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Thermodynamics of in situ formation of TiB₂ particulates in complex aluminium alloys for aeronautics

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Abstract. Aluminum complex alloy AlCuMgZn, reinforced by in-situ TiB₂ particles are fabricated via liquid metallurgy route based on the exothermic reactions between matrix alloy and inorganic salt mixture (K₂TiF₆ and KBF₄), at 750°C, at various time (60, 90 and 120 minutes). The XRD patterns revealed the formation of TiB₂. At working temperature by thermodynamic point of view (negative ΔG), some secondary reaction also was possible, and AlB₁₂, MgB₂ and MgB₁₂ can to form. The main alloying elements of AlCuMgZn alloy do not influence final reaction products. Increasing the reaction time from 60 to 120 minutes leads to agglomeration of TiB₂ particles. Form and dimensions of TiB₂ particles obtained after separation from aluminium matrix were determined by Transmission Electron Microscopy (TEM) and through Dynamic Light Scattering (Zetasizer Nano ZS Malvern).

Keywords: in-situ AlCuMgZn - TiB₂ composites, thermodynamics, TiB₂ particles, TEM, Dynamic Light Scattering (DLS).

1. Introduction

Aluminium matrix composites (AMCs) are very attractive materials in recent years. Discontinuously reinforced AMCs results in improved physical and mechanical properties that cannot be achieved using conventional engineering alloys. The progress in production techniques enabled researches to synthesize AMCs composites reinforced with various oxides, carbides and nitrides (Al₂O₃, TiC, TiB₂, ZrB₂ and AlN) particulates [1, 2].

In-situ fabrication of AMCs is a process, in which reinforcing phase is formed in the aluminium matrix gives better physical and mechanical properties than ex-situ AMCs due to good matrix / particle interface and finer reinforcement particles size

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[2-7]. In the last years have been realized many researches based on the exothermic reactions between the aluminium alloys (as matrix) and salt mixtures ($\text{KBF}_4 + \text{K}_2\text{TiF}_6$) [3, 5-15].

However, information related to the thermodynamics and also the characterization of TiAl_3 and TiB_2 particulates which is formed in this type of composites is very limited [4, 11, 12].

The objective of this paper is to present our results of the thermodynamics of in-situ TiB_2 particulates formed in Al-Cu-Mg-Zn / metallic boride composites.

Alloys from the quaternary system Al-Cu-Mg-Zn displays outstanding properties both as cast and after machining and specific heat. However, this system is not sufficiently studied, although it is used in high-tech industries, especially because of the large main alloying elements [16].

However, the fundamental understanding of the (Al) corner of this diagram, in particular, the liquidus projections and solidification surface are absent. For this reason, figure 1 represents the results obtained by the authors [16] based on many years of joint work upon this subject. Table 1 provides the corresponding non-variant phase reactions. One should mention that the latter take place at concentrations, which are quite different from those corresponding to known industrial alloys. For this reason, the most valuable information is contained in the isothermal cross-sections provided in figure 1 [16].

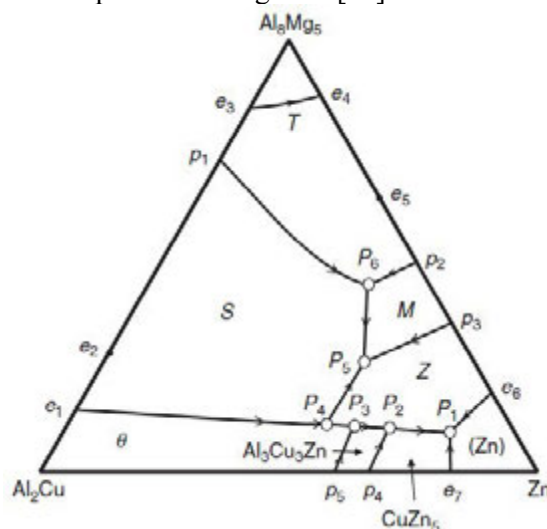


Fig. 1. Phase diagram Al-Cu-Mg-Zn: single-phase domains [16].

The CuMg_4Al_6 and $\text{Mg}_3\text{Zn}_3\text{Al}_2$ phases in ternary systems exist in a broad range of concentrations. In the quaternary system the phase domain occupied by the quaternary solid solution (the T-phase - cubic structure) is also quite broad (figure 1). The quaternary solid solution between compounds CuMgAl and MgZn_2 (the so-called M-phase) is characterized by hexagonal structure.

Table 1. Non-variant reactions in quaternary alloys of the Al-Cu-Mg-Zn system [16]

Point in figure 1	Phase reaction	Composition of liquid			T°C
		Zn(%)	Mg(%)	Cu(%)	
P ₁	$L + CuZn_5 \Rightarrow (Al) + (Zn) + Z$	91.1	2.2	3.4	350
P ₂	$L + Cu_3ZnAl_3 \Rightarrow (Al) + CuZn_5 + Z$	82.6	5.4	10.1	363
P ₃	$L + Al_2Cu \Rightarrow (Al) + Cu_3ZnAl_3 + Z$	77.2	3.0	9.8	377
P ₄	$L + Al_2CuMg + Al_2Cu \Rightarrow (Al) + Z$	6.5	6.5	38.9	482
P ₅	$L + Al_2CuMg \Rightarrow (Al) + Z + M$	-	-	-	< 467
P ₆	$L + T \Rightarrow (Al) + Al_2CuMg + M$	-	-	-	< 467

The solid solution formed by $Cu_6Mg_2Al_5$ and Mg_2Zn_{11} compounds (the Z-phase - cubic structure). The $CuAl_2$ phase practically does not dissolve magnesium and dissolves not more than 2% Zn. The $CuMgAl_2$ phase also has very limited solubility range and can dissolve less than 1% Zn. In alloys containing 4 ÷ 8% Zn and 0.5 ÷ 1.0% Cu, the lattice parameter increases with Mg content in solid solution [16].

2. Experimental procedure

In-situ composites with TiB_2 particles were fabricated in an electric furnace using a graphite clay crucible by direct reaction between complex aluminium melt and mixed salts KBF_4 , K_2TiF_6 and Na_3AlF_6 , at 750 ÷ 950°C. A preweighted mixture of inorganic salts was added into the molten metal using the stirring method.

Cryolite (Na_3AlF_6) was added for the metal bath protection and dissolution of the formed oxides. The characteristic of the salts and metals used are following:

- Potassium hexafluorotitanate (K_2TiF_6): molecular weight: 240.09 g/mol; appearance: white crystalline flakes; melting point: 780°C; composition: 99% min.; Cl ≤ 0.05%; $SO_4 \leq 0.01\%$; $H_2O \leq 0.05\%$; Pb ≤ 0.01%; $SiO_2 \leq 0.2\%$; Fe ≤ 0.02%; grit: 60 mesh - 5% max.; 200 mesh - 45 % min.; 300 mesh - 20% max.;
- Potassium tetrafluoroborate (KBF_4): molecular weight: 125.91 g/mol; density (20°C): 2.5 g/cm³; volumetric weight: 800 ÷ 1400 g/l; molar volum: 49.4 cm³; melting point: 530°C; solubility in water (20°C): 4.4 g/l; composition: > 98%; Fe ≤ 0.01%; $SO_4 \leq 0.02\%$; $SiO_2 \leq 0.4\%$; Cl ≤ 0.1%; Pb ≤ 0.0005%; Na ≤ 0.1%; Mg ≤ 0.05%; H_2O (110°C) ≤ 0.05%;
- Cryolite (Na_3AlF_6): molecular weight: 209.94 g/mol; appearance: white powder; density (20°C): 2.95 g/cm³; volumetric weight: 600 ÷ 1000 g/l; melting point: 1027°C; solubility in water (20°C): 0.42 g/l; composition: Na 30 ÷ 32%; Al 12 ÷ 13.5%; F ≥ 53.0%; Fe ≤ 0.03%; $SO_4 \leq 0.5\%$; $SiO_2 \leq 0.25\%$; $P_2O_5 \leq 0.03\%$; Cl ≤ 0.1%; Pb ≤ 0.0005%.
- AA 7xxx series aluminium alloys

Table 2. Chemical composition of 7xxx alloys, wt% [12]

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr	Al
EN AW 7050 AlZn6CuMgZr	0.12	0.15	2.0 ÷ 2.6	0.10	1.9 ÷ 2.6	0.04	5.7 ÷ 6.7	0.06	0.08 ÷ 0.15	rest
7050 - sample C	0.065	0.11	2.20	0.021	2.28	0.0025	5.95	0.035	0.09	rest

After the slag is removed, the composite was poured into cast iron mould in the form of bars of 10 mm diameter. The specimens from the cast composites were polished and etched with Keller reagent and examined by OM (optical microscopy) and X-ray diffractometer.

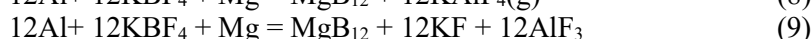
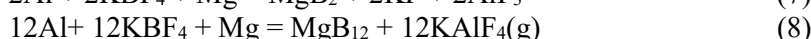
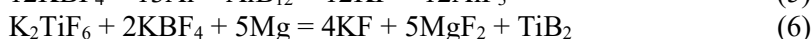
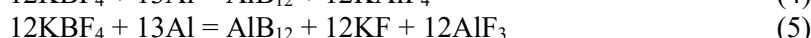
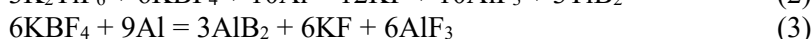
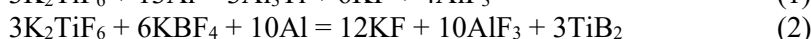
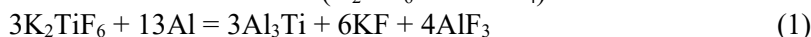
Samples of the composite materials was dissolved in concentrated HCl and powder of TiB₂ particle was examined using X-ray diffractometer.

3. Results and discussions

The studies presented in the literature refers specifically to less complex systems [2, 3, 5-10, 13-15], in terms of development and in-situ growth of particle reinforcement. For complex systems Al-Cu-Mg-Zn / K₂TiF₆ / KBF₄ [4, 11, 12] is interesting to see whether high concentrations of Cu (> 1.5%), Mg (> 2.2%) and Zn (> 5.4%) influence the final reaction products for reactions (1 ÷ 9).

According to calculation by T. Fan, G. Yang, and D. Zhang [10] results that free excess energy of TiB₂, and Al₃Ti formation may be influenced by various alloying elements in aluminium. Thus, the addition of Mg, Cu, Zn, Ni, Fe, V and La may intensify the formation of Al₃Ti and TiB₂.

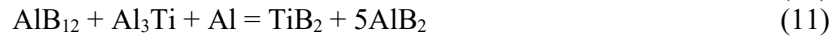
To highlight the thermodynamics of boride particle formation in aluminium complex 7xxx alloys, three times to react for produce TiB₂ (60, 90 and 120 minutes) were studies. From thermodynamic studies results 14 reactions, the aluminothermic reduction of salts (K₂TiF₆ and KBF₄) occurs:



Thermodynamic data computed with HSC Chemistry program indicates, in the temperature range 750 ÷ 950°C, possibility of Al₃Ti, TiB₂, AlB₂, AlB₁₂, MgB₂ and MgB₁₂ compounds formation, with negative ΔG°_T (table 3 for reactions 1 ÷ 7 and table 4 for reactions 8 ÷ 14).

At the working temperature, in the condition of exothermic reaction heat evolution, the Al₃Ti, TiB₂, AlB₂, AlB₁₂, MgB₂ and MgB₁₂ particles developed

from reaction (1 ÷ 9), can react resulting in-situ Al_3Ti / TiB_2 reinforced compound of aluminium matrix:



For determining the mechanism of thus reactions, an optical microscopy of the material in an intermediate state has been achieved (figure 1).

Table 3. Gibbs Free Energies of formation for the reaction 1 ÷ 7

T	deltaG1	deltaG2	deltaG3	deltaG4	deltaG5	deltaG6	deltaG7
K	kJ	kJ	kJ	kJ	kJ	kJ	kJ
973.15	-1124	-2474	-1354	-2484	-2127	-1410	-389
998.15	-1131	-2472	-1340	-2514	-2101	-1409	-384
1023.15	-1139	-2470	-1325	-2543	-2075	-1408	-379
1048.15	-1147	-2468	-1311	-2573	-2049	-1408	-374
1073.15	-1156	-2467	-1296	-2602	-2023	-1407	-369
1098.15	-1165	-2466	-1281	-2630	-1997	-1407	-364
1123.15	-1174	-2466	-1267	-2659	-1971	-1407	-359
1148.15	-1187	-2471	-1255	-2687	-1949	-1408	-355
1173.15	-1201	-2479	-1244	-2714	-1930	-1411	-352
1198.15	-1215	-2487	-1232	-2742	-1911	-1413	-348
1223.15	-1230	-2495	-1221	-2769	-1892	-1416	-344
1248.15	-1245	-2504	-1210	-2796	-1873	-1419	-340
1273.15	-1261	-2513	-1199	-2823	-1854	-1422	-336

Table 4. Gibbs Free Energies of formation for the reactions 8 ÷ 14

T	deltaG8	deltaG9	deltaG10	deltaG11	deltaG12	deltaG13	deltaG14
K	kJ	kJ	kJ	kJ	kJ	kJ	kJ
973.15	-2334	-1978	1	-580	-149	-358	-582
998.15	-2364	-1951	0	-579	-150	-355	-579
1023.15	-2393	-1925	-2	-577	-150	-352	-575
1048.15	-2422	-1898	-3	-576	-151	-348	-572
1073.15	-2450	-1872	-5	-574	-151	-345	-569
1098.15	-2478	-1845	-7	-573	-152	-342	-566
1123.15	-2506	-1818	-8	-571	-152	-339	-563
1148.15	-2534	-1797	-10	-570	-153	-336	-560
1173.15	-2561	-1777	-11	-568	-153	-332	-557

T	deltaG8	deltaG9	deltaG10	deltaG11	deltaG12	deltaG13	deltaG14
K	kJ	kJ	kJ	kJ	kJ	kJ	kJ
1198.15	-2588	-1757	-13	-567	-154	-329	-554
1223.15	-2615	-1738	-15	-565	-154	-326	-551
1248.15	-2641	-1718	-16	-564	-155	-322	-547
1273.15	-2667	-1698	-18	-562	-155	-319	-544

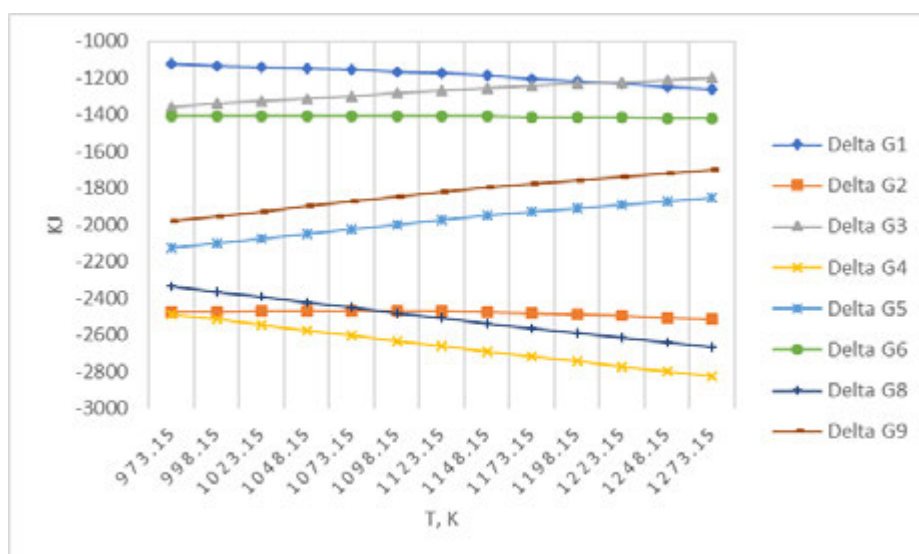


Fig. 2. Variation of standard free enthalpy (ΔG) in the temperature range 973.15 – 1273.15 K of the reactions 1 ÷ 6, 8 and 9.

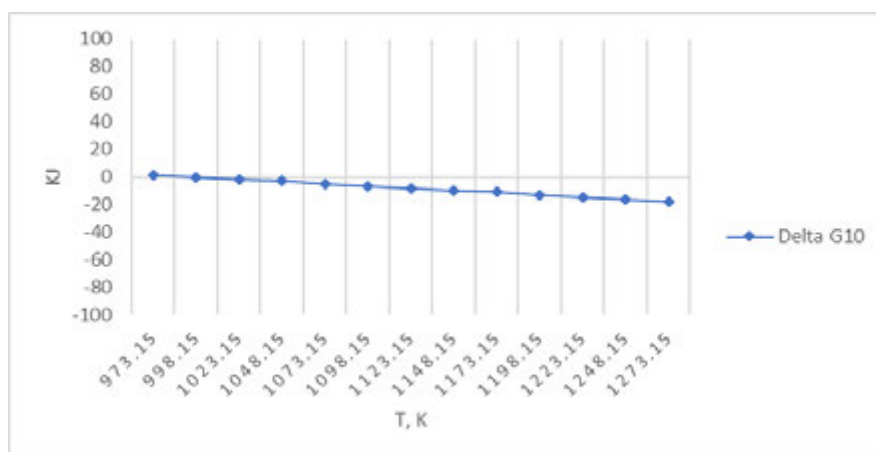


Fig. 3. Variation of standard free enthalpy (ΔG) in the temperature range 973.15 – 1273.15 K of the reaction 10.

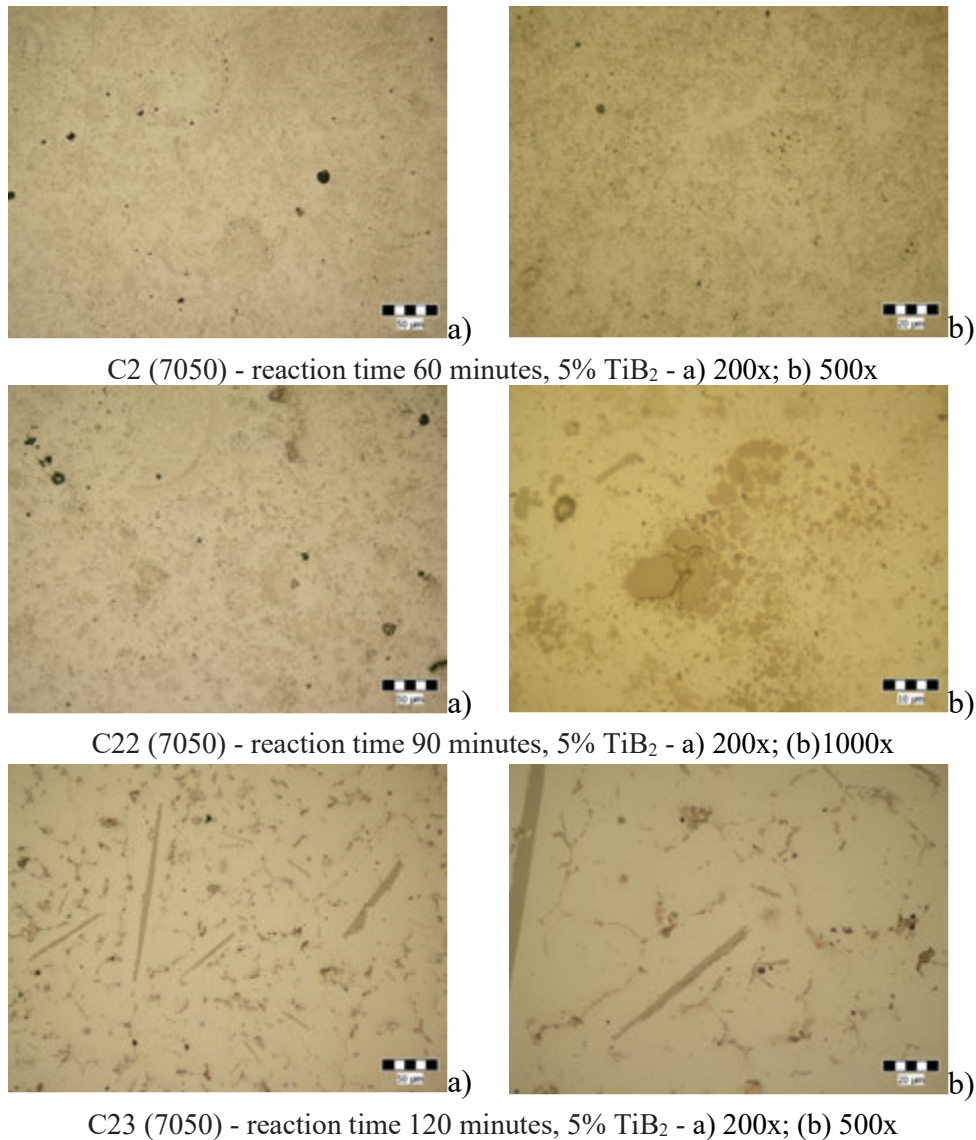
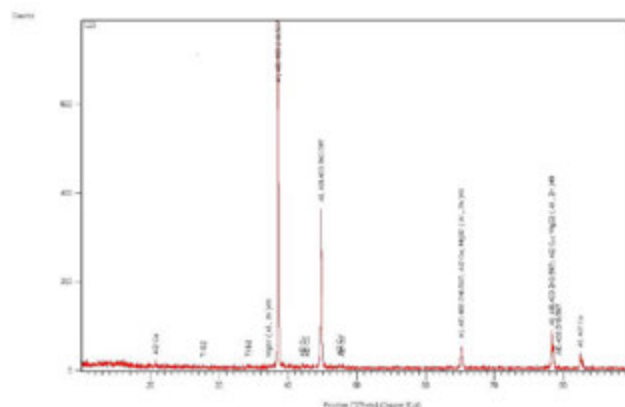


Fig. 4. Optical microstructures of composites with different concentrations of in-situ formed particles.

Increasing the reaction time from 60 to 120 minutes leads to the agglomeration of TiB_2 particles. Also, from the optical microscopy analysis, an increase in the concentration of TiAl_3 compounds can be observed at 120 minute reaction times, which means a change in the direction of the reaction (10), with the dissolution of TiB_2 .

In order to identify the TiB_2 particles, we performed the diffractometric analysis of the samples. Figures 2, 3 and 4 show the results of the diffractometric analysis for

the analyzed samples (5% TiB₂), the list of reaction products present in the analysed samples and the list of the corresponding peakings.



a)

No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale ...	SemiQua
1	<input type="checkbox"/>	01-071-3760	Aluminum	Al	51	0.465	-
2	<input type="checkbox"/>	00-052-0856	Aluminum Zinc	Al _{10.403} Zn _{0.597}	23	0.425	-
3	<input type="checkbox"/>	01-089-1980	Khatyrkite, s...	Al ₂ Cu	Un...	0.021	-
4	<input type="checkbox"/>	01-075-0967	titanium boride	Ti B ₂	8	0.018	-
5	<input type="checkbox"/>	00-039-0951	Aluminum M...	Mg ₃₂ (Al, Zn) ₄₉	2	0.039	-

b)

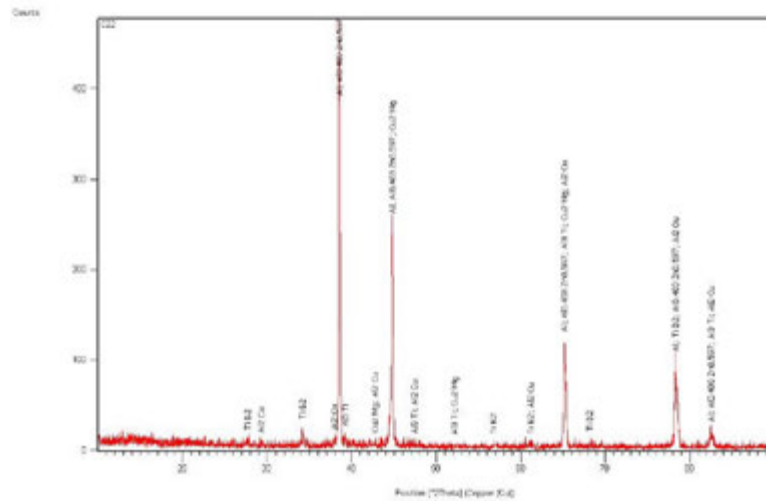
Date: 5/22/2014 Time: 13:36:52 File: C23

No.	Pos. [2Th]	d-spacing...	Rel. Int.	FWHM [°]	Matched by	Area [cts*°2Th]	Back
1	20.6847	4.29420	0.63	0.1181	01-089-1980	0.89	
2	27.6459	3.22672	0.27	0.1968	01-075-0967	0.38	
3	34.1627	2.62465	0.64	0.2362	01-075-0967	0.91	
4	37.1778	2.41843	0.47	0.1574	00-039-0951	0.66	
5	38.5416	2.33594	100.00	0.1968	01-071-3760, 00-...	141.86	
6	42.0777	2.14745	0.79	0.2362	01-089-1980	1.12	
7	42.7501	2.11522	0.96	0.3149	01-089-1980	1.36	
8	44.8034	2.02294	24.35	0.0984	01-071-3760, 00-...	34.54	
9	47.3701	1.91914	1.08	0.1968	01-089-1980	1.54	
10	47.8646	1.90047	0.59	0.1574	01-089-1980	0.83	
11	65.1685	1.43153	6.63	0.1968	01-071-3760, 00-...	9.40	

XRD crystallites size:
TiB₂ – 19,12 nm
Al – 35,84 nm

c)

Fig. 5. Diffractometric analysis (a) for the sample maintained 60 minutes, the list of compounds (b) and the list of peaks (c) with the crystallite dimensions.



a)

No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale ...	SemiQua
1	<input type="checkbox"/>	01-089-3657	Aluminum, syn	Al	52	0.684	-
2	<input type="checkbox"/>	01-071-5368	Titanium Bor...	Ti B2	18	0.042	-
3	<input type="checkbox"/>	00-052-0856	Aluminum Zinc	Al0.403 Zn0.597	32	0.457	-
4	<input type="checkbox"/>	03-065-7847	Aluminum Ti...	Al3 Ti	7	0.044	-
5	<input type="checkbox"/>	03-065-9042	Copper Magnes	Cu2 Mg	0	0.079	-
6	<input type="checkbox"/>	01-089-1981	Khatyrkite, s...	Al2 Cu	4	0.011	-

b)

No.	Pos. (°2Th)	d-spacing	Rel. Int.	FWHM (°)	Matched by	Area [int°2Th]	Height [cts]	Width [cts]
1	27.6986	3.22070	1.43	0.1574	01-071-5368	0.71	4.81	4.57
2	29.2917	3.04907	1.61	0.3149	01-089-1981	0.80	4.70	2.57
3	34.1764	2.62363	4.01	0.1181	01-071-5368	1.99	4.57	17.09
4	37.9521	2.37085	2.27	0.1968	01-089-1981	1.13	5.21	5.80
5	38.4975	2.33851	100.00	0.1181	01-089-3657,00...	49.66	5.23	426.34
6	39.1976	2.29834	2.83	0.1574	03-065-7847	1.41	5.25	9.06
7	42.7516	2.11515	1.14	0.3149	03-065-9042,01...	0.57	5.44	1.83
8	44.7704	2.02435	47.98	0.0984	01-089-3657,00...	23.83	4.89	245.47
9	47.4100	1.91762	4.44	0.9446	03-065-7847,01...	2.22	4.16	2.38
10	52.1691	1.75334	0.39	0.1181	03-065-7847,03...	0.19	3.38	1.65
11	56.7708	1.62166	2.58	0.6298	01-071-5368	1.28	2.95	2.06
12	61.2021	1.51444	2.71	0.4723	01-071-5368,01...	1.35	3.08	2.89
13	65.1708	1.43149	31.62	0.1378	01-089-3657,00...	15.70	3.74	115.55
14	68.1258	1.37642	0.82	0.0984	01-071-5368	0.41	3.82	4.22
15	78.2786	1.22036	47.99	0.1920	01-089-3657,01...	23.83	3.74	93.10
16	82.5082	1.16818	5.96	0.1440	01-089-3657,00...	2.96	3.75	15.41

c)

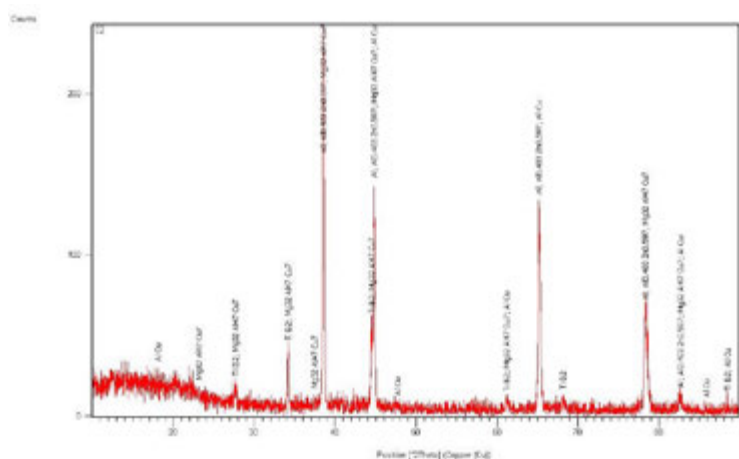
XRD crystallites size:

TiB₂ – 31,68nm

Al – 35,79nm

TiAl₃ – 31,49nm

Fig. 6. Diffractometric analysis (a) for the sample maintained 90 minutes, the list of compounds (b) and the list of peaks (c) with the crystallite dimensions.



a)

No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale ...	SemiQua
1	<input type="checkbox"/>	01-071-4624	Aluminum	Al	49	1.067	-
2	<input type="checkbox"/>	01-075-1045	titanium boride	Ti B2	39	0.200	-
3	<input type="checkbox"/>	00-052-0856	Aluminum Zinc	Al0.403 Zn0.597	29	0.627	-
4	<input type="checkbox"/>	00-019-0011	Aluminum C...	Mg32 Al147 Cu7	7	0.701	-
5	<input type="checkbox"/>	01-088-1713	Cupalite, syn	Al Cu	6	0.376	-

b)

Date: 5/22/2014 Time: 13:28:22

File: C2

No.	Pos. [2θ]	d-spacing	Rel. Int.	FWHM [°]	Matched by	Area [pts*2θ]	Backg
1	18.0833	4.90565	2.78	0.1181	01-088-1713	1.14	
2	23.1844	3.83657	1.74	0.1378	00-019-0011	0.71	
3	27.7015	3.22038	6.36	0.2362	01-075-1045; 00-...	2.60	
4	34.1691	2.62417	10.11	0.1181	01-075-1045; 00-...	4.13	
5	37.4436	2.40187	1.82	0.1574	00-019-0011	0.74	
6	38.5175	2.33734	69.05	0.1181	01-071-4624; 00-...	28.19	
7	44.4752	2.03710	14.98	0.1181	01-075-1045; 00-...	6.12	
8	44.7865	2.02366	32.59	0.0984	01-071-4624; 00-...	13.31	
9	47.7200	1.90589	2.81	0.6298	01-088-1713	1.15	
10	61.1936	1.51463	4.08	0.3149	01-075-1045; 00-...	1.67	
11	65.1740	1.43024	100.00	0.2400	01-071-4624; 00-...	40.83	
12	68.1182	1.37542	5.53	0.2880	01-075-1045	2.26	
13	78.2696	1.22048	78.76	0.1920	01-071-4624; 00-...	15.82	

XRD crystallites size:

TiB₂ – 29,65 nm

Al – 31,17 nm

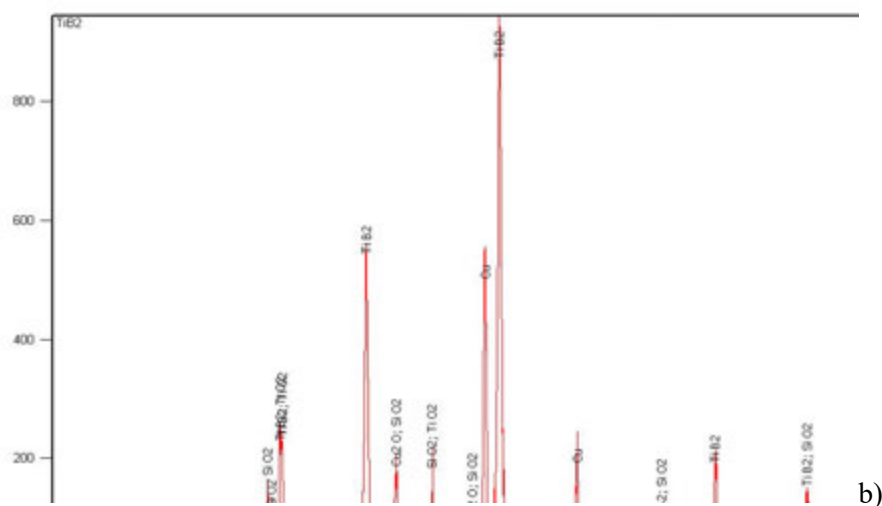
c)

Fig. 7. Diffractometric analysis (a) for the sample maintained 120 minutes, the list of compounds (b) and the list of peaks (c) with the crystallite dimensions.

4. Characterization of TiB₂ particles

After leaching in HCl of the composite and successive washings of solid material obtained, particles were analysed through X-ray diffraction (X-ray diffractometer – X’Pert PRO MPD, PANalytical) and fluorescence (X-ray Fluorescence Spectrometer – S8 Tiger). Form and dimensions of the TiB₂ particles were determined by Transmission Electron Microscopy (TEM) and through DLS technique (Dynamic Light Scattering – Zetasizer Nano ZS Malvern). The samples were spread in distilled water, homogenized in an ultrasonic box at different times. The amount of sample taken for the measurement was 1 ml and the temperature 25°C. Particle sizes were determined according to the intensity of the scattered light and the volume.

No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score
1	<input checked="" type="checkbox"/>	04-004-5881	Titanium Bo...	Ti B ₂	75
2	<input checked="" type="checkbox"/>	04-006-2601	Copper, syn	Cu	55
3	<input checked="" type="checkbox"/>	04-012-6327	Copper Oxide	Cu ₂ O	48
4	<input checked="" type="checkbox"/>	01-088-2487	Quartz, syn	Si O ₂	24
5	<input checked="" type="checkbox"/>	04-008-2840	Quartz, nat	Si O ₂	24



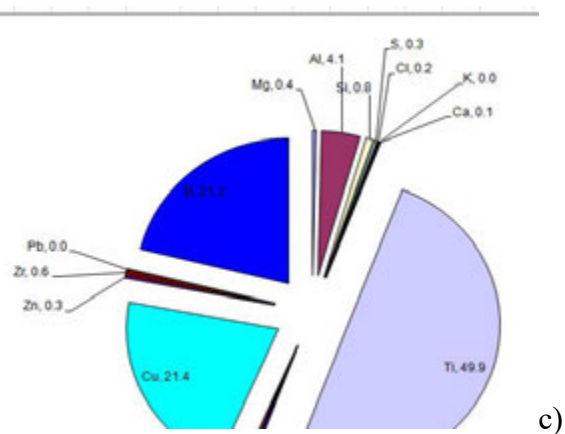


Fig. 8. Analysis of TiB₂ powders obtained:
a), b) - compound distribution (quantitative) and XRD diagram; c) elemental distribution.

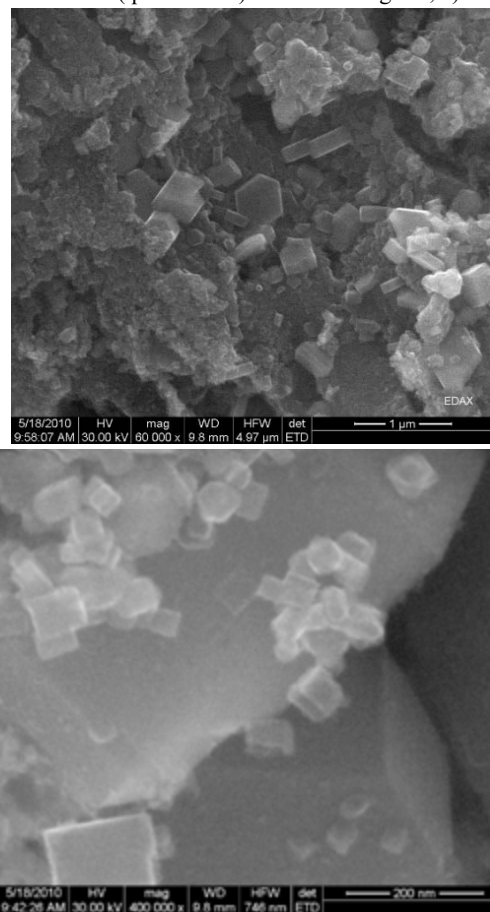


Fig. 9. The morphology of the TiB₂ particles, examined using transmission electron microscopy (TEM).

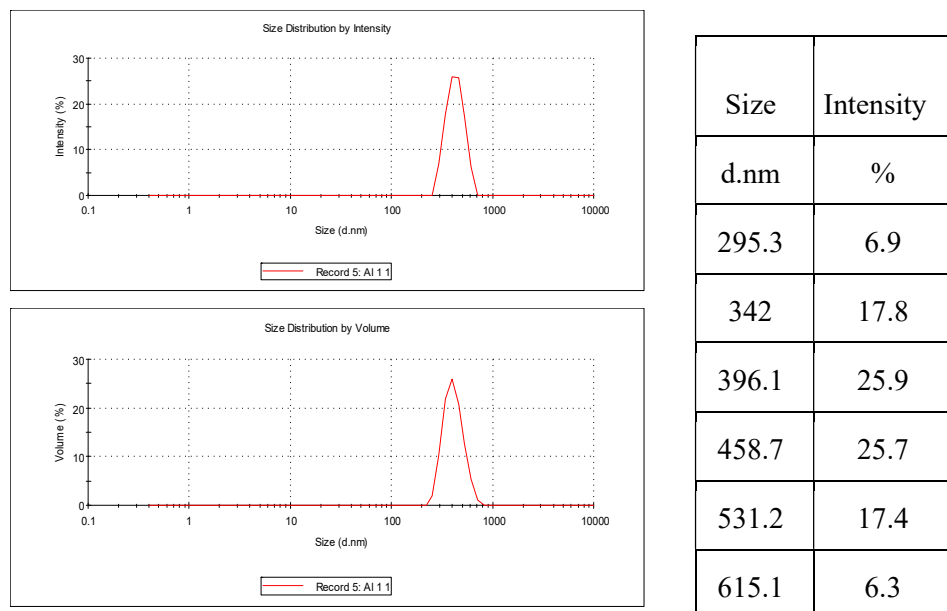
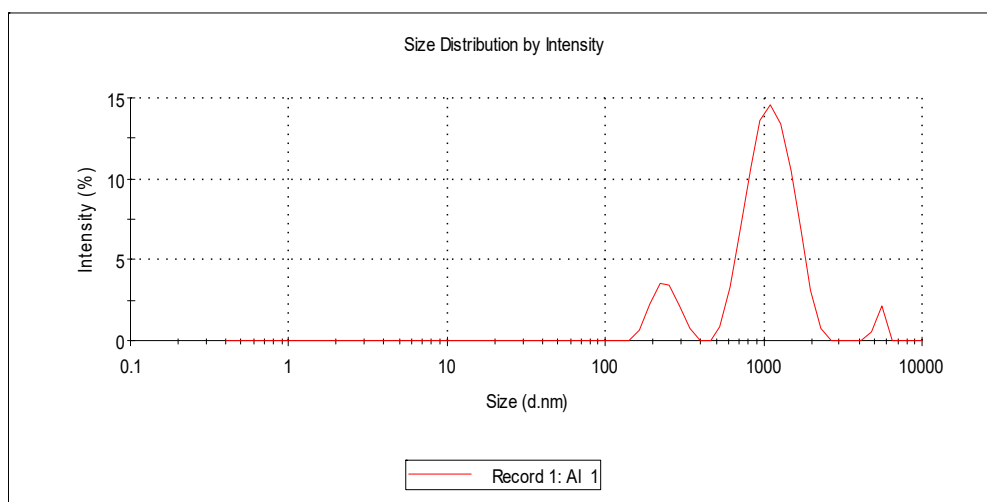
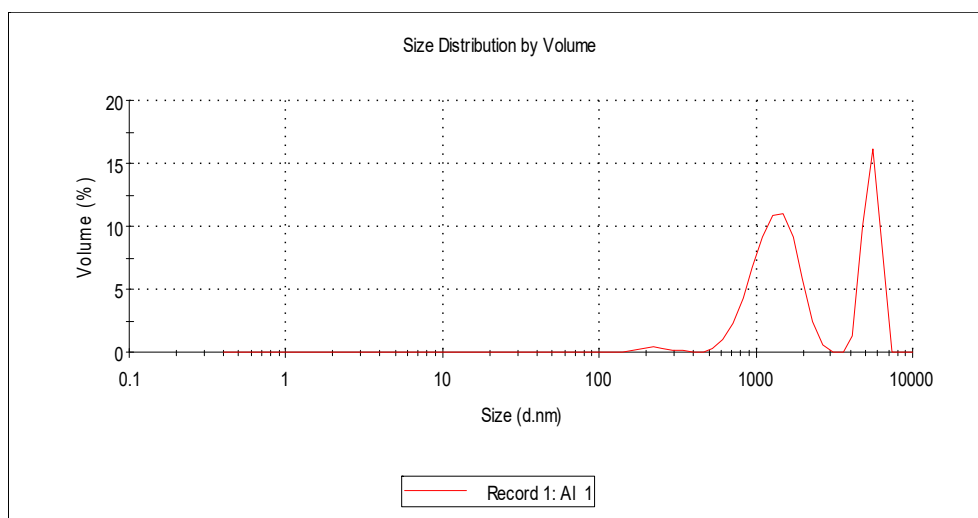


Fig. 10. Dimensional analysis of TiB₂ powders, determined by the DLS technique (dispersed particles) - Zetasizer Nano ZS Malvern.





Size	Intensity	Size	Intensity	Size	Intensity
d.nm	%	d.nm	%	d.nm	%
164.2	0.7	531.2	0.9	1281	13.4
190.1	2.3	615.1	3.3	1484	10.5
220.2	3.5	712.4	7	1718	6.7
255	3.4	825	10.8	1990	3.1
295.3	2.2	955.4	13.6	2305	0.8
342	0.8	1106	14.6	4801	0.5
				5560	2.1

Fig. 11. Dimensional analysis of TiB₂ powders, determined by the DLS technique (agglomerated particles) - Zetasizer Nano ZS Malvern.

5. Conclusions

- 1) In-situ AA 7050 / TiB₂ by reaction between potassium hexafluorotitanate (K₂TiF₆) and potassium tetrafluoroborate (KBF₄) are fabricated at 750°C.
- 2) Thermodynamic data, computed with HSC Chemistry program, indicates the possibility of TiB₂, Al₃Ti, AlB₂, AlB₁₂, MgB₂ and MgB₁₂ compounds formation, with negative ΔG°_T .

- 3) To highlight the mechanism of TiB_2 particle formation three time of reaction (60, 90 and 120 min.) were studied. Increasing the reaction time from 60 to 120 minutes leads to agglomeration of TiB_2 particles. Also, an increase of Al_3Ti concentration at 120 minute on observe by optical micrographies as a result of shifting the reaction (10) from right to left.
- 4) The XRD patterns revealed the formation of TiB_2 . Form and dimensions of TiB_2 particles obtained after separation from aluminium matrix were determined by Transmission Electron Microscopy (TEM) and through Dynamic Light Scattering (Zetasizer Nano ZS Malvern).
- 5) Only aluminium and magnesium from AlCuMgZn alloy can interacts with salts (K_2TiF_6 and KBF_4), but the influence of magnesium is negligible.

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