Thermodynamics of Interactions in Al-K_2TiF_6-KBF_4 System

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The aim of this paper is to present the thermodynamic calculus of in-situ TiB_2 formation in the aluminium matrix by the aluminothermic reduction of KBF_4 and K_2TiF_6 mixed salts at 750 – 950°C. The in-situ formed TiB_2 particles are very fine and thermodynamically more stable than other formed compounds (Al_3Ti, AlB_2). It is found that the silicon addition in aluminium hinder the formation of Al_3Ti and AlB_2, and almost has no effect on TiB_2. The XRD and SEM/EDS analysis of in-situ Al/TiB_2 composites indicates the formation of only TiB_2 reinforcement particles.

Keywords: thermodynamic, K_2TiF_6, KBF_4, Al, composite, in-situ reaction

In the last decades the aluminium matrix composites reinforced with ceramic particles represent a significant field in structural composite research. A wide variety of fabrication techniques have been explored for MMCs (metal matrix composite). Thus, they have been manufactured by diverse techniques such as powder metallurgy, deposition of matrix by atomization and cast methods.

In-situ method for manufacturing these composites, came into sight in the middle of'80, offering a thermodynamic stability of fine and disperse particles into the aluminium matrix due to the fact that germination and growth of reinforcement particles take place exact in the alloy matrix, ensuring a strong connection at the interface between particles and matrix.

In-situ fabrication of MMC_s is a process, in which reinforcing phase is formed in the matrix as a result of precipitation from the melt during its cooling and solidification. Dispersed phases of in-situ MMCs may consist of borides, carbides or intermetallic compounds.

In-situ synthesis of metal matrix composites (MMCs) gives better properties than ex-situ MMCs due to good particle/matrix interface and finer reinforcement particles size.

In the last years have been realized an important number of researches concerning the processing of Al/TiB_2 composite materials through in-situ methods. For obtaining these composites have been attempt some methods that are based on the exothermic reaction between the aluminum matrix and salts mixtures (K_2TiF_6 + KBF_4 + Na_3AlF_6) [1-8].

However information related to the thermodynamic of the exothermic reactions is very limited.

The objective of this paper is to present the results of the application of thermodynamic calculation of in-situ formation of TiB_2 particles in liquid aluminium matrix during the exothermic process via K_2TiF_6 and KBF_4 salts. The thermodynamic calculus was realized with HSC Chemistry 6 program.

Experimental part

The in-situ composites with Al-Mg-Si (6063) matrix and 5 - 12 vol.% TiB_2 particles were prepared in an electric furnace with KANTHAL resistance and graphite crucible by salts mixing process, at 750 – 950°C, in which KBF_4 and K_2TiF_6 salts were added in proper Ti:B ratio to the liquid metal. The melt was stirred for 10 – 15 min. and poured after the slag was cleared.

The samples for microstructure observations and X-ray diffraction analysis were cut from the composites. The microstructures of the polished samples were examined with optical microscope, scanning electron microscope (SEM) and energy dispersive X-ray microanalysis (EDS).

Thermodynamics of interaction processes of salts with aluminium melt

KBF_4 and K_2TiF_6 salts are thermodynamically stable in working temperatures interval (750 – 950°C), KBF_4 being less stable than K_2TiF_6 ($\left|\Delta G^0_{T(KBF4)}\right| < \left|\Delta G^0_{T(K2TiF6)}\right|$)(fig.1).

On these terms we cannot speak of dissociation of these salts:

$$KBF_4 \rightarrow KF + BF_{3(g)} \quad (1)$$

$$K_2TiF_6 \rightarrow 2\ KF + TiF_{4(g)} \quad (2)$$

KBF_4 suffered a polymorphous transformation by heating at 289°C passing from rhombic to cubic atomic structure [4, 11, 14]. Melting temperature of KBF_4 is very controversial, some authors indicating 570°C, and others being unable to identify it. The constitution water of K_2TiF_6 is lost at 375°C, and the formation of K_3TiOF_5 takes place at 562°C because of reaction with atmosphere humidity.

Also, the data from literature [1, 3, 8] confirm that in the presence of liquid aluminium the loss of constitution water take place at 375°C, and an exothermic reaction at 728°C suggest the beginning of precipitation of $TiAl_3$ compound.

In the presence of aluminium, KBF_4 can stand the same polymorphous transformation by heating at 289°C, and two exothermal reactions with the formation of AlB_{12} at 460 and 558°C are taking place [1, 2, 5].

An intensification of reaction at 558°C is found, at heating the salts mixture (K_2TiF_6 and KBF_4) in the presence of aluminium [1, 2, 9].

At the simultaneous introduction of those two salts in liquid aluminium, the interactions are very complex involving reactions in the melt, diffusion processes through boundary layer between metallic and salt melt, reactions

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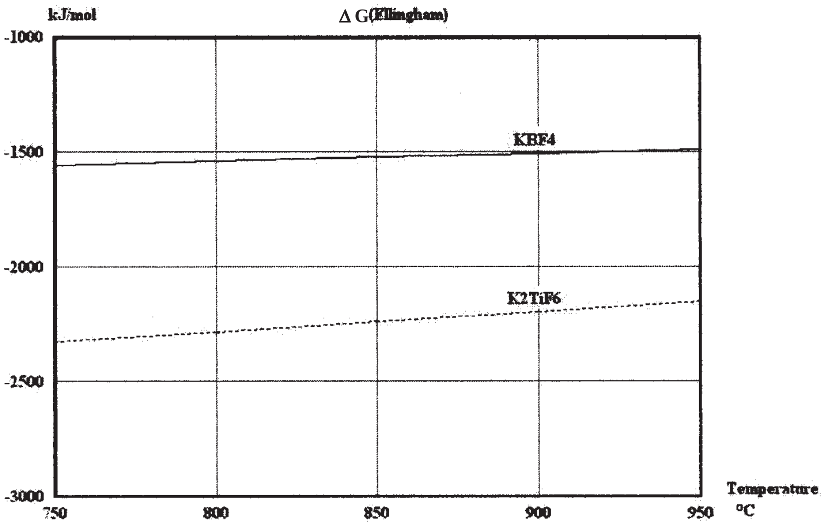

Fig. 1. Ellingham diagram $\Delta G_T^0 = f(T)$, at the formation of KBF_4 and K_2TiF_6

Table 1

RESULTS OF THERMODYNAMIC REACTION (3)

$3K_2TiF_6 + 6KBF_4 + 10Al = 3TiB_2 + 12KF + 10AlF_3$					
T, °C	ΔH, kJ	ΔS, J/K	ΔG, kJ	K	Log(K)
750	-254.,47	-70.2158	-2469.63	1.2E+126	126.0921
800	-2507.59	-37.8843	-2466.93	1.2E+120	120.0858
850	-2472.7	-6.11292	-2465.83	4.9E+114	114.6888
900	-2109.22	315.024	-2478.79	2.4E+110	110.3775
950	-2071.43	346.5618	-2495.33	3.7E+106	106.572
Formula	FM	Conc.	Amount	Amount	Volume
	g/mol	wt-%	mol	g	l or ml
Al	26.982	15.458	10.000	269.815	99.932
K_2TiF_6	240.087	41.264	3.000	720.261	0.000
KBF_4	125.902	43.278	6.000	755.411	301.561
	g/mol	wt-%	mol	g	l or ml
TiB_2	69.520	11.949	3.000	208.560	47.616
KF	58.097	39.941	12.000	697.160	281.113
AlF_3	83.977	48.111	10.000	839.767	270.893

K – equilibrium constant of reaction

within salt particle and the formation of some gaseous phases.

In the process proposed in this paper, the TiB_2 particles resulted by aluminothermique reduction of hexafluorotitanate (K_2TiF_6) and of tetrafluoroborate (KBF_4) with liquid aluminium:

$$3\ K_2TiF_6 + 6\ KBF_4 + 10\ Al = 3\ TiB_2 + 12\ KF + 10\ AlF_3 \quad (3)$$

Thermodynamic data of reaction (3) calculated by HSC Chemistry 6 are presented in the table 1 whence it results that ΔG is very negative in working interval (750 – 950°C), the reaction having a very high probability of development.

Aluminothermic reduction of the salts can take place according with reactions (4) and (5):

$$3\ K_2TiF_6 + 13\ Al = 3\ Al_3Ti + 6\ KF + 4\ AlF_3 \quad (4)$$

$$6\ KBF_4 + 9\ Al = 3\ AlB_2 + 6\ KF + 6\ AlF_3 \quad (5)$$

The calculated thermodynamic data (table 2 and 3) indicate the possibility of development of those two reactions in 750 – 950°C temperature interval, with negative ΔG_T^0.

From reactions (4) and (5) results the formation of Al_3Ti and AlB_2 compounds.

At the working temperature, in the conditions of exothermic reactions heat evolution, the Al_3Ti and AlB_2 particles developed from reactions (4) and (5) can rapidly react resulting in-situ TiB_2 reinforced compound in aluminium matrix:

$$3\ AlB_2 + 3\ Al_3Ti = 3\ TiB_2 + 12\ Al \quad (6)$$

The reaction has a negative ΔG_T^0 in the 750 - 950°C interval, in accordance with calculated data (table 4).

The compounds ($TiAl_3$, AlB_2, TiB_2, AlB_{12}) formed in Al-Ti-B system are presented in ternary diagram (fig. 2) [9-13].

Practically, at the aluminothermic reaction temperature, TiB_2 compound is thermodynamically more stable than $TiAl_3$, with negative ΔG_T^0 (fig. 3).

Also, Al_3Ti and AlB_{12} compounds can react at high temperatures and high maintaining time, in the presence of liquid Al to form TiB_2 and AlB_2:

$$AlB_{12} + Al_3Ti + Al = TiB_2 + 5\ AlB_2 \quad (7)$$

In accordance with calculated thermodynamic data (table 5), the reaction (7) is possible, having a high absolute value of negative free enthalpy.

This last reaction increases the number of reinforced particles (TiB_2) and leads to the dispersion of titanium boride in aluminium matrix.

Also, the titanium boride can directly result at the interface between liquid aluminium and flux. The TiB_2 particles formed in this way are more easily rejected to interdrenditic area in the course of composite solidification process.

For in-situ synthesis of Al/TiB_2 composites it is necessary, at the finish of aluminothermic reaction, to separate out TiB_2 as a precipitated phase.

A practical phase diagram in the aluminium corner at

Table 2
THERMODYNAMIC DATA CALCULATED FOR REACTION (4)

$3K_2TiF_6 + 13Al = 3Al_3Ti + 6KF + 4AlF_3$					
T, °C	ΔH, kJ	ΔS, J/K	ΔG, kJ	K	Log(K)
750	-812.629	319.0785	-1139.09	1.44E+58	58.15874
800	-776.118	353.9165	-1155.92	1.85E+56	56.26826
850	-739.08	387.6482	-1174.47	4.22E+54	54.62581
900	-537.716	565.3095	-1200.91	2.99E+53	53.47506
950	-499.173	597.482	-1229.98	3.39E+52	52.53083
Formula	FM	Conc.	Amount	Amount	Volume
	g/mol	wt-%	mol	g	l or ml
K_2TiF_6	240.087	67.250	3.000	720.261	0.000
Al	26.982	32.750	13.000	350.760	129.911
	g/mol	wt-%	mol	g	l or ml
Al_3Ti	128.845	36.090	3.000	386.534	0.000
KF	58.097	32.547	6.000	348.580	140.557
AlF_3	83.977	31.363	4.000	335.907	108.357

Table 3
THERMODYNAMIC DATA CALCULATED FOR REACTION (5)

$6KBF_4 + 9Al = 3AlB_2 + 6KF + 6AlF_3$					
T, °C	ΔH, kJ	ΔS, J/K	ΔG, kJ	K	Log(K)
750	-1921.02	-582.255	-1325.29	4.63E+67	67.66517
800	-1924.32	-585.41	-1296.09	1.23E+63	63.09137
850	-1926.95	-587.805	-1266.76	8.29E+58	58.91836
900	-1765.11	-444.57	-1243.56	2.37E+55	55.37424
950	-1765.94	-445.265	-1221.31	1.45E+52	52.1605
Formula	FM	Conc.	Amount	Amount	Volume
	g/mol	wt-%	mol	g	l or ml
KBF_4	125.902	75.674	6.000	755.411	301.561
Al	26.982	24.326	9.000	242.834	89.938
	g/mol	wt-%	mol	g	l or ml
AlB_2	48.602	14.606	3.000	145.805	45.707
KF	58.097	34.919	6.000	348.580	140.557
AlF_3	83.977	50.475	6.000	503.860	162.536

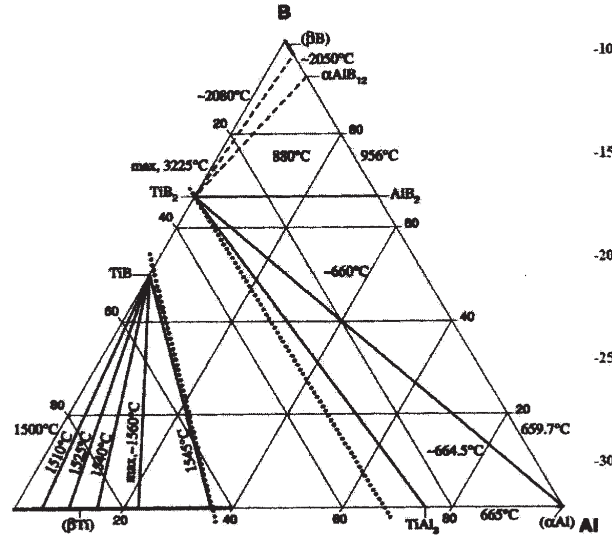

Fig. 2. The projection of partial surface of solidus in Al-Ti-B system

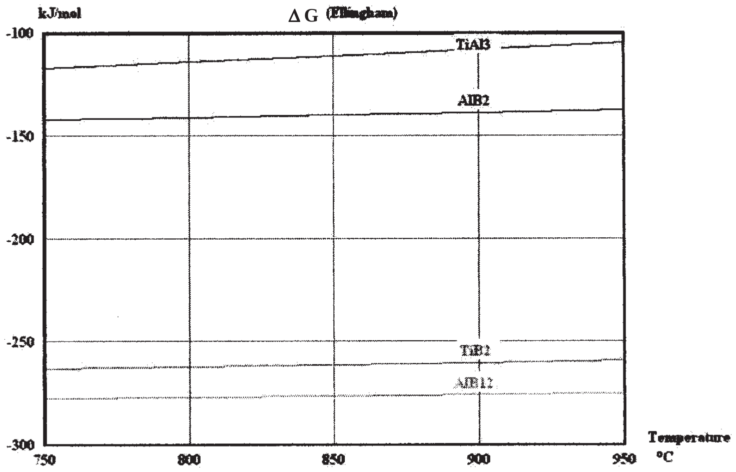

Fig. 3. Ellingham diagram ΔG_T^0 = f(T), at the formation of $TiAl_3$, AlB_2, TiB_2 and AlB_{12} compounds

Table 4
THERMODYNAMIC DATA CALCULATED FOR REACTION (6)

$3AlB_2 + 3Al_3Ti = 3TiB_2 + 12Al$					
T, °C	ΔH, kJ	ΔS, J/K	ΔG, kJ	K	Log(K)
750	192.1755	192.9607	-5.25229	1.854241	0.268166
800	192.854	193.609	-14.9175	5.322981	0.726155
850	193.3308	194.044	-24.6096	13.95154	1.144622
900	193.6057	194.284	-34.3186	33.74173	1.528167
950	193.6774	194.3445	-44.035	75.97552	1.880674
Formula	FM	Conc.	Amount	Amount	Volume
	g/mol	wt-%	mol	g	l or ml
AlB_2	48.602	27.389	3.000	145.805	45.707
Al_3Ti	128.845	72.611	3.000	386.534	0.000
	g/mol	wt-%	mol	g	l or ml
TiB_2	69.520	39.178	3.000	208.560	47.616
Al	26.982	60.822	12.000	323.778	119.918

Table 5
THERMODYNAMIC DATA CALCULATED FOR REACTION (7)

$AlB_{12} + Al_3Ti + Al = TiB_2 + 5AlB_2$					
T, °C	ΔH, kJ	ΔS, J/K	ΔG, kJ	K	Log(K)
750	-638.406	-59.8303	-577.19	2.95E+29	29.46961
800	-638.407	-59.8321	-574.198	8.93E+27	27.95093
850	-638.334	-59.7657	-571.208	3.69E+26	26.56754
900	-638.186	-59.6372	-568.223	2.01E+25	25.30229
950	-637.964	-59.4521	-565.245	1.38E+24	24.14082
Formula	FM	Conc.	Amount	Amount	Volume
	g/mol	wt-%	mol	g	l or ml
AlB_{12}	156.702	50.140	1.000	156.702	61.452
Al_3Ti	128.845	41.227	1.000	128.845	0.000
Al	26.982	8.633	1.000	26.982	9.993
	g/mol	wt-%	mol	g	l or ml
TiB_2	69.520	22.244	1.000	69.520	15.872
AlB_2	48.602	77.756	5.000	243.008	76.178

1000K (fig. 4) has been done [14]. It shows that when $x_{Ti} \cdot x_B^2 > 10^{-14.9}$, TiB_2 can be separated out as a distinguished phase in hatched area (x_{Ti} şi x_B are the atomic fractions of titanium and boron in the system Al – Ti - B).

When the alloying component (Si or Mg) in the aluminium matrix is added, the influence of alloying element addition on the precipitation reaction in the melt can come from changes of the components concentration and activity coefficient, namely Δx_i and $\Delta\gamma_i$, where $\Delta\gamma_i$ can be calculated from the Wilson equation and using an extended Miedema model.

In a quaternary system the Wilson equation can be rewritten as:

$$\lg\gamma_i = 1-\ln(1-x_jA_{j/i}-x_kA_{k/i}-x_hA_{h/i})-\frac{x_i}{1-x_jA_{j/i}-x_kA_{k/i}-x_hA_{h/i}}-\frac{x_j(1-A_{i/j})}{1-x_iA_{i/j}-x_kA_{k/j}-x_hA_{h/j}}-\frac{x_k(1-A_{i/k})}{1-x_iA_{i/k}-x_jA_{j/k}-x_hA_{h/k}}-\frac{x_h(1-A_{i/h})}{1-x_iA_{i/h}-x_jA_{j/h}-x_kA_{k/h}}$$

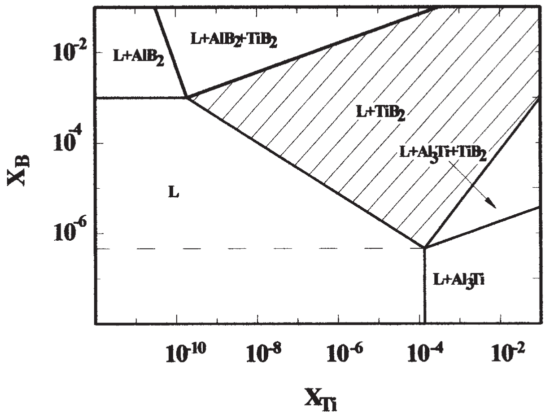

Fig. 4. Phase diagram for the system Al-Ti-B (Al corner) using logarithmic scales

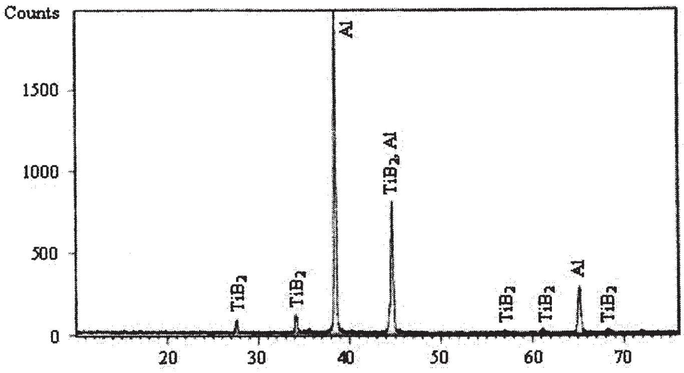

Fig. 7. XRD pattern of 6063/TiB_2 in -situ composite

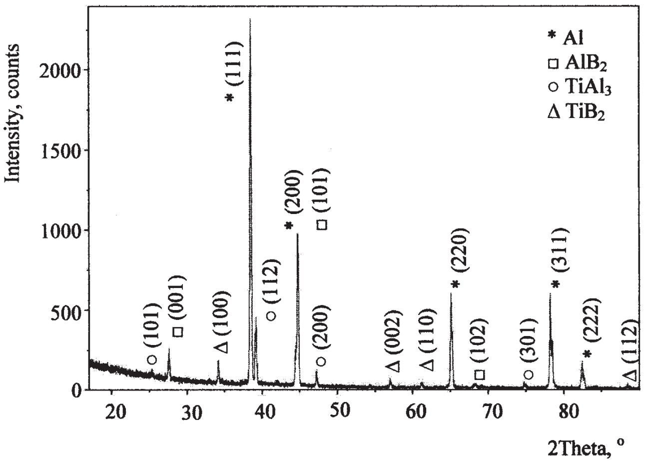

Fig. 5.X-ray diffraction patterns of Al/TiB_2 composite

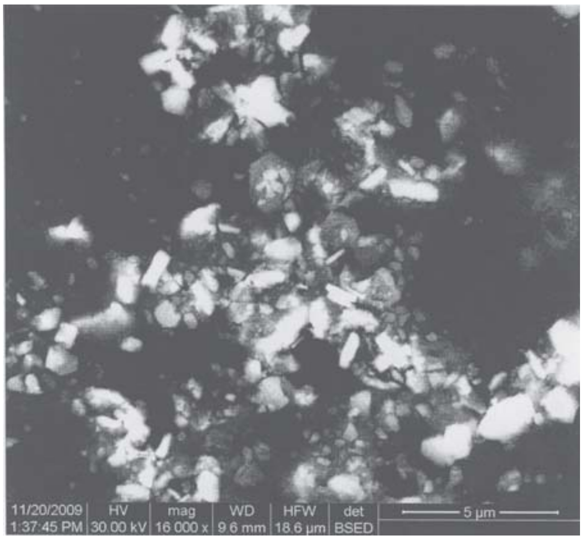

Fig. 8. SEM micrograph of Al/TiB_2 composite

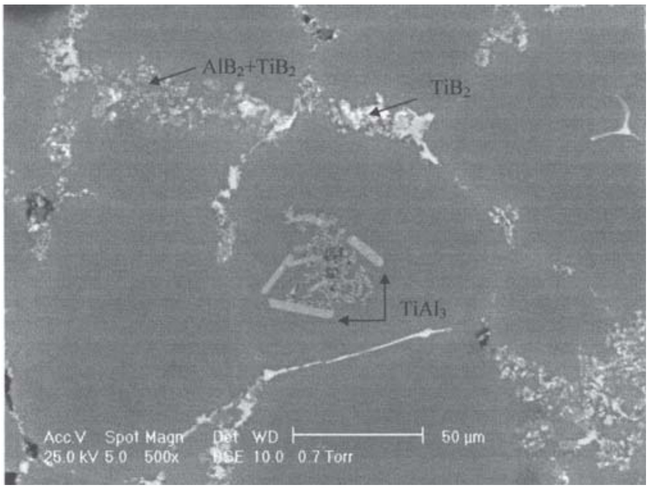

Fig. 6. SEM micrograph of Al/TiB_2 composite

In this relation $A_{h/i}$, ..., $A_{k/j}$ are Wilson adjustable parameters.

According to the calculated activities of different components in the aluminium melt, it was concluded that the excess free energy for the formation of TiB_2, Al_3Ti, and AlB_2 can be affected by different alloying element additions [4]. The results show that the addition of Mg, Cu, Zr, Ni, Fe, V, and La with low content can promote the formation of Al_3Ti and TiB_2.

Aluminium matrix alloy with Si and Mg addition (6xxx alloys) in our experiment can hinder the formation of Al_3Ti and AlB_2 and almost has no effect on TiB_2 [4].

Figure 5 shows the XRD patterns of Al/TiB_2 composites for reaction (6), progressing. It indicates that the present phases in the composite are α-Al, Al_3Ti, AlB_2 and TiB_2. SEM micrograph of Al/TiB_2 composite is presented in figure 6. The result of the XRD analysis for completely finished reaction (3) (fig. 7) indicates that the present phases in the composite are α-Al and TiB_2 particles.

Figure 8 shows the SEM micrograph of Al/TiB_2 composite for reaction (6) finished. It can be observed that TiB_2 particles are mostly less than 1 μm in size.

Conclusions

In the KBF_4-K_2TiF_6-Al system, the TiB_2 particles were formed in-situ in the aluminium matrix in the 750 – 950°C interval.

The calculated thermodynamic data by HSC Chemistry 6 indicate a negative value of ΔG_T^0 of the reaction:

$$3\,K_2TiF_6 + 6\,KBF_4 + 10\,Al = 3\,TiB_2 + 12\,KF + 10\,AlF_3$$

At the working temperature the Al_3Ti and AlB_2 particles can react with result of in-situ TiB_2 reinforced compound. Practically, at the aluminothermic reaction temperature, TiB_2 compound is thermodynamically more stable than Al_3Ti.

The reaction between Al_3Ti and AlB_{12} in the presence of liquid aluminium, increases the number of reinforced TiB_2 particles and leads to the dispersion of these particles in aluminium matrix.

The formation of TiB_2, Al_3Ti and AlB_2 particles can be affected by different alloying element additions. Aluminium matrix alloy with Si addition in our experiment can hinder the formation of Al_3Ti and AlB_2 and almost has no effect on TiB_2, according to the calculated excess free energy for the formation of these particles.

The XRD and SEM/EDS analysis of in-situ Al/TiB_2 composites, as produced by aluminothermic reduction of K_2TiF_6 and KBF_4 salts indicates the formation of only TiB_2 reinforcement particles.

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