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Research article

Научная статья



Sintering and thermokinetic modeling of the phase evolution in thermite powder mixtures under controlled heating

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Abstract. The behavior of compacted mixtures of metal powders (Al, Ti) and recycled metalworking wastes ($\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C}$) during vacuum sintering under controlled heating was investigated to assess the possibility of producing in situ metal–matrix composites containing oxide strengthening particles. The starting materials were titanium and aluminum powders (particle size $<160\text{ }\mu\text{m}$ and $<100\text{ }\mu\text{m}$, respectively) and a powder produced from recycled steel chips ($<300\text{ }\mu\text{m}$). The resulting samples exhibited a heterogeneous phase composition, which was examined by X -ray diffraction (CuK_α radiation, XRD-6000 diffractometer) and optical microscopy (Axiovert 200MAT). A pronounced difference was observed between the aluminum- and titanium-based systems: the former exhibited a distinct thermal peak, whereas the latter showed smooth temperature behavior without thermal spikes. A thermokinetic model describing the multi-stage reactions in both systems was developed. The model incorporates metallothermic reduction and intermetallic formation reactions. Formal kinetic parameters were estimated using a semi-empirical approach and refined by comparison with experimental data. The governing equations, including the heat balance equation and the system of kinetic rate equations, were solved numerically using a semi-implicit Euler method, while mass conservation and atomic balance were verified. The initial composition of the samples was varied in the calculations – accounting for oxygen, carbon, and the $\text{Fe}/\text{Fe}_2\text{O}_3$ ratio in the steel-chippowder – to reproduce the experimentally observed product compositions. The calculated and experimental results showed qualitative agreement.

Keywords: metal-matrix composite, vacuum sintering, metallothermic reactions, intermetallics, thermokinetic model

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Спекание и термокинетическое моделирование эволюции состава термитных смесей в условиях регулируемого нагрева

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Аннотация. Проанализировано поведение прессовок из смесей порошков металлов (Al, Ti) и переработанных отходов металлообработки ($\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C}$) в условиях вакуумного спекания при регулируемом нагреве для исследования возможности получения *in situ* металлматричных композиционных материалов с упрочняющими оксидными частицами. В качестве исходных материалов использованы порошки титана и алюминия с фракциями $d < 160$ мкм и < 100 мкм соответственно, а также порошок переработанной стружки из стали размером менее 300 мкм. В результате проведенного эксперимента обнаружен неоднородный фазовый состав образцов, который исследовали с помощью рентгеновского дифрактометра XRD-6000 с CuK_α -излучением и оптического микроскопа «Axiovert 200MAT». Продемонстрировано существенное различие в поведении систем на основе алюминия и титана: первая система характеризуется ярко выраженным термическим пиком, а во второй – превращения идут в спокойном режиме. Предложена термокинетическая модель процесса, учитывающая стадийность превращений для обеих систем. Учтены металлотермические реакции и реакции образования интерметаллидов. Дана оценка формально-кинетическим параметрам реакций с помощью полуэмпирического подхода. Полученные параметры корректировались при сравнении с экспериментом. Модель реализована численно с помощью полунявного метода Эйлера. Проверялись закон сохранения массы и неизменность числа атомов. Начальный состав образцов в расчетах варьировался (за счет учета присутствия кислорода, углерода и соотношения железа и оксида железа в стружке) таким образом, чтобы в результате синтеза получить состав продуктов, максимально приближенный к результатам эксперимента. Получено качественное соответствие теории и эксперимента.

Ключевые слова: металлматричный композит, вакуумное спекание, металлотермические реакции, интерметаллиды, термокинетическая модель

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Introduction

The *in-situ* formation of strengthening particles in metal–matrix composites (MMCs) has become a focal point in powder-processing technologies owing to applications across the aerospace, automotive, and energy sectors, and it continues to attract sustained interest from diverse research groups [1–4]. The spectrum of MMCs obtainable by powder routes is broad – in terms of both matrix chemistries and sets of strengthening phases. Of particular interest are systems built from chemically reactive powder components, where reactions between constituents synthesize the strengthening phases *in-situ* as micron-scale inclusions. This is largely characteristic of combustion-synthesis routes that rely on metallothermic reactions [5–9]. Such reactions are typically strongly exothermic, which helps sustain the synthesis process. Creating the strengthening particles directly during

composite fabrication is advantageous for interfacial bonding with the surrounding matrix. However, when a mixture permits metallothermic reduction (one metal reducing another), the presence of additional constituents can markedly redirect reaction pathways because local interaction conditions vary across different regions of the compact [10].

The problem becomes even less straightforward if one component of the powder mixture is itself a complex material – namely, a metallic base containing oxide inclusions – produced by recycling steel chips [11].

Here, the feasibility of producing metal–matrix composites from $\text{Al–Fe}_2\text{O}_3\text{–Fe}$ and $\text{Ti–Fe}_2\text{O}_3\text{–Fe}$ powder mixtures (optionally containing carbon) under sintering in a vacuum chamber is assessed, together with a theoretical description based on a thermokinetic model that accounts for the kinetics of the principal reactions.

1. Experimental

1.1. Materials and methods

Phase evolution under vacuum sintering with a controlled heating program (sintering temperature 1173–1473 K; 60-min hold) was examined for powder systems based on $\text{Ti-Al-Fe}_2\text{O}_3/(\text{Fe} + \text{C})$ using the following representative mixtures (from several possible combinations): $\text{Al} + (\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C})$ and $\text{Ti} + (\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C})$. Titanium powder TPP-8 (main fraction $d < 160 \mu\text{m}$) and aluminum powder PA-4 ($d < 100 \mu\text{m}$) were used to prepare the mixtures. As an analogue of the $\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C}$ composition, a powder produced from recycled steel 45 chips with a particle size not exceeding $300 \mu\text{m}$ was employed; its characteristics are described in detail in [11]. The component ratios in the mixtures were calculated to be sufficient both for metallothermic reduction and for intermetallic formation. The quantitative compositions of the powder mixtures under study are given in Table 1.

Selection of proportions for the aluminum-containing mixtures was guided by the binary Al-Fe phase diagram. The first option corresponds to the $\alpha\text{-AlFe}_3$ field, while the second lies predominantly in the $\text{Al}_3\text{Fe/AlFe}$ phase region. Both options imply exothermic reactions.

The titanium-containing mixture comprised 75 wt. % Ti and 25 wt. % steel chips, which favors the formation of a matrix basis in the resulting composite as a solid solution of iron and oxygen in titanium.

Microstructural characterization was performed by optical microscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD). The following instruments were used: Axiovert 200MAT optical microscope (Carl Zeiss, Germany), Mira 3 LMU SEM (Tescan, Czech Republic), and XRD-600 (Shimadzu, Japan) and DRON-8 (Russia) diffractometers with CuK_α radiation. Phase identification employed the PDF-4+ database and POWDER CELL 2.4 for full-profile analysis.

According to [11], chips oxidized in water and then milled form oxide-coated steel-chip fragments with an Fe core, containing dissolved carbon (≈ 1.5 wt. %).

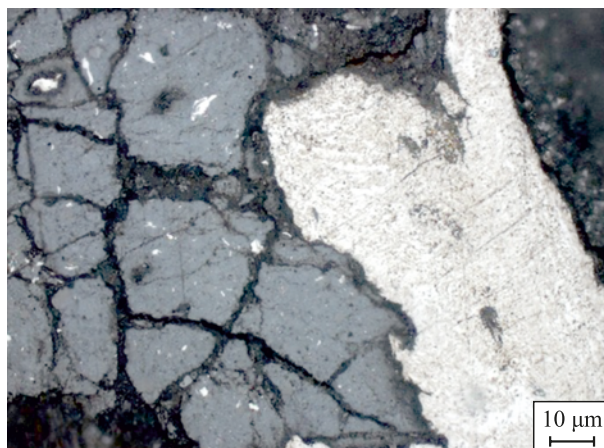


Fig. 1. Microstructure of the recycled steel 45 chips after oxidation and crushing

Light areas correspond to the steel core, dark areas to the iron oxide layer

Рис. 1. Микроструктура переработанной стружки из стали 45 после процедур окисления и дробления

Светлая область – стальная сердцевина,
темная – слой из оксидов железа

Although carbide phases were not detected by XRD, the presence of carbon in the steel-chip particles was confirmed by energy-dispersive X-ray spectroscopy (EDS). Carbon content, measured with a LECO ONH-836 gas-impurity analyzer (USA), showed a broad distribution (0.8–1.6 wt. %), reflecting the substantial heterogeneity of the processed steel-chip-derived particles. Their surfaces bear iron-oxide regions ($\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3/\text{FeO}$) [11], with the oxide fraction reaching $\approx 50\text{--}70\%$. Because these oxide layers are highly nonuniform (Fig. 1), the contact between a chip-derived particle and Al or Ti powder depends on the local surface domain encountered. Within the same mixture, the second component can therefore contact metallic iron (carbon steel) and iron oxides simultaneously.

1.2. Experimental results

Under vacuum sintering at $T_s = 1273 \text{ K}$, a heterogeneous phase assemblage was identified for both $\text{Al} + (\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C})$ formulations [12]. The pressed compacts of aluminum powder with milled, oxidized

Table 1. Composition of the investigated powder mixtures, wt. %

Таблица 1. Состав исследуемых порошковых смесей, мас. %

Mixture	Composition	Ti	Al	Recycled steel chips ($\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C}$)
1	$\text{Al} + (\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C})$	–	25	75
		–	60	40
2	$\text{Ti} + (\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C})$	75	–	25

steel chips lost structural integrity and disintegrated into separate fragments. The selected sintering conditions were sufficient to initiate a cascade of reactions, yielding Fe–Al intermetallics together with oxide strengthening particles. Residual (unreacted) iron was also detected in the products (Fig. 2). Oxygen was transferred almost entirely from the iron oxides to aluminum, forming Al_2O_3 , and FeAl constituted the dominant volumetric fraction of the product.

With increasing aluminum content in the compact, the reaction products contained a substantial fraction of residual, unreacted constituents, attributable to a decrease in the overall exothermicity of the reactions.

The second formulation, $\text{Ti} + (\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C})$, is less exothermic. Since the solubility of iron in β -Ti reaches 22 at. % at $T_s = 1358 \text{ K}$ and drops to 0.34 at. % in α -Ti at 673 K, it was expected that part of the iron would react with titanium to form intermetallics. It was also anticipated that titanium would be sufficient to interact with oxide inclusions present in the recycled steel-chip powder. Experimentally, the steel-chip powder in the $\text{Ti} + (\text{Fe} + \text{Fe}_2\text{O}_3 + \text{C})$ mixture exhibited good sinterability, with predominantly diffusional interaction with iron and oxygen migration from iron oxides into the titanium matrix. It is plausible that carbon contained in the chips enhances sintering via diffusion into titanium; however, its amount is too low to produce titanium carbide at levels detectable by X-ray diffraction. Interaction of free iron with titanium in the presence of oxide inclusions does not impede interdiffusion. The phase set and phase fractions depend on the sintering temperature; nevertheless, in all cases the pro-

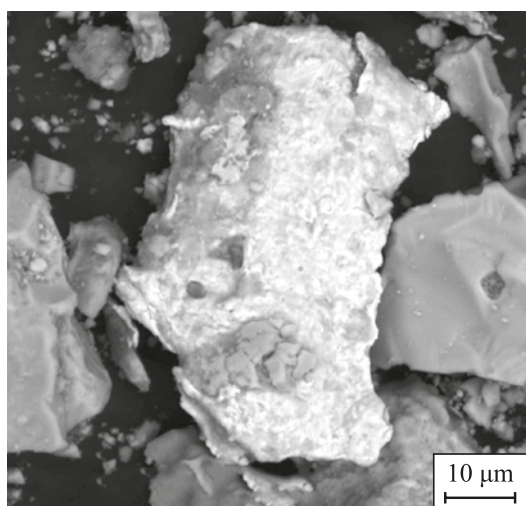


Fig. 2. Microstructure of a fragment of the sintered material 25 % Al + 75 % (Fe + Fe_2O_3 + C)

Рис. 2. Микроструктура фрагмента спеченного материала 25 % Al + 75 % (Fe + Fe_2O_3 + C)

ducts are dominated by a titanium-based solid solution (Fig. 3). At lower temperatures, the products contain a nonstoichiometric TiO_2 -based oxide (18 wt. %) and residual Fe_2O_3 (32 wt. %) originating from the steel-chip particles. Iron from these particles reacts with titanium to yield up to 20 wt. % of the equiatomic intermetallic TiFe. At a higher sintering temperature (1473 K), no unreacted constituents remain, and two types of α -Ti-based solid solutions form with different dissolved Fe and O contents; small inclusions of Ti_2Fe , TiFe_2 , or TiFe are also observed. Oxides are not detected as a separate phase under these conditions (Fig. 3).

The results reported in [13; 14] provided the basis for constructing thermokinetic models that capture the staged nature of phase formation.

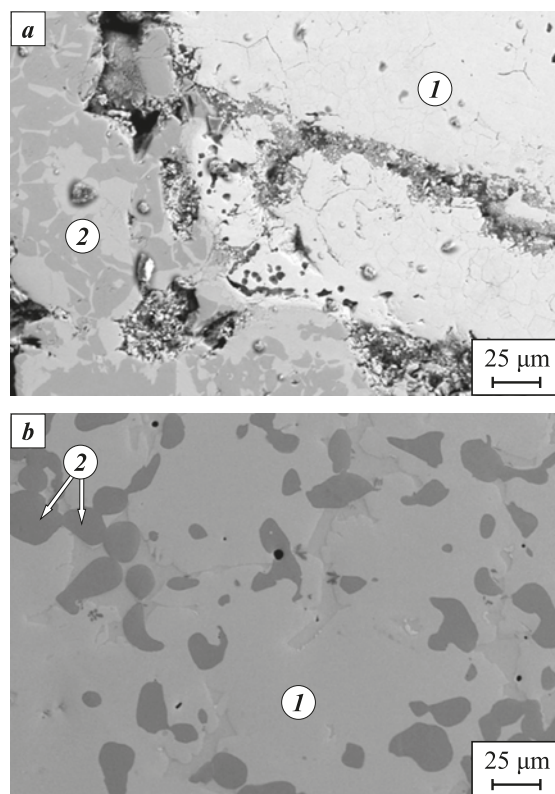


Fig. 3. Microstructure of sintered compacts from the mixture 75 % Ti + 25 % (Fe + Fe_2O_3 + C) at temperatures $T_s = 1173 \text{ K}$ (a) and 1473 K (b)

- a: 1 – regions of residual iron with oxide inclusions;
2 – α -Ti of variable composition with TiFe inclusions;
b: 1 – α -Ti of variable composition with dissolved iron and oxygen, with small TiFe_2 or TiFe inclusions;
2 – α -Ti regions depleted in iron with small Ti_2Fe inclusions

Рис. 3. Микроструктура спеченных прессовок из смеси 75 % Ti + 25 % (Fe + Fe_2O_3 + C) при температурах $T_s = 1173 \text{ K}$ (a) и 1473 K (b)

- a: 1 – область остатков железа с оксидными включениями;
2 – α -Ti переменного состава с включениями TiFe;
b: 1 – α -Ti переменного состава с растворенными железом и кислородом, небольшими включениями TiFe_2 или TiFe; 2 – области α -Ti, обедненные железом с небольшими включениями Ti_2Fe

2. Sintering model with detailed kinetics

2.1. Heat balance

The thermokinetic model accounts for the sample temperature change arising from the controlled external heating program and from heat release by chemical reactions. Owing to the small sample size, temperature gradients within the compact are neglected (a lumped-capacitance assumption); estimates justifying this approximation are given in [15]. The heat-balance equation has the form

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

where T is the temperature; t is time; V and S are the compact volume and surface area; c and ρ are the heat capacity and density of the pressed powder mixture; W_{ch} is the total heat release due to chemical reactions; σ is the Stefan–Boltzmann constant; ε is the surface emissivity of the compact; α is the heat-transfer coefficient (in vacuum it may be taken as zero); T_e is the ambient temperature (if Newton cooling is included).

The vacuum-chamber wall temperature T_w follows a linear law:

$$T_w = T_0 + at, \text{ for } T < T_s,$$

and

$$T_w = T_s, \text{ for } T \geq T_s, \quad (2)$$

where a is the heating rate and T_s is the sintering temperature.

Within the interval $T_{\min} - T_{\max}$, melting is assumed to occur, with the liquid-phase fraction (η_L) varying from 0 to 1:

$$\begin{aligned} \eta_L &= 0 \text{ for } T \leq T_{\min}, \\ \eta_L &= \left(\frac{T - T_{\min}}{T_{\max} - T_{\min}} \right)^2 \text{ for } T_{\min} < T \leq T_{\max}, \\ \eta_L &= 1 \text{ for } T > T_{\max}. \end{aligned} \quad (3)$$

Here, $T_{\min}$ is the lowest melting temperature among the reagents and reaction products in the chosen system, and $T_{\max}$ is the highest one (see Table 2).

Within the melting interval, the (specific) heat capacity is given by

$$c = \left(c_s + \frac{Q_{\text{eff}}}{m} \frac{\partial \eta}{\partial T} \right) (1 - \eta_L) + c_L \eta_L, \quad (4)$$

Table 2. Melting points of the starting substances and selected reaction products

Таблица 2. Температуры плавления исходных веществ и некоторых продуктов

Phase (compound)	T_m , K	Phase (compound)	T_m , K
Al	903,3	Ti–Al*	1513–1733
Fe	1811	Ti–Fe*	1273–1723
Ti	1941	Al–Fe*	825–1583
Fe ₂ O ₃	1838	FeAl ₂ O ₄	1713
Al ₂ O ₃	2345	Ti ₃ FeO ₂	–**
TiO ₂	2116	TiC	3473

* Intermetallic phases in the corresponding binary system.

** An unstable compound that decomposes before melting (at $T = 1273$ K).

where c_s is the heat capacity of the mixture in the solid state, c_L is the heat capacity of the mixture in the liquid state; Q_{eff} is the effective enthalpy of fusion (J/mol); m is the mean molar mass of the mixture of reagents and reaction products.

Heat release from chemical reactions is given by

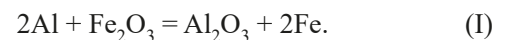
$$W_{\text{ch}} = \sum_{i=1}^n Q_i \Phi_i, \quad (5)$$

where n is the number of reactions; Φ_i are the reaction rates; Q_i are the reaction enthalpies (heat effects).

2.2. Model of phase composition evolution during sintering

Because the detailed mechanisms of most solid-state reactions are rarely known and the steps involved often comprise a mix of physicochemical processes, it is most appropriate to use a reduced-chemistry model that explicitly tracks the formation of the experimentally observed phases.

In the Al-containing system (where aluminum has the lowest melting temperature), the dominant exothermic step is expected to be the aluminothermic reduction of iron oxide:



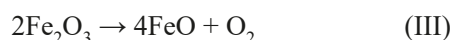
The reduced iron then reacts with excess aluminum to form intermetallic phases. Owing to the large reaction enthalpies, phase formation is expected to occur predominantly in the liquid phase and to be accompanied by the appearance of agglomerates [16]. At the same time, as noted in [17], direct reaction

between aluminum and iron oxides during combustion is preceded by the partial decomposition sequence $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$. Thin plates of FeAl_2O_4 , have been observed in [17] as a result of the interaction between FeO and the amorphous Al_2O_3 film that invariably coats aluminum:

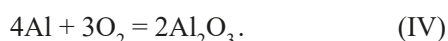


Iron aluminates such as FeAl_2O and FeAl_2O_4 commonly appear in the $\text{Al-Fe}_2\text{O}_3$ system, which is unfavorable for further reduction of iron oxides – especially in the presence of Al_2O_3 [18].

In the $\text{Al-Fe}_2\text{O}_3$ system, an additional step may occur

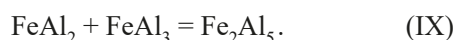
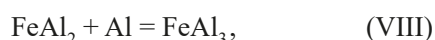
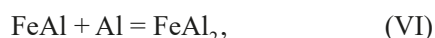


followed by oxidation of aluminum:



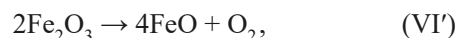
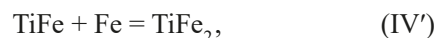
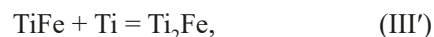
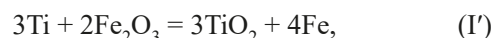
The Al-Fe phase diagram contains several intermetallic phases (Fig. 4). The diagram was constructed using the Thermo-Calc Software (open version) with the TCBIN: TC Binary Solutions v1.1 database.

Formation of intermetallic phases proceeds via the reactions



The FeAl intermetallic is not shown on the diagram; however, it is known to form by ordering of the $\alpha\text{-Fe(Al)}$ solid solution. Fe_3Al is a metastable phase that appears via a second-order phase transformation from FeAl [19]. Carbon present in the processed chips could, in principle, participate in the synthesis of aluminum carbide (Al_4C_3), but the sintering schedule and mixture composition do not provide sufficient carbon or temperature to initiate the corresponding reaction.

In the second case ($\text{Ti-Fe}_2\text{O}_3\text{-Fe-C}$ system), iron is the lowest-melting component (see Table 2). According to [20], the thermite reaction $\text{Ti-Fe}_2\text{O}_3$ proceeds through several steps – reduction of Fe_2O_3 by Ti to form Fe and TiO_2 , followed by the formation of the metastable intermetallic Ti_2Fe . Allowing for partial decomposition of iron oxide, the presence of carbon, and the formation of intermetallic phases (Fig. 4, *b*), the reaction set can be written as:



The notation for species concentrations (C_k) for each system is given in Tables 3 and 4.

For each reaction network, the kinetic equations can be written as

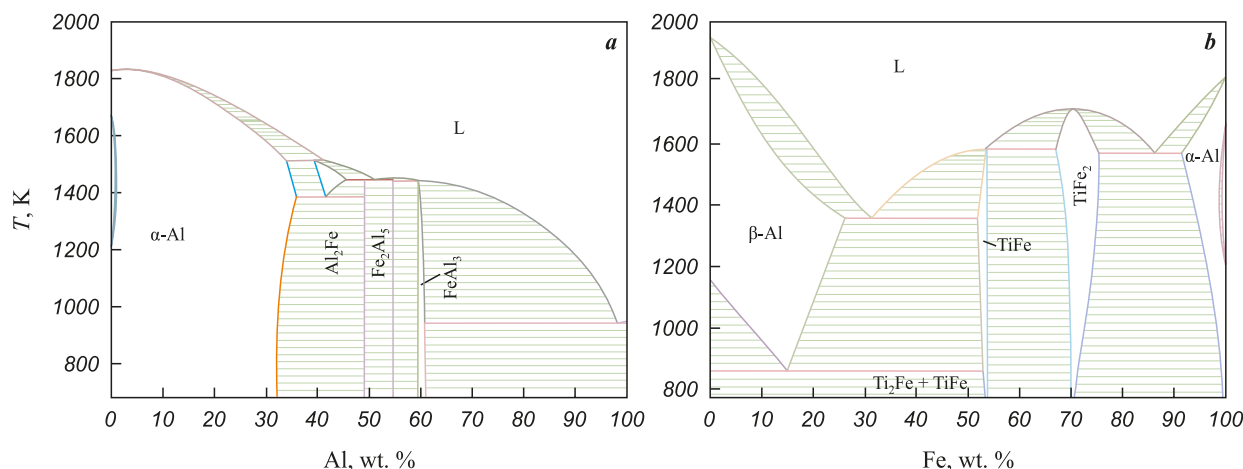


Fig. 4. Phase diagrams of the Al-Fe (a) and Ti-Fe (b) systems

Рис. 4. Диаграммы состояния Al-Fe (a) и Ti-Fe (b)

$$\frac{dC_k}{dt} = \sum_{k=1}^r \nu_{ki} \Phi_i, \quad (6)$$

where ν_{ki} are the stoichiometric coefficients of component k in reaction i ; r is the number of reactions, Φ_i are the reaction rates. We assume that the reaction rates follow an Arrhenius temperature dependence and depend on concentrations according to the law of mass action:

$$\Phi_i = k_i(T) \prod_k C_k^{n_{ki}}. \quad (7)$$

Here, n_{ki} are the exponents equal in absolute value to the corresponding stoichiometric coefficients;

$$k_i = k_{i0} \exp\left(-\frac{E_i}{RT}\right), \quad (8)$$

where k_{i0} are the pre-exponential factors; E_i are the activation energies; R is the universal gas constant. The rate expressions for all reactions are given in Table 5.

Thus, for the first system we require 27 formal kinetic parameters k_{i0} , E_i , Q_i , and for the second – 24. Using

published parameters for overall reactions in SHS-type mixtures [21] is not feasible. One reason is the strong dependence of parameters on the determination method, mixture processing, heating rate, etc. Another is the lack of data for most steps. Even for one of the most studied thermite mixtures (Al–Fe₂O₃), published values are inconsistent [22], including the reaction enthalpies. For example, for reaction (VI) in the Al-containing system, [23] gives: $\Delta H = -851.4$ kJ/mol, whereas [16] reports $\Delta H \approx -752$ kJ/mol.

The entropies and enthalpies of reactions were obtained using Hess's law:

$$\Delta H_{298}^0 = \sum_{\text{products}} \nu_{ki} \Delta H_{298}^0 - \sum_{\text{reagents}} \nu_{ki} \Delta H_{298}^0, \quad (9)$$

$$\Delta S_{298}^0 = \sum_{\text{products}} \nu_{ki} \Delta S_{298}^0 - \sum_{\text{reagents}} \nu_{ki} \Delta S_{298}^0, \quad (10)$$

where the first terms on the right-hand side are sums of the parameters for the reaction products, and the second terms are the parameters for the reactants (reagents in the formula). However, tabulated values

Table 3. Concentration designations for the Al + (Fe + Fe₂O₃) system

Таблица 3. Обозначения концентраций для системы Al + (Fe + Fe₂O₃)

Species	Concentration	Species	Concentration
Al	C_1	Fe ₂ Al ₅	C_7
Fe	C_2	Al ₂ O ₃	C_8
FeAl	C_3	Fe ₂ O ₃	C_9
FeAl ₂	C_4	FeO	C_{10}
Fe ₃ Al	C_5	O ₂	C_{11}
FeAl ₃	C_6	FeAl ₂ O ₄	C_{12}

Table 4. Concentration designations for the Ti + (Fe₂O₃ + Fe + C) system

Таблица 4. Обозначения концентраций для системы Ti + (Fe₂O₃ + Fe + C)

Species	Concentration	Species	Concentration
Ti	C_1	TiFe ₂	C_7
Fe	C_2	TiC	C_8
Fe ₂ O ₃	C_3	FeO	C_9
TiO ₂	C_4	O ₂	C_{10}
TiFe	C_5	Ti ₃ FeO ₂	C_{11}
Ti ₂ Fe	C_6		

Table 5. Reaction rate expressions

Таблица 5. Скорости реакций

Al-containing system	Reaction rate	Ti-containing system	Reaction rate
1) Al + Fe = FeAl	$\Phi_1 = k_1 C_1 C_2$	1) 3Ti + 2Fe ₂ O ₃ = 3TiO ₂ + 4Fe	$\Phi_1 = k_1 C_1^3 C_3^2$
2) FeAl + Al = FeAl ₂	$\Phi_2 = k_2 C_1 C_3$	2) Ti + Fe = TiFe	$\Phi_2 = k_2 C_1 C_2$
3) FeAl + 2Fe = Fe ₃ Al	$\Phi_3 = k_3 C_1^2 C_3$	3) TiFe + Ti = Ti ₂ Fe	$\Phi_3 = k_3 C_1 C_5$
4) FeAl ₂ + Al = FeAl ₃	$\Phi_4 = k_4 C_1 C_4$	4) TiFe + Fe = TiFe ₂	$\Phi_4 = k_4 C_2 C_5$
5) FeAl ₂ + FeAl ₃ = Fe ₂ Al ₅	$\Phi_5 = k_5 C_4 C_6$	5) Ti + C = TiC	$\Phi_5 = k_5 C_1 C_8$
6) 2Al + Fe ₂ O ₃ = Al ₂ O ₃ + 2Fe	$\Phi_6 = k_6 C_1^2 C_9$	6) 2Fe ₂ O ₃ → 4FeO + O ₂	$\Phi_6 = k_6 C_3^2$
7) 2Fe ₂ O ₃ → 4FeO + O ₂	$\Phi_7 = k_7 C_9^2$	7) Ti + O ₂ = TiO ₂	$\Phi_7 = k_7 C_1 C_{11}$
8) FeO + Al ₂ O ₃ = FeAl ₂ O ₄	$\Phi_8 = k_8 C_9 C_{10}$	8) TiO ₂ + Ti ₂ Fe = Ti ₃ FeO ₂	$\Phi_8 = k_8 C_4 C_6$
9) 4Al + 3O ₂ = 2Al ₂ O ₃	$\Phi_9 = k_9 C_1^4 C_{11}^3$		

are not available in the literature for all compounds. For this reason, approximate semi-empirical methods were used to obtain preliminary estimates of the formal kinetic parameters (Table 6). The parameter-estimation procedure is described in detail in [15].

For each system, the problem (which comprised 10 and 9 ordinary differential equations of the form (6) for the Al- and Ti-containing systems, respectively, plus the heat-balance equation (1)) was solved numerically using a semi-implicit Euler method. In every run, mass conservation and atomic balance were verified. Calculations were performed at constant ΔS_{298}^0 and ΔH_{298}^0 . The reaction orders were adjusted during the numerical solution. For the first system, we obtained:

$$k_{01} = 10^{17}, k_{02} = 10^{22}, k_{03} = 3 \cdot 10^{22}, k_{04} = 10^{22},$$

$$k_{05} = 10^{22}, k_{06} = 8 \cdot 10^{19}, k_{07} = 6 \cdot 10^{15},$$

$$k_{08} = 10^{15}, k_{09} = 10^{24} \text{ s}^{-1}.$$

For the second system, the adjustments affected two pre-exponential factors and the activation energy of one reaction:

$$k_{05} = 3 \cdot 10^{19} \text{ c}^{-1}, k_{06} = 6 \cdot 10^{23} \text{ s}^{-1},$$

$$E_6 = 150,255 \text{ J/mol}.$$

A single scaling factor applied to all reactions was 10^{-17} for the Al-containing system and $7.5 \cdot 10^{-13}$ for the Ti-containing system. The criterion for selecting this factor was the characteristic reaction time under the experimental conditions.

2.3. Numerical analysis results

Calculated temperature and composition profiles for reactive sintering of the studied systems are shown in Figs. 5–7. The typical temperature curves differ for the Al- and Ti-containing mixtures (Fig. 5). In the former, a temperature spike appears upon reaction initiation at $T = 700\text{--}900 \text{ K}$. In the latter, there is no pronounced spike, although a wavy temperature curve is observed.

Such behavior is often ascribed to thermocouple sensitivity; however, the calculations indicate that it may also arise from the interplay of coupled physico-chemical processes.

As noted above, the exact oxide composition in the chips is unknown. Accordingly, the modeling allows for different choices of initial data (Table 7). We assume the presence of two iron oxides – FeO and Fe_2O_3 . Fe_3O_4 can, to first approximation, be treated as a combination of FeO and Fe_2O_3 and is therefore not included explicitly. In addition, the numerical experiment accounts for adsorbed oxygen and alumina on particle surfaces. Only under this assumption does the model reproduce the amount of Al_2O_3 observed experimentally in the products. The numerical study further enables exploration over a wide range of initial compositions, which is difficult to achieve experimentally.

No such complications arose for the Ti system, although the initial composition of the powder mixture can likewise be varied numerically.

Composition-evolution results for different initial data are presented in Figs. 6 and 7. We find that

Table 6. Formal kinetic parameters obtained using a semi-empirical approach

Таблица 6. Формально-кинетические параметры, найденные с помощью полужемпирического подхода

Al + (Fe + Fe_2O_3)					Ti + (Fe_2O_3 + Fe + C)				
Reaction No.	ΔS_{298}^0	k_{0i}	E	ΔH_{298}^0	Reaction No.	ΔS_{298}^0	k_{0i}	E	ΔH_{298}^0
1	–26.10	10^{15}	32,104.53	–30.7	1	–0.36	$9 \cdot 10^{13}$	15,710.04	–1155.0
2	–25.15	10^{15}	31,218.18	–33.7	2	–3.47	10^{14}	18,730.20	–44.6
3	–36.10	$3 \cdot 10^{15}$	36,638.25	–93.0	3	–40.92	10^{16}	78,275.70	–49.1
4	–26.38	10^{15}	32,365.77	–37.6	4	–40.43	10^{16}	77,496.60	–45.4
5	–24.95	10^{15}	47,960.92	–161.5	5	–161.62	$3 \cdot 10^{22}$	17,970.00	–209.0
6	–38.48	$8 \cdot 10^{15}$	43,655.07	–760.0	6	274.20	$6 \cdot 10^{26}$	15,255.54	584.0
7	274.30	$6 \cdot 10^{26}$	15,260.94	584.0	7	–183.32	10^{22}	10,348.02	–933.0
8	–5.40	10^{14}	22,621.50	–122.0	8	10.60	$2 \cdot 10^{14}$	32,147.00	–173.3
9	–626.86	10^{45}	34,299.18	–3164.0					
Notes. Units: $[\Delta S_{298}^0] = \text{J}/(\text{mol} \cdot \text{K})$; $[k_{0i}] = \text{s}^{-1}$; $[E] = \text{J/mol}$; $[\Delta H_{298}^0] = \text{kJ/mol}$. Reaction numbers follow Table 5.									

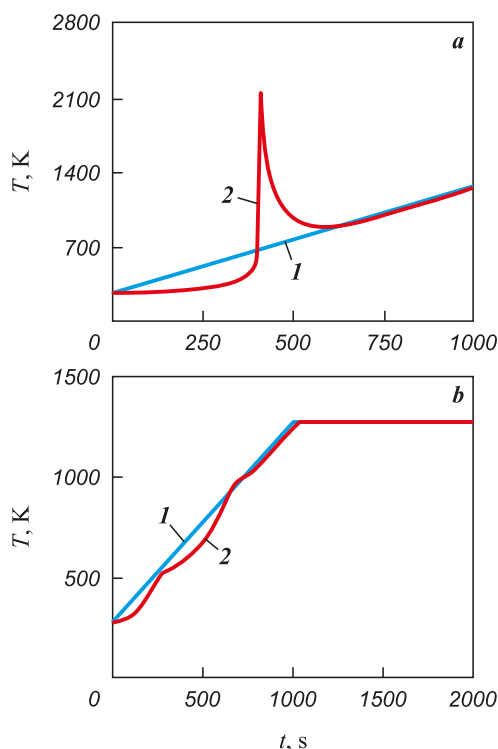


Fig. 5. Typical temperature curves for the composition with (a) and titanium (b)

Mixtures compositions 2 from Table 7

Sintering temperature $T_s = 1273$ K

1 – heater temperature; 2 – sample temperature

Рис. 5. Типичное поведение температурных кривых для состава с алюминием (a) и титаном (b)

Составы смесей 2 из табл. 7

Температура спекания $T_s = 1273$ K

1 – температура нагревателя; 2 – температура образца

the product composition can vary substantially. For the Al-containing system (Fig. 6), the products always contain Fe_3Al and FeAl_3 intermetallics in different proportions, as well as Al_2O_3 . The reduction of iron is the fastest reaction. FeAl is not observed in the products. The mixed oxide appears only when the initial mixture contains Al_2O_3 , FeO , and oxygen; in that case, Fe_2Al_3 is also present. The experimental data are best matched by Composition 2, which includes oxygen and oxide in the starting mixture.

The phase composition of the Ti compact also evolves (Fig. 7). All reactions proceed actively over a time interval shorter than the total sintering time. For all initial compositions, the products always contain the intermetallic Ti_2Fe and unreacted Ti. TiFe appears as an intermediate during sintering. In three variants, the product contains Ti_3FeO_2 . In the second variant, the starting mixture contains a small amount of iron oxide, hence its role is minor; however, Fe_2O_3 most closely reflects the experimental conditions. Under the experimental conditions, the product con-

tains 91 wt. % of α -Ti solid solution + Ti_2Fe and α -Ti solid solution + TiFe . In this case, Fe_2O_3 is insufficient to form TiO_2 . In the other three variants, TiO_2 appears as an intermediate that is consumed rapidly to form the complex oxide.

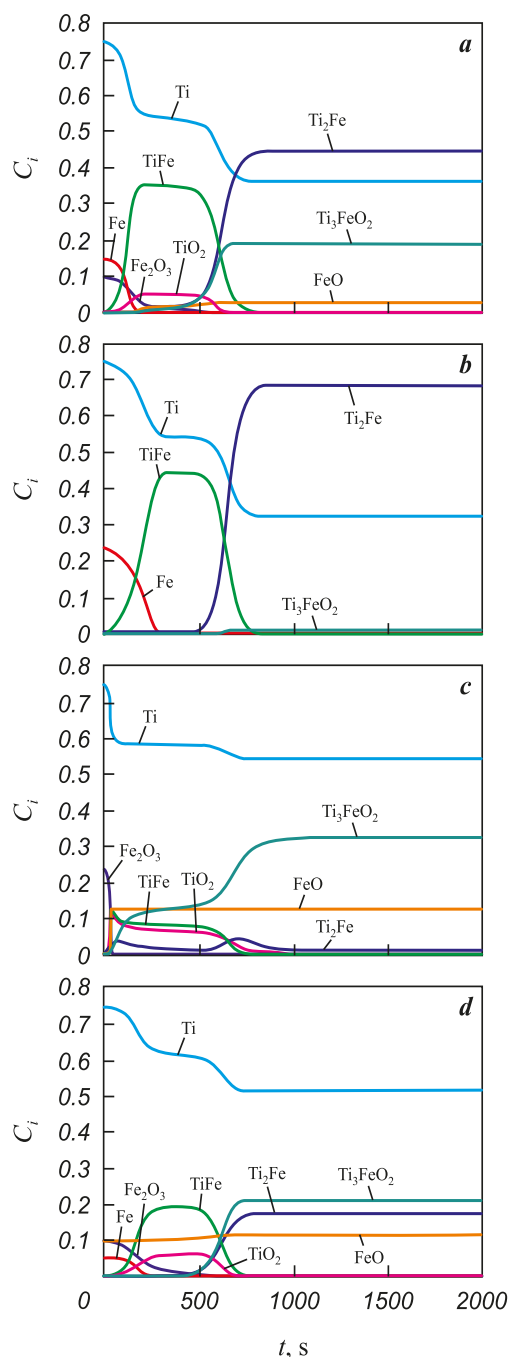


Fig. 6. Phase composition evolution of the aluminium compact during sintering

The initial composition corresponds to Table 7

Al-based mixtures: a – composition 1, b – 2, c – 3, d – 4

Рис. 6. Изменение фазового состава прессовки с алюминием в условиях спекания

Начальный состав соответствует табл. 7

Составы с Al: a – состав 1, b – 2, c – 3, d – 4

Table 7. Initial data for calculations

Таблица 7. Начальные данные для расчетов

Composition No. (numerical experiment)	Initial composition of the Al-containing mixture, wt. %						Initial composition of the Ti-containing mixture, %				
	Al	Fe ₂ O ₃	Fe	FeO	O ₂	Al ₂ O ₃	Ti	Fe ₂ O ₃	Fe	FeO	C
1	0.25	0.45	0.30	–	–	–	0.75	0.100	0.150	–	–
2	0.25	0.20	0.30	0.15	0.05	0.05	0.75	0.010	0.239	–	0.001
3	0.25	0.15	0.30	0.20	0.50	0.05	0.75	0.239	0.010	–	0.001
4	0.60	0.20	0.20	–	–	–	0.75	0.100	0.050	0.10	–

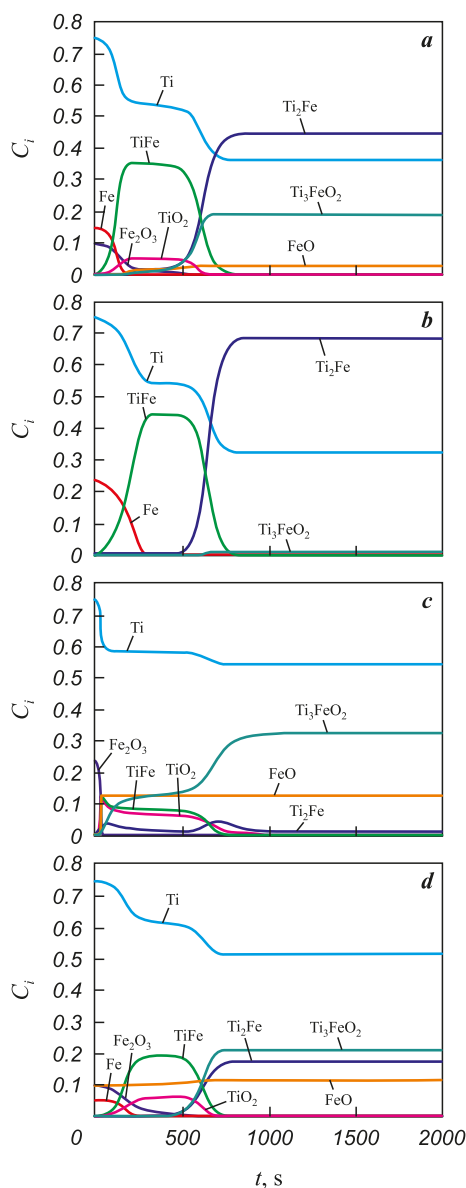


Fig. 7. Phase composition evolution of the titanium compact during sintering

The initial composition corresponds to Table 7
Ti-based mixtures: a – composition 1, b – 2, c – 3, d – 4

Рис. 7. Изменение фазового состава прессовки с титаном в условиях спекания

Начальный состав соответствует табл. 7
Составы с Ti: a – состав 1, b – 2, c – 3, d – 4

Conclusion

This study demonstrates good agreement between the proposed thermokinetic model and experimental data for multicomponent powder mixtures – recycled steel-chip powder with aluminum or titanium – under vacuum sintering. Consistent with the experiments, the calculations predict substantial heat release upon heating Al + (Fe + Fe₂O₃ + C) mixtures, whereas Ti + (Fe + Fe₂O₃ + C) sinters in a steady regime. In the former case, aluminum carbide was not included in the model because of the low sintering temperature; in the latter, titanium carbide formed only in trace amounts. No carbides were detected experimentally in either system.

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V. S. Safronova – development of the computational program, performing calculations, and analysis of the research results.

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