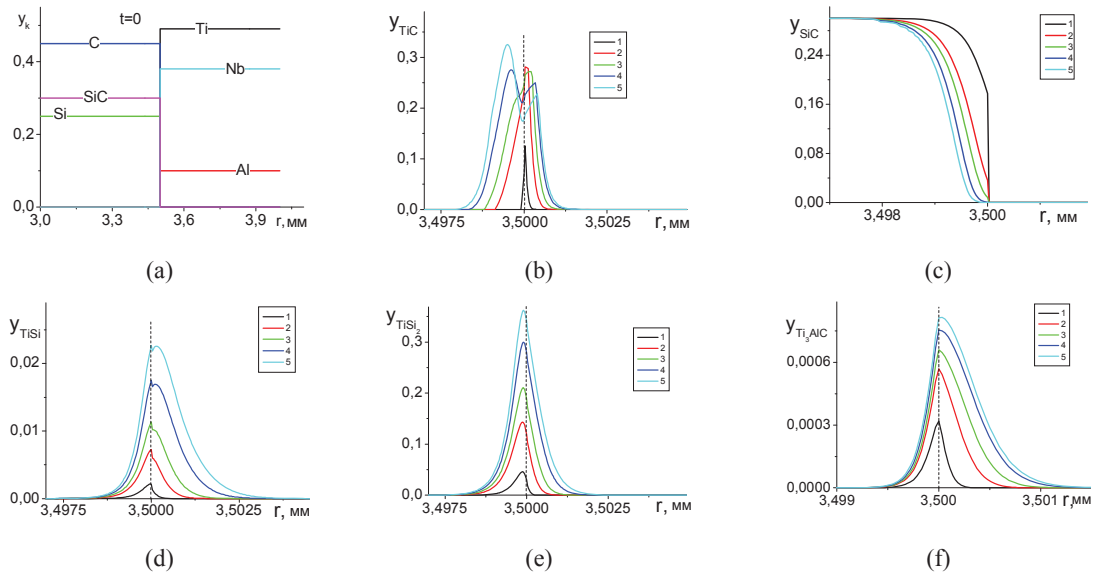
FIGURE 1. Phase concentrations distribution near interface at different moments of time; $T = 1100$ K, $P = 2000$ atm. $t = 0$ (a), 1. 5 (b), 30 (c), 60 (d), 120 (e), 180 min (f)

RESULTS AND DISCUSSION

The dynamics of the formation of certain phases is shown in Fig. 1. Dotted line corresponds to an interface. Initial composition is presented in Fig. 1(a). It is shown that in such conditions titanium carbide forms close to both sides of interface due to titanium diffusion into fiber and due to carbon diffusion into intermetallide matrix (Fig. 1(b)). Silicon carbide is consumed in the reactions (Fig. 1(c)).
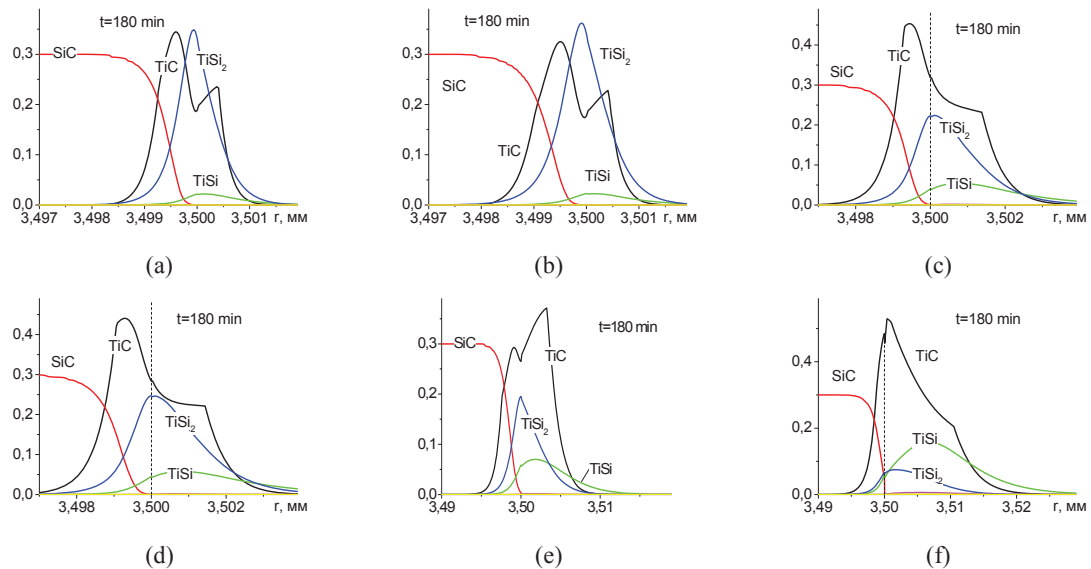
FIGURE 2. Phase distribution along transient zone after synthesis: (a) $T = 1100$ K, $P = 1500$ atm; (b) $T = 1100$, $P = 2000$; (c) $T = 1200$, $P = 1000$; (d) $T = 1200$, $P = 1500$; (e) $T = 1270$, $P = 1500$; (f) $T = 1400$; $P = 1000$
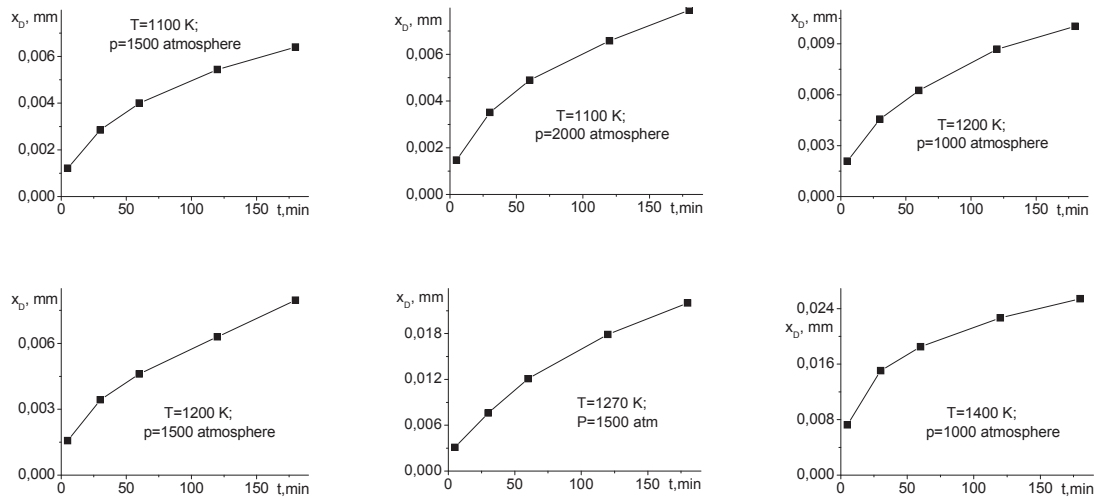
FIGURE 3. Thickness of diffusion zone in time for different temperature and pressure

Two types of titanium silicide occur near the interface (Fig. 1(d and e)) in various proportion depending on the given temperature and pressure. Triple compounds (for example, Ti_3AlC, Fig. 1(f)) form in small quantity.

The primary location of phases depends essentially on the synthesis conditions. However, in any case, titanium carbide initially forms near a fiber and then neighbored by the region of silicides. The relative composition of the transient zone can vary for different synthesis conditions (Fig. 2) that affect effective mechanical and physical properties of composites [2–4] and their residual strength.

It is clear that temperature and pressure growth leads to diffusion acceleration and reaction zone extension. Zone, where new phases appear is less then diffusion zone, usually in 2–3 time. During this period of time the size of the chemical reactions zone stops changing. This is explained by the growth of the intermediate layer, which retards the diffusion.

Let determine diffusion zone thickness using difference between coordinates x_0 in fiber where Al or Ti concentration equal to 10% on their initial value, and coordinate x_f in alloy where concentration Si or C equal 10% on their initial value. Thickness of diffusion zone depends essentially on given temperature and pressure that is shown in Fig. 3.

SUMMARY

Thus, suggested model allows forecasting the thickness and the phase composition of transient layer between fiber and matrix forming during composite synthesis under given temperature and pressure. If it necessary to mark, that chemical reaction set can vary depending on small concentrations of admixtures presenting in alloys. However, thermodynamical approach to formal kinetic parameters calculation helps to reduce a number of unknown parameters. This model could be supplemented by local mechanical stresses calculation.

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