Features of the Synthesis of TiCAl (Fe_2O_3/TiO_2) Metal Matrix Composites under Nonequilibrium Conditions

<u>Anna Knyazeva</u>
Institute Strength Physics and Materials Science SB RAS, Tomsk Polytechnic University, Tomsk, Russia

Elena Korosteleva
Institute Strength Physics and Materials Science SB RAS, Tomsk Polytechnic University, Tomsk, Russia

Ivan Nikolaev
Tomsk Polytechnic University, Tomsk, Russia

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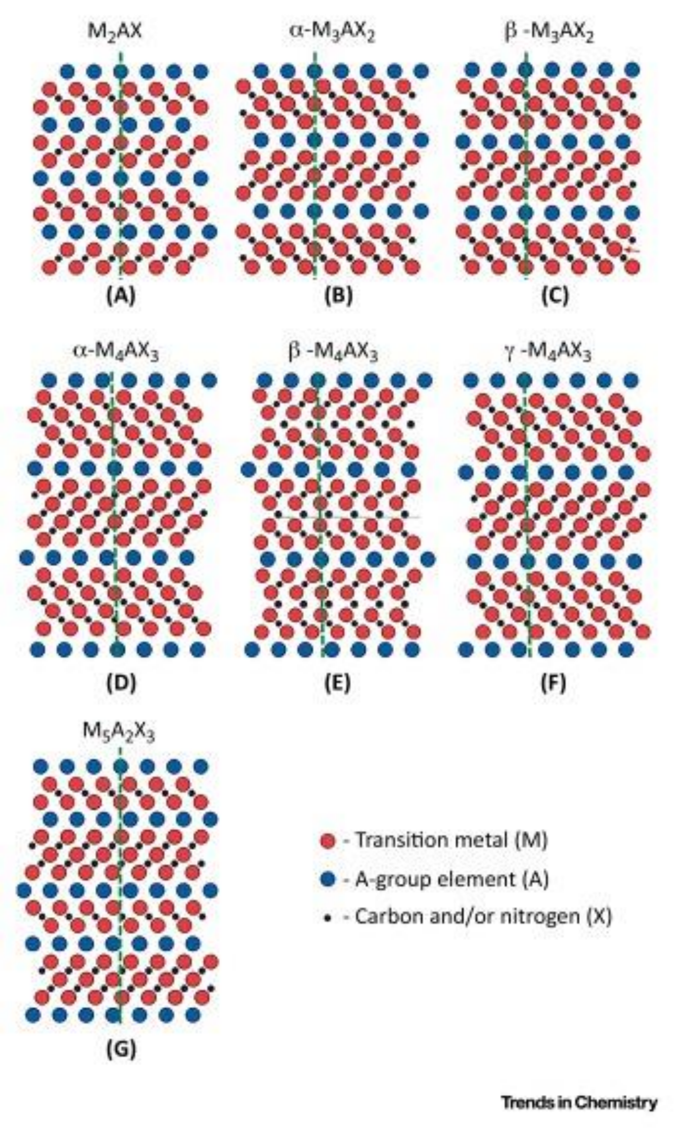
The synthesis of composites in the ***Ti-C-Al***, ***Ti-Al-C-Fe_2O_3*** and ***Ti-Al-C-TiO_2*** systems which is accompanied by the formation of ***MAX*** phases and intermetallic compounds with different properties was studied theoretically and experimentally.

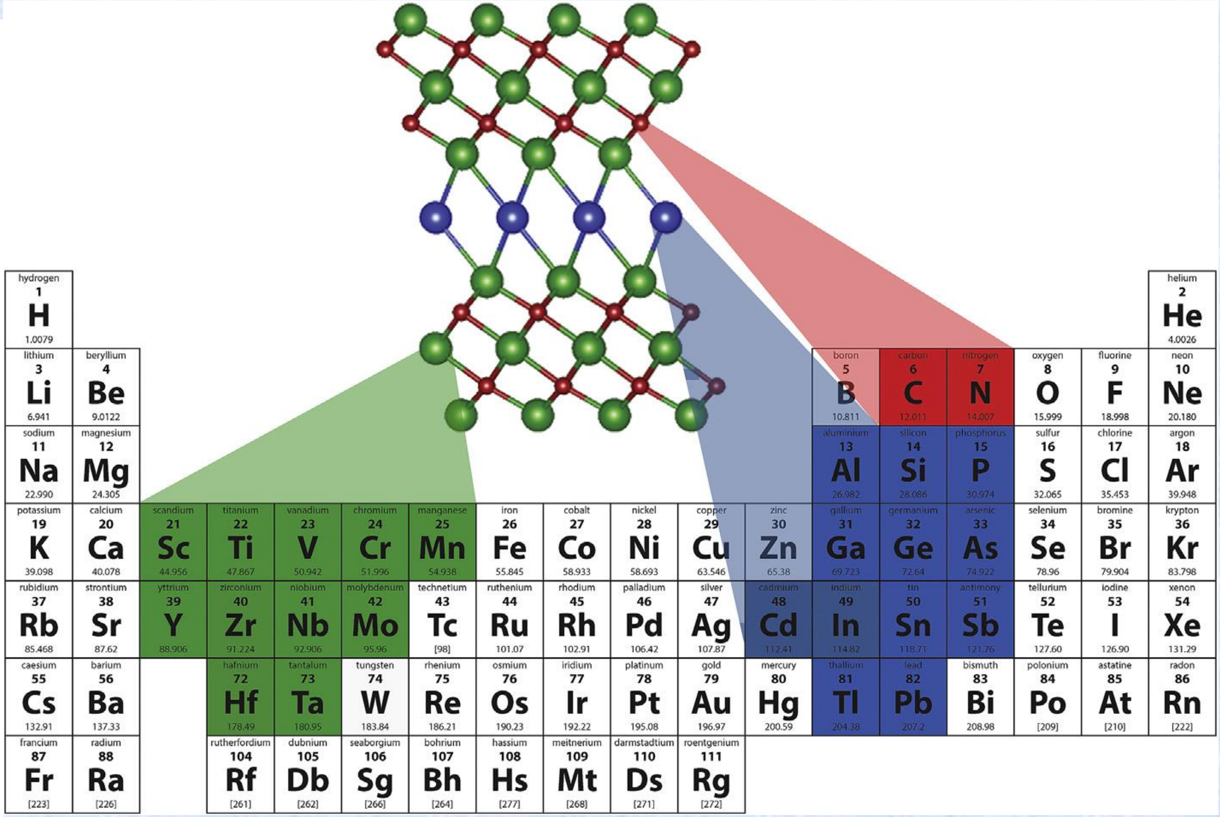
An attempt was made to determine under what conditions (and for which the compositions of the starting powder compositions) composite powders with fundamentally different properties are formed, caused by not only the inclusion properties, but also the matrix structure.

The result of the synthesis is a metal matrix composite or ceramic composite depending on the composition of the initial powders.

Using of metallothermal reactions to obtain composites with oxide inclusions (***Ti-Al-C-Fe_2O_3*** and ***Ti-Al-C-TiO_2***) results in appearance of the nonequilibrium phases that not predicted from preliminary thermodynamic evaluation.

What does mind MAX-phases?



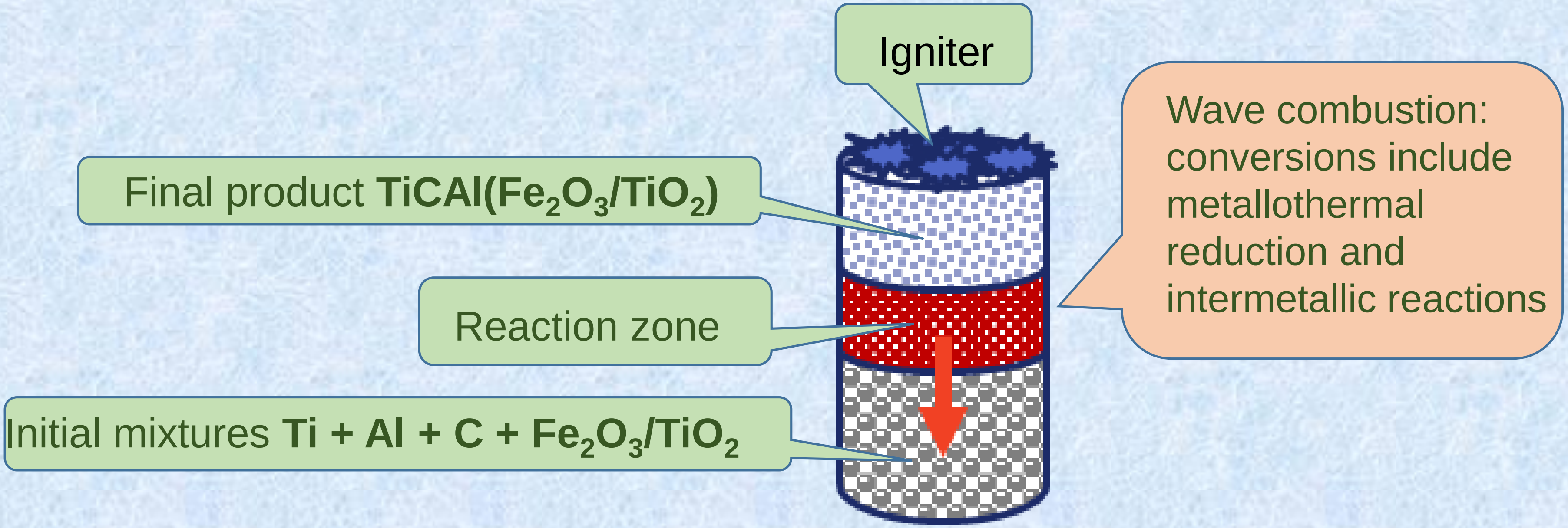


Among the many MAX phases synthesized to date, the compounds Ti_2AlC, Ti_2AlN, Ti_3AlC_2 and Ti_3SiC_2 in titanium-based materials are the most interesting in terms of physical and mechanical properties.

Materials and procedure

Industrial powders: Ti (≤ 160 μm)
Al (≤ 60 μm)
C (carbon black) (≤ 6 μm)
Fe_2O_3 (≤80 μm)
TiO_2 (≤60 μm)

Compositions:
a) Ti – Al – C
b) Ti – Al – C – Fe_2O_3
c) Ti – Al – C –TiO_2



Thermodynamics and kinetics

Among the possible reactions involving the **MAX** phases, the following are possible:

***$TiC+Al+Ti=Ti_2AlC$*;**

***$TiC+TiAl=Ti_2AlC$*;**

$2TiC+TiAl_3=TiAlC_2+2Al$

Some of the thermodynamically possible reactions in the **Ti-C** system:

$Ti + C \rightarrow TiC$ $\quad 2Ti + C \rightarrow Ti_2C$

$Ti_2C \rightarrow Ti + TiC$ $\quad TiC + Ti_2C \rightarrow Ti_3C_2$

$TiC_2 \rightarrow Ti + 2C$ $\quad Ti + 2C \rightarrow TiC_2$

$Ti_3C_2 = 2TiC + Ti$

Possible reactions of the intermetallic compounds formation in **Ti – Al** system:

$Ti + Al = TiAl$; $\quad TiAl + 2Ti = Ti_3Al$;

$TiAl + 2Al = TiAl_3$;

$2Ti + TiAl_3 = 3TiAl$ et al.

Possible reactions:

For TiO_2 – Al – C:

$$3TiO_2 + 4Al = 3Ti + 2Al_2O_3$$

$$Ti + Al \rightarrow TiAl$$

$$Ti + C \rightarrow TiC$$

$$TiAl + TiC \leftrightarrow Ti_2AlC$$

Mathematical model

The mathematical model of the composite synthesis by combustion generally takes into account the stage of the reaction initiation in the igniter; the non-stoichiometric composition of the reaction mixture; the formation of nonequilibrium phases; the accumulation of the liquid phase; and the course of the reactions in the solid phase, in the two-phase region, in the temperature range from solidus to liquidus, and in liquid phase.

The combustion model includes heat equations of the form:

$$c_k \rho_k \frac{\partial T_k}{\partial t} = \frac{\partial}{\partial x}\left(\lambda_k \frac{\partial T_k}{\partial x} \right) + W_{ch} -$$

$$- \frac{2\alpha}{R_k}\left(T_k - T_0\right) - \frac{2\varepsilon_0 \sigma_0}{R_k}\left(T_k^4 - T_0^4\right),$$

where the index "k = 1" relates to the igniter, the index "r = 2" relates to the ignited mixture, T is the temperature, t is the time; x - spatial coordinate;
λ_k, c_k, ρ_k – effective thermal conductivity, heat capacity and the density of layers; α – heat loss coefficient to the environment; σ_0 - Stefan-Boltzmann constant; ε_0 – effective degree of blackness, R_k - the layers radii, and W_{ch} - summary heat release in reactions

$$W_{ch} = \sum_{i=1}^{r} W_i$$

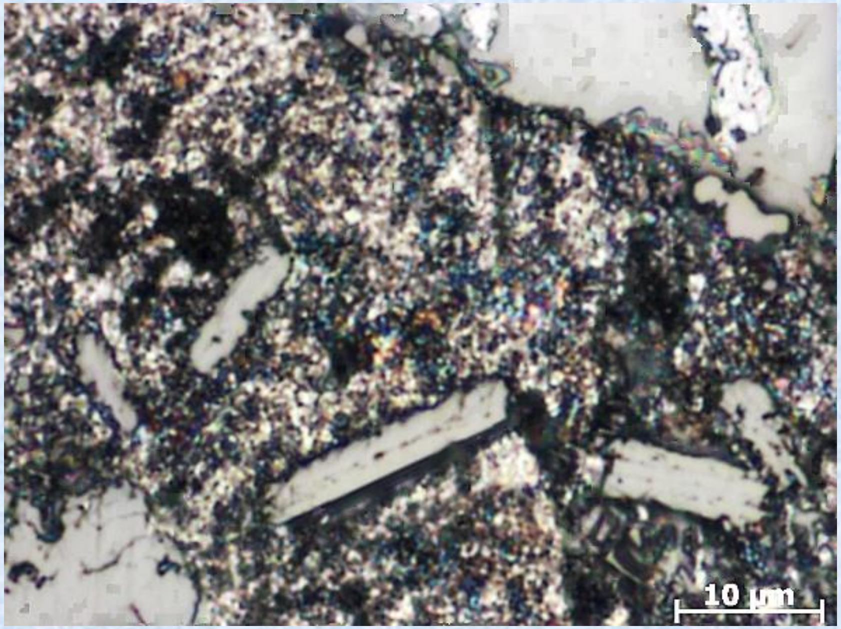
Kinetic equation system describes the possible conversions and irreversible phase formation.

Experiments

I. Composition Ti – Al – C

Phase distribution in products synthesized OF Ti–Al–C composition

Target (estimated) phase composition	Actual phase, wt.%		
	TiC	Al	$TiAl_3$
(TiC)+10 wt. %Al	83	12	5
(TiC)+20 wt. %Al	80	15	5
(TiC)+30 wt. %Al	61	35	4
(TiC)+40 wt. %Al	58	38	4
(TiC)+50 wt.%Al	57	40	3



Microstructure of the synthesized composite TiC – 40 wt. % Al

II. Composition Ti – Al – C – Fe_3O_2

Mixtures of the initial powders were prepared using different combinations of reacting components:

A) A composition expected to synthesize the titanium monoaluminide TiAl and intermetallic compound Fe_2Ti;

B) A reaction mixture in which titanium dioxide and complex triple intermetallic compounds of the type ($Fe_xAl_yTi_z$) should be synthesized;

C) The composition expected after the synthesis was similar to the previous one, but a different combination of the initial powders was used

Target Compositions and Powder Mixtures used in Ti–Al–C–Fe_3O_2 composites

Composition option	Reagent balance Fe_2O_3 /Al	Target composition (estimated phases after synthesis)	Initial powders used, wt. %			
			Ti	C	Al	Fe_2O_3
A	0.47	TiC + Al_2O_3 + Fe_2Ti + TiAl	55.2	2.1	28.6	14.1
B	0.59	TiC + Al_2O_3 + TiO_2 + ($Fe_xAl_yTi_z$)	52.8	1.1	28.9	17.2
C	0.22	TiC + Al_2O_3 + TiO_2 + ($Fe_xAl_yTi_z$)	35.4	0.7	52.3	11.5

Actual phase content in synthesized products of **Ti–Al–C–Fe_3O_2** compositions

Phases, wt.%	Target composition		
	A	B	C
TiC	4(14)	7 (20)	2(9)
Al_2O_3	7(25)	11(29)	21(26)
FeAl	10(14)	19 (35)	19(45)
Ti_2AlC	29(40)	20(23)	
$TiFe_{0.5}Al_{1.5}$	29(37)		
Ti_3Al		13	
$TiAl_3$			16
Al			10(12)

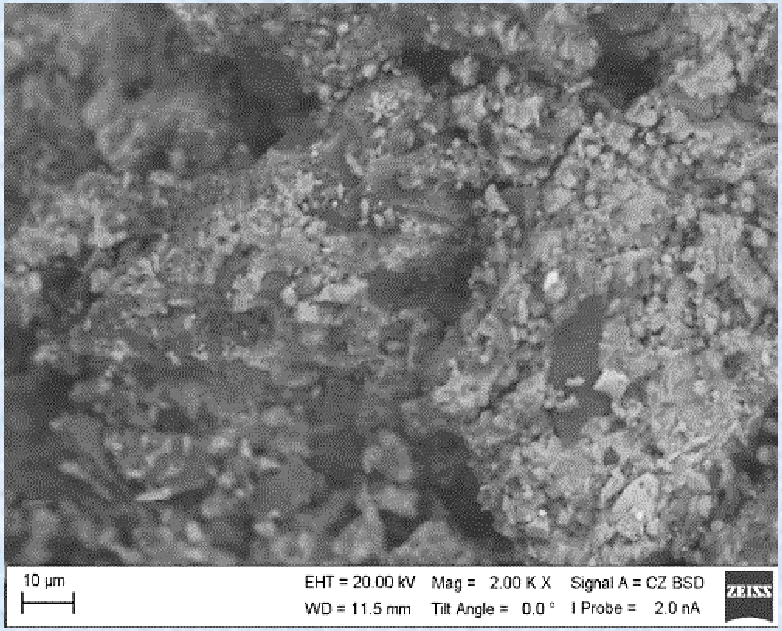
Table shows two variants of the quantitative composition of the synthesis products for each of the three reaction mixtures studied: the first number is the minimum content and the second (in brackets) is the maximum phase content.

From the data analysis of Tables, it follows that the aluminothermal reaction of the iron reduction from iron oxide by aluminium ($Fe_2O_3+2Al \rightarrow Al_2O_3+2Fe$) is leading and proceeds to the end, because the iron oxide residues were not found in the synthesis products.

III. Composition Ti – Al – C – TiO_2

Phase composition of synthesis products Ti–Al–C–TiO_2

Reaction mixture composition, wt. %				Phase composition of the synthesis products			
				Estimated	Actual, wt. %		
TiO_2	Al	C	Ti		TiC	Al_2O_3	Ti_2AlC
50.0	22.5	7.5	20.0	Al_2O_3+TiC+Ti	73	16	11



Morphology of the powder particles in SHS products of the TiO_2-Al-C-Ti reaction mixture

Conclusion

- During the synthesis of composites by combustion, a nonequilibrium phase composition is formed, which can be predicted only based on thermokinetic models, including a set of possible chemical stages.
- The determination of the formal kinetic parameters of the reactions is a separate problem.
- The composition of the synthesis products, in addition to intermetallic phases, includes Ti_2AlC phase. This phase can be synthesized both in combination with iron oxide and with the use of titanium dioxide.
- A number of phases supposed in the final product were not fixed. Perhaps these phases formed during the synthesis process, but their lifetime was short due to rapidly changing thermokinetic conditions that led to their decomposition.
- On the other hand, phases that were not supposed to be after synthesis were fixed.

Thank you very much for attention