

Journal of Engineering Sciences and Innovation

Volume 4, Issue 3 / 2019, pp. 285-300

Technical Sciences Academy of Romania www.jesi.astr.ro

B. Chemical Engineering, Materials Science and Engineering

Received 8 July 2019 Received in revised from 26 August 2019 Accepted 3 September 2019

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

PETRU MOLDOVAN, MIHAI BUŢU *

Polytechnica University of Bucharest, Splaiul Independentei nr. 313, Bucharest, Romania

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 (K_2TiF_6 and KBF_4), 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 - TiB_2 composites, thermodynamics, TiB_2 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

^{*} Correspondence address: mihaibutu@yahoo.com

[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 (KBF₄ + K_2TiF_6) [3, 5-15].

However, information related to the thermodynamics and also the characterization of TiAl₃ and TiB₂ 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 insitu TiB₂ 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 CuMg₄Al₆ and Mg₃Zn₃Al₂ 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 MgZn₂ (the so-called M-phase) is characterized by hexagonal structure.

| 140 | | 1 410 1 11 0 | a ng ni s. |) 500 m [10] | |
|------------|--|--------------|---------------|---------------------|-------|
| Point in | Phase reaction | Com | position of l | iquid | T⁰C |
| figure 1 | | Zn(%) | Mg(%) | Cu(%) | |
| P 1 | $L + Cu Zn_5 \Longrightarrow (Al) + (Zn) + Z$ | 91.1 | 2.2 | 3.4 | 350 |
| P2 | $L + Cu_3ZnAl_3 \Rightarrow (Al) + CuZn_5 + Z$ | 82.6 | 5.4 | 10.1 | 363 |
| P3 | $L + Al_2Cu \Rightarrow (Al) + Cu_3ZnAl_3 + Z$ | 77.2 | 3.0 | 9.8 | 377 |
| P4 | $L + Al_2CuMg + Al_2Cu \Longrightarrow (Al) + Z$ | 6.5 | 6.5 | 38.9 | 482 |
| P5 | $L + Al_2CuMg \Rightarrow (Al) + Z + M$ | - | - | - | < 467 |
| P6 | $L + T \Rightarrow (Al) + Al_2CuMg + M$ | - | - | - | < 467 |

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

The solid solution formed by $Cu_6Mg_2Al_5$ and Mg_2Zn_{11} compounds (the Z-phase - cubic structure). The CuAl₂ phase practically does not dissolve magnesium and dissolves not more than 2% Zn. The CuMgAl₂ phase also has very limited solubility range and can dissolve less than 1% Zn. In alloys containing $4 \div 8\%$ Zn and $0.5 \div 1.0\%$ 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 KBF₄, K₂TiF₆ and Na₃AlF₆, at 750 ÷ 950°C. A preweighted mixture of inorganic salts was added into the molten metal using the stirring method.

Cryolite (Na₃AlF₆) 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 (K₂TiF₆): molecular weight: 240.09 g/mol; appearance: white crystalline flakes; melting point: 780°C; composition: 99% min.; Cl $\leq 0.05\%$; SO₄ $\leq 0.01\%$; H₂O $\leq 0.05\%$; Pb $\leq 0.01\%$; SiO₂ $\leq 0.2\%$; Fe $\leq 0.02\%$; grit: 60 mesh 5% max.; 200 mesh 45 % min.; 300 mesh 20% max.;
- Potassium tetrafluoroborate (KBF₄): molecular weight: 125.91 g/mol; density (20°C): 2.5 g/cm³; volumetric weight: 800 \div 1400 g/l; molar volum: 49.4 cm³; melting point: 530°C; solubility in water (20°C): 4.4 g/l; composition: > 98%; Fe $\le 0.01\%$; SO₄ $\le 0.02\%$; SiO₂ $\le 0.4\%$; Cl $\le 0.1\%$; Pb $\le 0.0005\%$; Na $\le 0.1\%$; Mg $\le 0.05\%$; H₂O (110°C) $\le 0.05\%$;
- Cryolite (Na₃AlF₆): molecular weight: 209.94 g/mol; appearance: white powder; density (20°C): 2.95 g/cm³; volumetric weight: 600 \div 1000 g/l; melting point: 1027°C; solubility in water (20°C): 0.42 g/l; composition: Na 30 \div 32%; Al 12 \div 13.5%; F \ge 53.0%; Fe \le 0.03%; SO₄ \le 0.5%; SiO₂ \le 0.25%; P₂O₅ \le 0.03%; Cl \le 0.1%; Pb \le 0.0005%.
- AA 7xxx series aluminium alloys

288 Moldovan P., Buțu M. / Thermodinamics of in situ formation of TiB₂ particulates...

| 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 |

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

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 TiB_2 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 / K_2TiF_6 / KBF_4 [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 TiB_2 (60, 90 and 120 minutes) were studies. From thermodynamic studies results 14 reactions, the aluminothermic reduction of salts (K_2TiF_6 and KBF_4) occurs:

| $3K_2TiF_6 + 13Al = 3Al_3Ti + 6KF + 4AlF_3$ | (1) |
|---|-----|
| $3K_2TiF_6 + 6KBF_4 + 10Al = 12KF + 10AlF_3 + 3TiB_2$ | (2) |
| $6KBF_4 + 9Al = 3AlB_2 + 6KF + 6AlF_3$ | (3) |
| $12KBF_4 + 13Al = AlB_{12} + 12KAlF_4$ | (4) |
| $12KBF_4 + 13AI = AIB_{12} + 12KF + 12AIF_3$ | (5) |
| $K_2TiF_6 + 2KBF_4 + 5Mg = 4KF + 5MgF_2 + TiB_2$ | (6) |
| $2Al + 2KBF_4 + Mg = MgB_2 + 2KF + 2AlF_3$ | (7) |
| $12Al + 12KBF_4 + Mg = MgB_{12} + 12KAlF_4(g)$ | (8) |
| $12Al + 12KBF_4 + Mg = MgB_{12} + 12KF + 12AlF_3$ | (9) |

Thermodynamic data computed with HSC Chemistry program indicates, in the temperature range 750 \div 950°C, possibility of Al₃Ti, TiB₂, AlB₂, AlB₁₂, MgB₂ and MgB₁₂ compounds formation, with negative ΔG^{o}_{T} (table 3 for reactions 1 \div 7 and table 4 for reactions 8 \div 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 $(1 \div 9)$, can react resulting in-situ Al₃Ti / TiB₂ reinforced compound of aluminium matrix:

| $AlB_2 + Al_3Ti = TiB_2 + 4Al$ | (10) |
|---|------|
| $AlB_{12} + Al_3Ti + Al = TiB_2 + 5AlB_2$ | (11) |
| $MgB_{12} + Al = AlB_{12} + Mg$ | (12) |
| $MgB_{12} + 5Mg = 6MgB_2$ | (13) |
| $AlB_{12} + 5Al = 6AlB_2$ | (14) |

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

| - | | | | U | | | | |
|---|---------|---------|---------|---------|---------|---------|---------|---------|
| I | Т | deltaG1 | deltaG2 | deltaG3 | deltaG4 | deltaG5 | deltaG6 | deltaG7 |
| I | K | kJ |
| I | 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 |
| I | 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 |
| I | 1273.15 | -1261 | -2513 | -1199 | -2823 | -1854 | -1422 | -336 |

Table 3. Gibbs Free Energies of formation for the reaction $1 \div 7$

Table 4. Gibbs Free Energies of formation for the reactions $8\div14$

| Т | 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 |

| 290 Moldovan P. | , Buţu M. / | / Thermodine | amics of in | situ forma | tion of TiB_2 | particulates |
|------------------------|-------------|--------------|-------------|------------|-----------------|--------------|
| | | | | ./ | ./ = | |

| Т | 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 \div 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.



C2 (7050) - reaction time 60 minutes, 5% TiB₂ - a) 200x; b) 500x



C22 (7050) - reaction time 90 minutes, 5% TiB₂ - a) 200x; (b)1000x



C23 (7050) - reaction time 120 minutes, 5% TiB₂ - a) 200x; (b) 500x 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% TiB_2), the list of reaction products present in the analysed samples and the list of the corresponding peakings.



| 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 | | XRD crystallites size |
| 7 | 42.7501 | 2.11522 | 0.96 | 0.3149 | 01-089-1980 | 1.36 | | $TiB_2 = 10.12 \text{ nm}$ |
| 8 | 44.8034 | 2.02294 | 24.35 | 0.0984 | 01-071-3760;00 | 34.54 | | $11B_2 - 19,121111$ |
| 9 | 47.3701 | 1.91914 | 1.08 | 0.1968 | 01-089-1980 | 1.54 | | Al – 35,84 nm |
| 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 | (c) | |
| | | | | - | | | \sim | |

b)

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.



| XRD crystallites size: |
|------------------------|
| $TiB_2 - 31,68nm$ |
| Al – 35,79nm |
| $TiAl_3-31,\!49nm$ |
| |

¹b)

293

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.

23.83

2.22

1.28

15,70

0.41

2.96

1.8

245.47

2.38

1.65

2.06

2.85

4.22

93.10

15.41

c)

115.55

4.89

4.16

3.38

2.95

3.08

3.74

3.82

3.74

42.7516

44.7704

47.410

52 1691

56.770

61.2021

65.1708

68.1258

78.2786

82.5082

2.02435

1.91762

1.75334

1.62166

1.51444

1.43149

1.37642

1.22036

1.16818

1.14

47.98

4.44

0.39

2.58

2.71

31.62

47.99

5.96

0.82

0.0984 01-089-3657,00-

0.9446 03-065-7947-01

0.1181 03-065-7847,03-

0.4723 01-071-5368,01

0.1378 01-089-3657,00-

0.0984 01-071-5368 0.1920 01-089-3657,01

0.1440 01-089-3657,00-

0.6298

01-071-5368

294 Moldovan P., Buţu M. / Thermodinamics of in situ formation of TiB₂ particulates...



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.

295

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 | | 04-004-5881 | Titanium Bo | Ti B2 | 75 |
| | | 04-006-2601 | Copper, syn | Cu | 55 |
| 3 | | 04-012-6327 | Copper Oxide | Cu2 O | 48 |
| 4 | | 01-088-2487 | Quartz, syn | Si O2 | 24 |
| 1 | 5.4 | 04 000 7040 | Dutile and | T: 00 | 20 |







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^{o}_{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 incease 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 TiB₂. 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).

5) Only aluminium and magnesium from AlCuMgZn alloy can interacts with salts (K₂TiF₆ and KBF₄), but the influence of magnesium is negligible.

References

[1] Moldovan P., Compozite cu matrice metalică, Editura PRINTECH, București, 2008, p. 17.

[2] Zhao D.G., Liu X.F., Pan Y.C., Bian X.F., Liu X.J., *Microstructure and mechanical properties of in situ synthesized (TiB₂+Al₂O₃)/Al-Cu composites, J. Mater. Process. Technol., 189, Issue 1-3, 6 July 2007, p. 237-241.*

[3] Geng J., Liu G., Hong T., Wang M., Chen D., Ma N., Wang H., *Tuning the microstructure features of* in-situ *nano TiB₂/Al-Cu-Mg composites to enhance mechanical properties*, Journal of Alloys and Compounds, **775**, 15 February 2019, p. 193-201.

[4] Ma Y., Geng J., Chen Z., Wang M., Chen D., Ji G., Ji V., Wang H., *Experimental study of the mechanisms of nanoparticle influencing the fatigue crack growth in an* in-situ *TiB₂/Al-Zn-Mg-Cu composite*, Engineering Fracture Mechanics, **207**, 15 February 2019, p. 23-35.

[5] Mohanavel V., Rajan K., Arul C., Senthil P.V., *Production, Microstructure and Mechanical behavior of AA6351/TiB₂ composite synthesized by direct melt reaction method*, Materials Today, Proceedings, Vol. 4, 2017, p. 3315–3324.

[6] Ramesh C.S., Pramod S., Keshavamurthy R., A study on microstructure and mechanical properties of Al 6063 - TiB_2 in situ composites, Mater. Sci. Eng. A, **528**, Issue 12, February 2011, p. 4125-4132.

[7] Kumar S., Chakraborty M., Sarma V.S., Murty B.S., *Tensile and wear behaviour of in situ Al-7Si/TiB*₂ *particulate composites*, Wear, **265**, 2008, p. 134-142.

[8] Moldovan P., Butu M., Popescu G., Buzatu M., Usurelu E., Soare V., Mitrica D., *Thermodynamics of interactions in Al-K*₂*TiF*₆*-KBF*₄ *system*, Rev. Chim. (Bucharest), **61**, Vol. 9, 2010, p. 828-832.

[9] Ramesh C.S., Ahamed A., Channabasappa B.H., Keshavamurthy R., *Development of Al 6063 - TiB₂ in situ composites*, Materials and Design, **31**, 2010, p. 2230-2236.

[10] Fan T., Yang G., Zhang D., *Thermodynamic effect of alloying addition on in situ reinforced TiB*₂/*Al composites*, Metallurgical and Materials Transactions A, **36**, Issue 1, February 2005, p. 225-233.

[11] Rajan M., Ramabalan S., Dinaharan I., Vijay S.J., *Synthesis and characterisation of in situ formed titanium diboride particulate reinforced AA 7075 aluminum alloy cast composites*, Materials and Design, Vol. 44, 2013, p. 438-445.

[12] Butu M., Moldovan P., Marcu F.D., Berbecaru A., Stancel C.D., Rosu L., Ungureanu I., *Thermodynamics of in situ production of aluminium matrix composites. Comparative analysis*, Rev. Materiale Plastice Vol. 53, Issue 3, 2016, p. 428-433.

[13] Buțu M., Moldovan P., Uşurelu E., Mitrică D., *The mechanism and kinetics of TiB*₂ *nanoparticles and microparticles formation via aluminothermic reaction*, Rev. Chim. (Bucharest), 62, Vol. 7, 2011, p. 723-726.

[14] Vivekanada A. S., Balasivanandha Prabu S., Paskaramoorthy R., *Influence of process parameters of aluminothermic reduction process on grain refinement of in-situ Al/TiB2 composites*, Materials Today, Proceedings, Vol. 5, Issue 1, 2018, p. 1071-1075.

300 Moldovan P., Buţu M. / Thermodinamics of in situ formation of TiB_2 particulates...

[15] Han Y., Liu X., Bian X., In situ TiB₂ particulate reinforced near eutectic Al-Si alloy composites, Composites, Part A, Vol. 33, March 2002, p. 439-444.
[16] Zolotorevsky V. S., Belov N. A., Glazoff M. V., Casting aluminium alloys, Elsevier Science, 2007, p. 544.