Thermodinamics of *in situ* Production of Aluminium Matrix Composites

Comparative analysis

MIHAI BUTU[1], PETRU MOLDOVAN[1], FLORIN DRAGOS MARCU[1]*, ANDREI BERBECARU[1], CONSTANTIN DOMENIC STANCEL[1], LUCIAN ROSU[1], IONEL UNGUREANU[2]

[1]University Politehnica of Bucharest, Materials Science and Engineering Faculty, 313 Splaiul Independetei, 060042, Bucharest, Romania

[2]ALRO S.A., 116 Pitesti Str., 230048, Slatina, Romania

The aim of this work is to examine the role of alloying elements (Cu, Mg, Zn) in the complex reactions occurring in the heterogeneous system Al-Cu-Mg-Zn/K_2TiF_6/KBF_4 at high temperatures. The paper presents theoretical and experimental studies to obtain aluminothermic reactions of composite AA7xxx/TiB_2, putting into evidence the thermodynamic calculations and X-ray diffraction resulting compounds.

Keywords: Al-Cu-Mg-Zn, TiB_2, aluminium matrix composites, XRD

Metal matrix composites (MMC) proved to be a class of materials with the potential to replace a large number of materials used in automotive industry, aerospace, electronics, defence and in the manufacture of sports equipment, where the requirement for lightweight parts with high strength is increasing.

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.

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 [1] 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.

An important peculiarity of this phase diagram is that the three phases of the Al-Mg-Zn system and the three phases of the Al-Cu-Mg system form continuous solid solutions. It is important that in the Al-Cu-Mg system, the CuMgAl and $Cu_6Al_2Mg_7$ compounds are not in equilibrium with (Al) and additions of zinc are required so that these equilibria could take place. There are three domains corresponding to continuous solid solution formed by the phases $CuMg_4Al_6$ and $Mg_3Zn_3Al_2$, $MgZn_2$ and CuMgAl, and $Cu_6Mg_2Al_5$ and Mg_2Zn_{11}.

The $CuMg_4Al_6$ and $Mg_3Zn_3Al_2$ 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 (fig.1). The quaternary solid solution between compounds

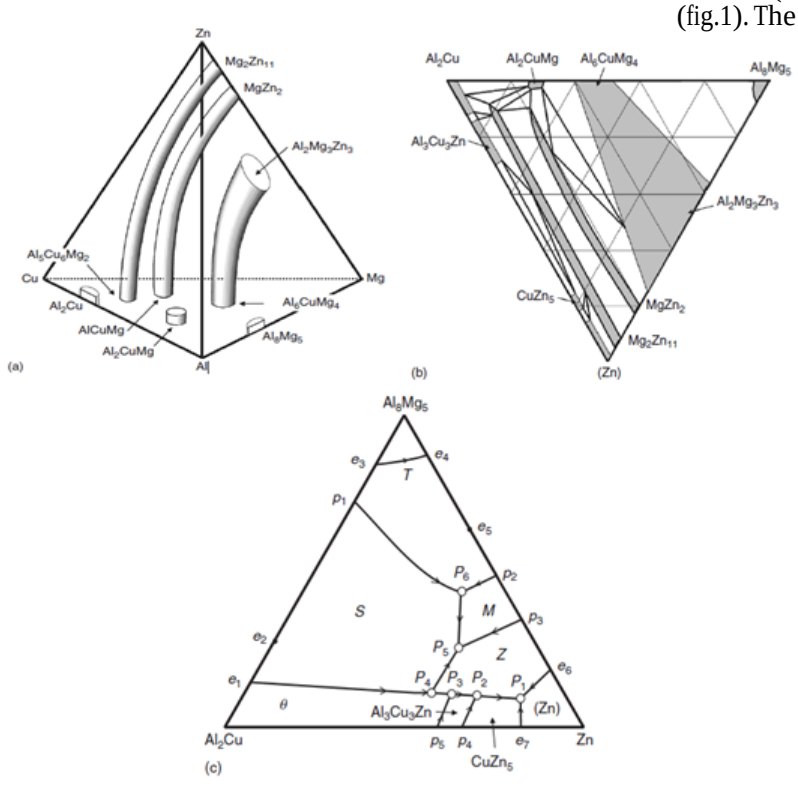


Fig. 1. Phase diagram Al–Cu–Mg–Zn: (a) polythermal diagram, (b) distribution of phase fields in the solid state in the aluminum corner, and (c) single-phase domains [1]

* *email: dragosmarcu@yahoo.com*

Point in figure 1	Phase reaction	Composition of liquid (%)			T°C
		Zn	Mg	Cu	
P_1	$L + Cu\ Zn_5 \Rightarrow (Al) + (Zn) + Z$	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

Table 1
NON VARIANT REACTIONS IN QUATERNARY ALLOYS OF THE Al-Cu-Mg-Zn SYSTEM

CuMgAl and $MgZn_2$ (the so-called M-phase) is characterized by hexagonal structure. 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 [1].

Experimental part

The method proposed in the experiments is the aluminothermic reaction of potassium hexafluorotitanate (K_2TiF_6) which provides titanium, potassium tetra-fluoroborate (KBF_4) which provides boron, AA7xxx series alloys (AA7050 and AA7075) for the intake of aluminum and having a matrix function, in the presence of cryolite (Na_3AlF_6) in order to avoid formation of the aluminum oxide barrier (Al_2O_3).

The reinforcement element obtained in-situ is TiB_2. Aluminothermic reactions possible in this system, according to the literature are:

$$3K_2TiF_6 + 6KBF_4 + 10Al = 4K_3AlF_6 + 6AlF_3 + 3TiB_2 \quad (1)$$
$$3K_2TiF_6 + 6KBF_4 + 10Al = 3TiB_2 + 12KF + 10AlF_3 \quad (2)$$
$$3K_2TiF_6 + 13Al = 3Al_3Ti + 6KF + 4AlF_3 \quad (3)$$
$$6KBF_4 + 9Al = 3AlB_2 + 6KF + 6AlF_3 \quad (4)$$
$$3AlB_2 + 3Al_3Ti = 3TiB_2 + 12Al \quad (5)$$
$$AlB_{12} + Al_3Ti + Al = TiB_2 + 5AlB_2 \quad (6)$$

The studies presented in the literature refers specifically to less complex systems [1, 2, 4, 6 - 10], in terms of development and in-situ growth of particle reinforcement. For complex systems Al-Cu-Mg-Zn/ K_2TiF_6/ KBF_4 [12-14] 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) ÷ (6).

According to calculation by T. Fan, G. Yang, and D. Zhang [16] results that free excess energy of TiB_2, and Al_3Ti 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 Al_3Ti and TiB_2. In addition Mg reduce the salts as aluminium (table 2).

$$K_2TiF_6 + 2KBF_4 + 5Mg = 4KF + 5MgF_2 + TiB_2 \quad (7)$$

Magnesium dissolved in the Al-Zn-Mg-Cu matrix can affect reaction in the melt, influencing separation of TiB_2 particle as separate phase.

The influence of alloying elements on precipitation reactions may result from changes in concentration of the components (Δx_i) and the activity coefficient ($\Delta\gamma_i$). $\Delta\gamma_i$ can be calculated from Wilson equation and using extended Miedema model [17].

The chemical compositions of the matrix metals used in the experiments, which bring excess aluminum in the reactions (1) ÷ (4) and (6) are shown in table 3.

	T	Cp	H	S	G	Reference
1	$K_2TiF_6+2KBF_4+5Mg=4KF+5MgF_2+TiB_2$					
2	T	deltaH	deltaS	deltaG	K	Log(K)
3	K	kJ	J/K	kJ		
4	1100.000	-1419.562	-11.494	-1406.919	6.525E+066	66.815
5	1200.000	-1286.151	106.186	-1413.575	3.439E+061	61.536
6	1300.000	-1260.637	126.606	-1425.225	1.866E+057	57.271
7						
8	K_2TiF_6		Extrapolated form		398.000	K

Table 2
THERMODYNAMICAL VALUES OF REACTION (7) CALCULATED WHITH HSC CHEMISTRY 8.0 SOFTWARE

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr	Al
AA7050 - Sample C	0.065	0.11	**2.20**	0.021	**2.28**	0.0025	**5.95**	0.035	0.09	Bal.
AA7075 - Sample D	0.14	0.23	**1.52**	0.13	**2.45**	0.20	**5.47**	0.043	0.01	Bal.

Table 3
CHEMICAL COMPOSITION OF AA7XXX SERIES ALLOYS, wt. %

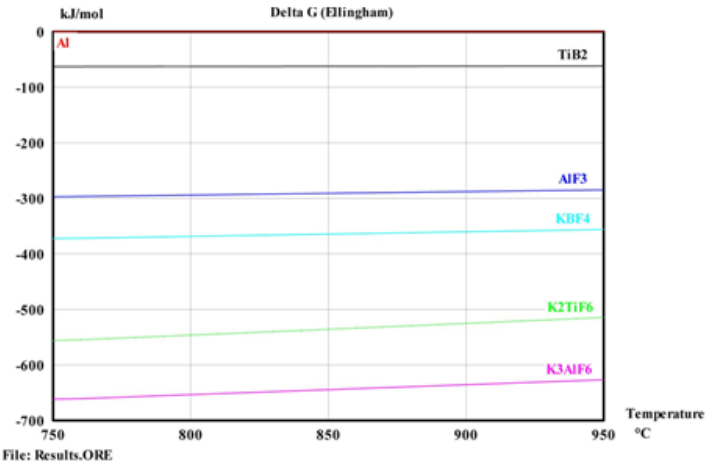


Fig. 2. Ellingham diagram $\Delta G^o_T = f(t)$ when forming reactive species for reaction (1)

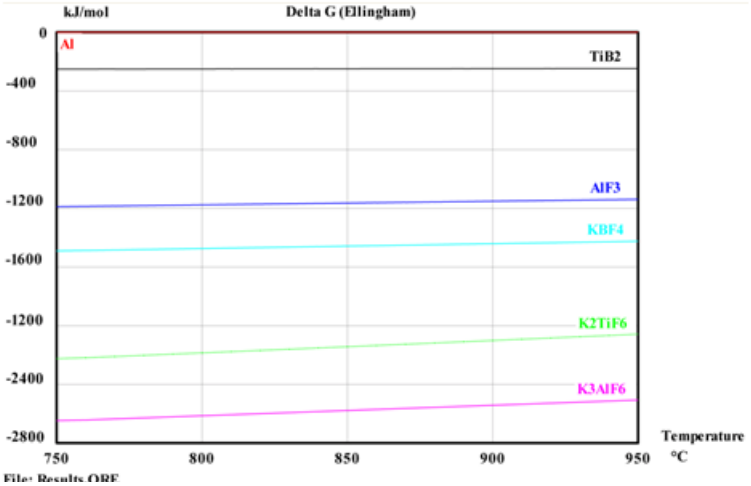


Fig. 3. Ellingham diagram $\Delta G^{o}_{T} = f(t)$, for reaction (2)

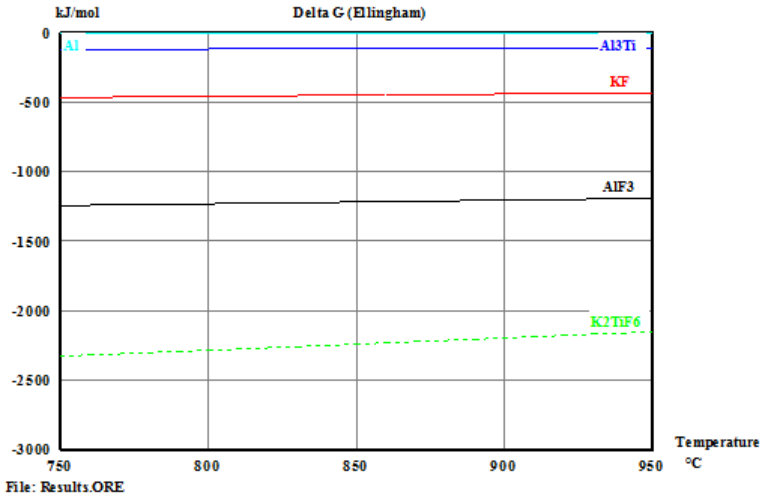


Fig. 4. Ellingham diagram $\Delta G^{o}_{T} = f(t)$ for reaction (3)

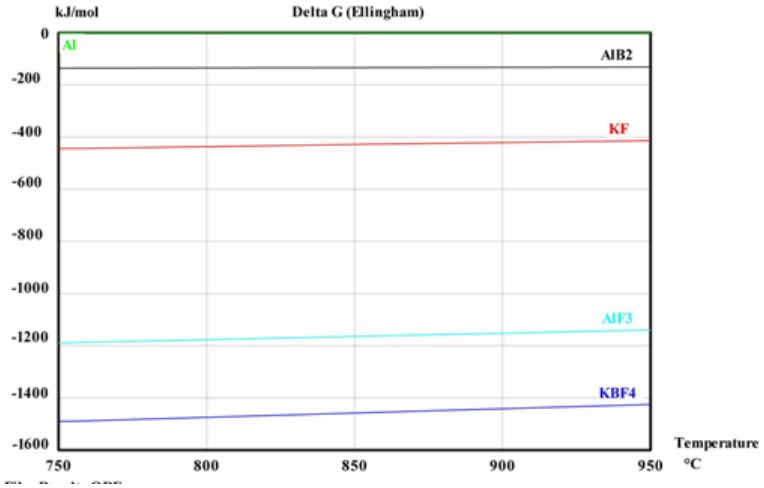


Fig. 5. Ellingham diagram $\Delta G^{o}_{T} = f(t)$ for reaction (4)

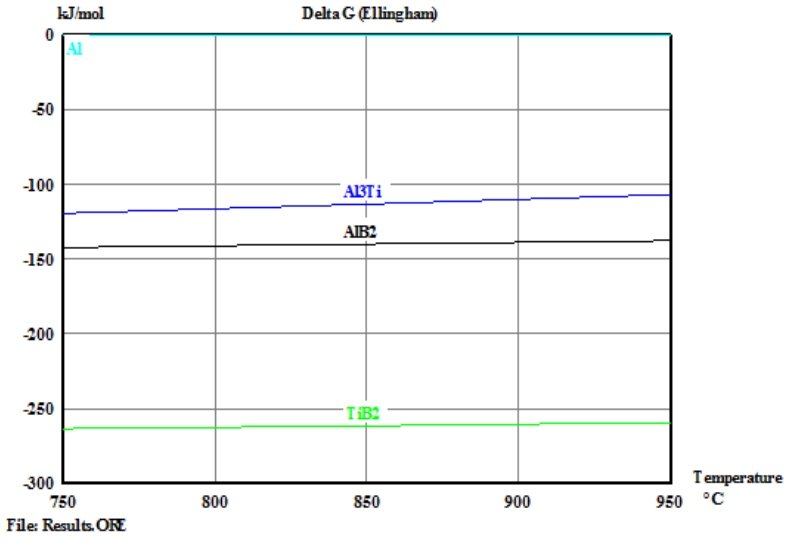


Fig. 6. Ellingham diagram $\Delta G^{o}_{T} = f(t)$ for reaction (5)

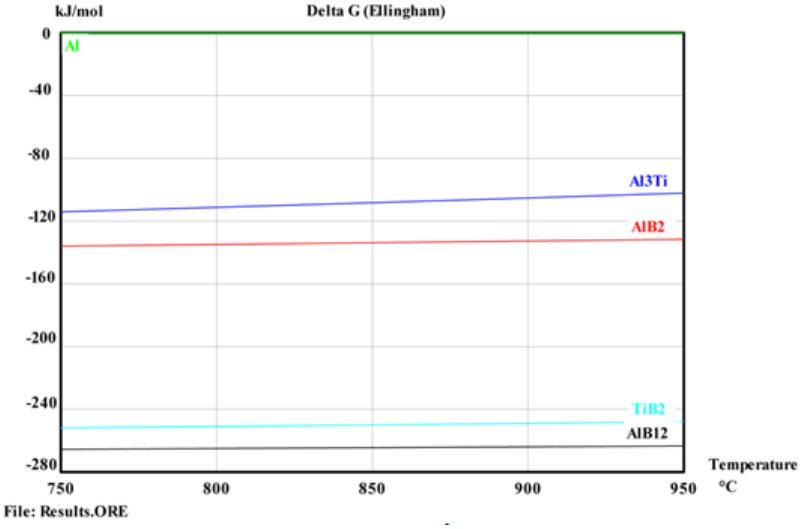


Fig.e 7. Ellingham diagram $\Delta G^{o}_{T} = f(t)$ for reaction (6)

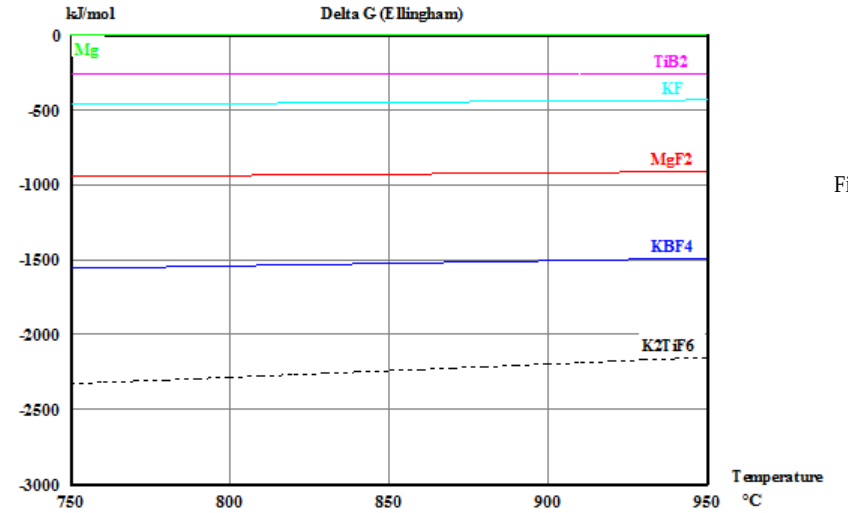


Fig. 8. Ellingham diagram $\Delta G^{o}_{T} = f(t)$, for reaction (7)

T	ΔG1, kJ	ΔG2, kJ	ΔG3, kJ	ΔG4, kJ	ΔG5, kJ	ΔG6, kJ	ΔG7, kJ
1023	-2994.66	-2469.64	-1139.05	-441.791	-1.741	-577.199	-336.624
1033	-2995.11	-2468.97	-1142.27	-439.849	-2.385	-576.601	-336.560
1043	-2995.64	-2468.37	-1145.57	-437.905	-3.028	-576.002	-336.500
1053	-2996.24	-2467.83	-1148.93	-435.959	-3.673	-575.404	-336.446
1063	-2996.91	-2467.35	-1152.37	-434.01	-4.318	-574.806	-336.398
1073	-2997.65	-2466.94	-1155.87	-432.06	-4.963	-574.207	-336.354
1083	-2998.46	-2466.59	-1159.44	-430.107	-5.608	-573.609	-336.315
1093	-2999.34	-2466.31	-1163.08	-428.153	-6.254	-573.011	-336.282
1103	-3000.29	-2466.09	-1166.79	-426.198	-6.9	-572.413	-336.253
1113	-3001.32	-2465.93	-1170.57	-424.241	-7.547	-571.815	-336.230
1123	-3002.41	-2465.84	-1174.41	-422.282	-8.194	-571.217	-336.212
1133	-3003.57	-2466.66	-1178.75	-420.464	-8.84	-570.62	-336.270
1143	-3004.8	-2469.58	-1184.17	-418.985	-9.488	-570.022	-336.492
1153	-3006.11	-2472.57	-1189.65	-417.505	-10.135	-569.425	-336.719
1163	-3007.48	-2475.62	-1195.21	-416.024	-10.782	-568.828	-336.952
1173	-3008.91	-2478.74	-1200.82	-414.542	-11.43	-568.232	-337.189
1183	-3010.42	-2481.92	-1206.51	-413.06	-12.077	-567.636	-337.432
1193	-3011.99	-2485.17	-1212.26	-411.577	-12.725	-567.04	-337.680
1203	-3013.64	-2488.47	-1218.07	-410.094	-13.373	-566.444	-337.933
1213	-3015.35	-2491.85	-1223.95	-408.61	-14.021	-565.849	-338.191
1223	-3017.12	-2495.28	-1229.89	-407.126	-14.669	-565.254	-338.453

Table 4
GIBBS FREE ENERGIES OF FORMATION FOR THE REACTIONS (1) – (7)

For the species involved in the reactions (1) ÷ (7) but also for the reaction products there have been built Ellingham diagrams $\Delta G^{o}_{T} = f(t)$.

Reaction (6) increases the number of reinforcing particles (TiB_2) and leads to the dispersion of titanium diboride phase in the the aluminum matrix.

As a general conclusion, the above reactions are most likely to obtain in-situ composites AA7050/TiB_2 and AA7075/TiB_2. In table 4 standard free energies of formation for the reactions studied are centralized, in the temperature range 1023÷1223K, and in figure 8 is presented their evolution with temperature.

TiB_2 particles contribute to grain refining [18], considering that it passes from a dendritic structure, with a coarse grain size to one with a finer granulation when increasing concentration of TiB_2.

In order to identify TiB_2 particles, we performed a diffractometry analysis on the samples.

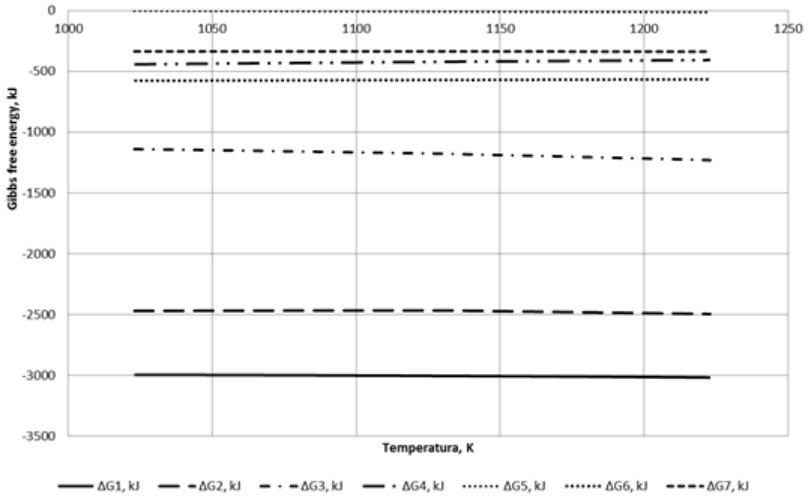
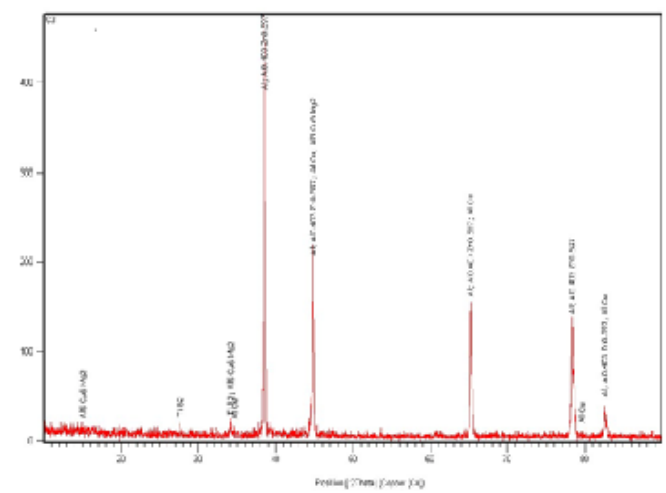


Fig. 9. Variation whith temperature of standard energy

a



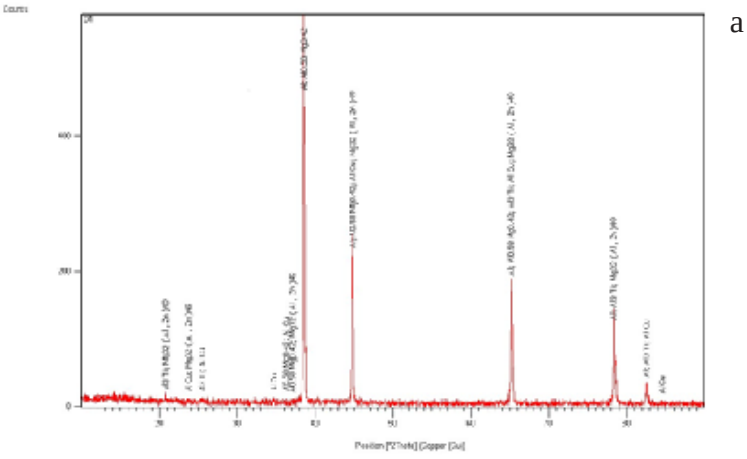
b

No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale ...	SemiQua
1	☐	01-071-4634	Aluminum	Al	66	0.900	-
2	☐	01-075-0967	titanium boride	Ti B2	18	0.052	-
3	☐	00-052-0856	Aluminum Zinc	Al0.403 Zn0.597	27	0.499	-
4	☐	03-065-1228	Aluminum C...	Al Cu	6	0.171	-
5	☐	03-065-1852	Aluminum C...	Al5 Cu6 Mg2	3	0.144	-

XRD crystallites size: TiB_2 – 19.12 nm; Al – 30.96 nm

Fig. 10. XRD pattent (a) for the sample C3 – 7.5% TiB_2, (b) the list of compounds

a

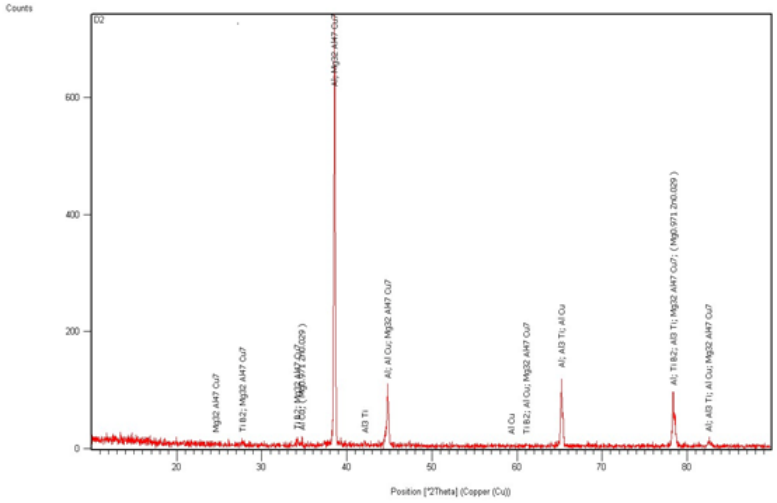


b

No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale ...	SemiQua
1	☐	01-071-4624	Aluminum	Al	61	0.824	-
2	☐	00-052-0856	Aluminum Zinc	Al0.403 Zn0.597	39	0.586	-
3	☐	03-065-1228	Aluminum C...	Al Cu	8	0.147	-
4	☐	00-019-0011	Aluminum C...	Mg32 Al47 Cu7	6	0.772	-
5	☐	03-065-7847	Aluminum Ti...	Al3 Ti	2	0.767	-

XRD crystallites size: $TiAl_3$ – 35.54 nm; Al – 36.95 nm

Fig. 11. XRD pattent (a) for the sample D1 – 2.5% TiB_2, (b) list of compounds



a

Fig. 12. XRD pattent (a) for the sample D2-5% TiB_2, (b) list of compounds

b

No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale ...	SemiQua
1	☐	01-071-4624	Aluminum	Al	51	0.670	-
2	☐	01-085-2083	titanium dibo...	Ti B2	14	0.028	-
3	☐	01-072-5006	Aluminum Ti...	Al3 Ti	2	0.180	-
4	☐	03-065-1228	Aluminum C...	Al Cu	5	0.077	-
5	☐	00-019-0011	Aluminum C...	Mg32 Al47 Cu7	7	0.544	-
6	☐	01-071-9628	Magnesium Z...	(Mg0.971 Zn0.0...	0	0.017	-

XRD crystallites size: $TiAl_3$ – 26.06 nm; Al – 25.75 nm; TiB_2 – 25.26 nm

To highlight the evolution of particle morphology for $TiAl_3$ to TiB_2, calculations were made to determine crystallite size using Debye-Scherrer formula.

Conclusions

In terms of thermodynamic, the most likely reactions are (1) and (2) in the complex system Al-Cu-Mg-Zn/K_2TiF_6/KBF_4. The main reaction product is TiB_2, the compound displaying the highest importance in developing AA7050 and AA7075 composite metallic materials.

Other intermetallic compounds obtained upon solidification of MMC's are typical compounds of the Al-Cu-Mg-Zn system, combinations of Mg-Al-Cu, Mg-Zn, Al-Cu, Al-Zn, with different degrees of substitution between the elements.

The proposed process, aluminothermic reaction between AA7xxx series alloys, potassium hexafuorotitanite (K_2TiF_6) and potassium tetrafluoroborate (KBF_4), in the presence of cryolite (Na_3AlF_6) leads to the production of composite materials with different concentrations of reinforcing elements (TiB_2), depending on the initial amount of salts used.

The main alloying elements, Cu, Zn and Mg, do not influence final reaction products of the reactions (1) ÷ (7). Only magnesium may interact with salts (K_2TiF_6 and KBF_4), reaction having a high enough absolute value.

References

1.HAN, Y., LIU, X., BIAN, X., Composites, no. 33, Part A, 2002, p. 439
2.KUMAR, S., CHAKRABORTY, M., SARMA, V.S., MURTY, B.S., Wear, no. 265, 2008, p. 134
3.LI, P., LI, Y., WU, Y., MA, G., LIU, X., Mater. Sci. Eng. A, no. 546, 2012, p. 146
4.ZHAO, D.G., LIU, X.F., PAN, Y.C., BIAN, X.F., LIU, X.J., J. Mater. Process. Technol. No.189, 2007, p. 237
5.MALLIKARJUNA, C., SHASHIDHARA, S.M., MALLIK, U.S., PARASHIVAMURTHY, K.I., Materials and Design no. 32, 2011, p. 3554
6.RAMESH, C.S., AHAMED, A., CHANNABASAPPA, B.H., KESHAVAMURTHY, R., Materials and Design no. 31, 2010, p. 2230
7.RAMESH, C.S., PRAMOD, S., KESHAVAMURTHY, R., Mater. Sci. Eng. A, no. 528, 2011, p. 4125
8.BUTU, M., MOLDOVAN, P., USURELU, E., MITRICA, D., Rev. Chim. (Bucharest), **62**, no. 7, 2011, p. 723
9.MOLDOVAN, P., BUTU, M., POPESCU, G., BUZATU, M., USURELU, E., SOARE, V., MITRICA, D., Rev. Chim. (Bucharest), **61**, no. 9, 2010, p. 828
10.USURELU, E., MOLDOVAN, P., BUTU, M., CIUCA, I., DRAGUT, V., U.P.B. Scientific Bulletin, Vol. 73, 3, 2011, p. 205
11.DRAGUT, D.V. MOLDOVAN, P., BUTU, M., Rev. Chim. (Bucharest), **63**, no. 9, 2012 p. 925
12.MARCU, D., BUTU, M., MOLDOVAN, P., BERBECARU, A., COSAC, A., U.P.B. Sci. Bull., Series B, 2014, p. 183
13.RAJAN, M., RAMABALAN, S., DINAHARAN, I., VIJAY, S.J., Materials and Design, 44, 2013, p. 438
14.RAJAN, M., RAMABALAN, S., DINAHARAN, I., VIJAY, S.J., Archives Civil Mechan. Eng., 2015
15.ZOLOTOREVSKY, V.S., BELOV, N.A., GLAZOFF, M.V., Casting Aluminum Alloys, Elsevier Ltd., 2007
16.FAN, T., YANG, G., ZHANG, D., Metall. Mat. Trans. A, no. 36, , Issue 1, 2005, p. 225
17.USURELU, E.M., PhD. Thessis, University Politehnica of Bucharest, 2011
18.MOLDOVAN, P., POPESCU, G., BUTU, M., APOSTOLESCU, I., Finisarea granulaiei aliajelor de aluminiu, Editura Politehnica Press, Bucuresti, 2006.

Manuscript received: 12.01.2016