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ON THE MECHANISM AND THERMODYNAMICS OF THE PRECIPITATION OF TIB_2 PARTICLES IN 6063 MATRIX ALUMINUM ALLOY

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S-au adus contribuții la mecanismul şi termodinamica precipitării nanoparticulelor şi microparticulelor de TiB_2 *în aliajul matrice AA6063(AlMgSi), la fabricarea compozitului in situ* Al/TiB_2*. Evoluția formării particulelor de* TiB_2 *din reacția aluminotermică în sistemul* $Al\text{-}KBF_4\text{-}K_2TiF_6$ *a fost analizată prin microscopie optică şi electronică si de asemenea prin difracție cu raze X. De asemenea, a fost examinat rolul adaosului de magneziu in sistemul Al-Ti-B-Mg, asupra stabilității particulelor de* TiB_2 *(entalpia liberă de exces).*

Contributions to the mechanism and thermodynamics of the precipitation of the TiB_2 *nanoparticles and microparticles in AA6063(AlMgSi) matrix alloy at the* Al/TiB_2 *in situ composite fabrication were proposed. The evolution of* TiB_2 *particles formation from aluminothermic reaction in the* $Al\text{-}KBF_4\text{-}K_2TiF_6$ *system was analized through optical and electron microscopy and also through X-ray diffraction. The role of the magnesium addition in the Al-Ti-B-Mg system, on the stability of* TiB_2 *particles (excess free energy) was also examined.*

Keywords: TiB_2 particles, in situ composite, mechanism, thermodynamics

1. Introduction

Aluminum matrix composites have emerged as an important class of materials for structural, thermal, wear, transportation and other applications, primarily as a result of their ability to exhibit superior strength to weight ratio and strength - to - cost ratio when compared to equivalent monolithic commercial alloys [1-2].

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In-situ processes involve the synthesis of composites such that desirable reinforcements, matrices and interfaces are formed during processing.

New in-situ processing techniques, in which the reinforcements are in-situ synthesized in a metallic melt by chemical reactions have been developed [3]. Some of these technologies include high-temperature synthesis (SHS), mechanical alloying (MA) and flux-assisted synthesis (FAS).

In the in-situ methods reinforcements are clean, thermodynamically stable, resulting in strong interfacial bonding and finer in size and their distribution in the matrix is more uniform. Applications of in-situ composites include wear part for values, chute liners, pumps, jet mill nozzles, heat exchangers [4].

Among the various reinforcing particles TiB_2 is particularly attractive because it possesses many desirable properties, such as high hardness, low density, high melting temperature, high modulus and high corrosion resistance [5].

The successful synthesis of in-situ composites involves good understanding of mechanism and thermodynamics of reactions in order to obtain the desirable end product.

This paper aims to investigate the mechanism and thermodynamics of in-situ formation of TiB_2 particles during aluminothermic process between aluminum alloys and KBF_4 and K_2TiF_6 salts.

2. Experimental

The composites were fabricated by mixing potassium tetrafluoroborate (KBF_4), potassium hexafluorotitanate (K_2TiF_6) and cryolite (Na_3AlF_6), preheated at 300˚C for 2 hours to remove any trace of moisture and added into the AA6063 alloy (0.62 wt.% Mg, 0.44 wt.% Si) melt overheated at 1000 to 1200K. Cryolite salt plays two roles: one is akting as activator, decreasing activation energy and accelerating the reaction, the other is reacting with Al_2O_3 to form drosses. In the molten state, the salt mixture was slowly added, and stirred by a graphite rod for 10 minutes.

The crucible, containing the aluminum alloy, was heated under argon atmosphere and set to reach thermal equilibrium at a chosen temperature. Slag formed during the reaction between aluminum (6063 alloy) and mixed salts were skimmed thoroughly before pouring the molten composite.

The in-situ composite was poured in a graphite-coated cast iron die.

The cast samples were cut for microscopic analysis (OM, SEM/EDS) and for X-ray diffraction analysis.

The samples were prepared after quenching, using Buswell's reagent (10 ml HNO_3, 1 ml HF, 89 ml H_2O, 0.1 ml $CuSO_4.5H_2O$) [6].

3. Results and Discussion

3.1. Mechanism of in-situ formation of TiB_2

We can consider that in-situ process mechanism of formation of TiB_2 particles is based on the partial reactions:

$2KBF_4 + 3Al = AlB_2 + 2KAlF_4$ (1)
$3K_2TiF_6 + 13Al = 3TiAl_3 + K_3AlF_6 + 3KAlF_4$ (2)
$AlB_2 + TiAl_3 = TiB_2 + 4Al$ (3)

The aim is to achieve a suitable fraction of finally dispersed TiB_2 particles of optimum size [7] by moving into the Liquid (L) – TiB_2 two phase region in the ternary phase diagram and thus avoid the formation of Al_3Ti compound (Fig. 1).

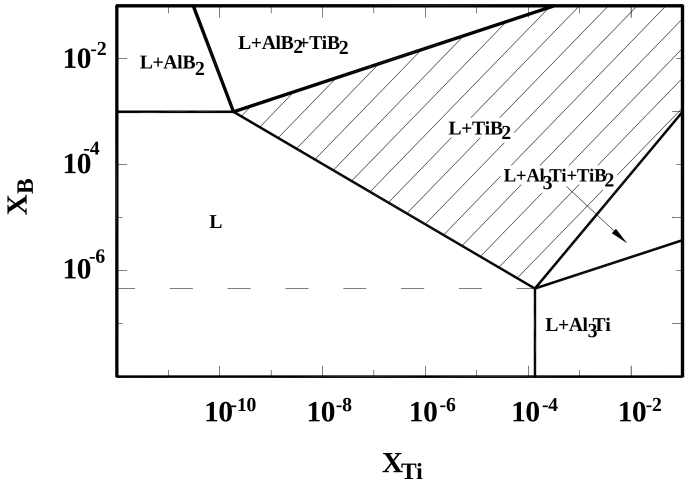


Fig. 1. Aluminum corner of the A-Ti-B ternary system [8] at 1000K

Donaldson, Squire and Stokes [9] have examined the reaction between salts and aluminum by XRD analysis of the slag, as well as the transfer efficiency of titanium and boron from salts to aluminum matrix by chemical analysis of the alloy. The following reactions are suggested:

$9K_2TiF_6 + 12Al \leftrightarrow 9(KF.AlF_3) + 3(3KF.AlF_3) + 9\underline{Ti}$ (4)
$2K_2TiF_6 \leftrightarrow 4KF + 2\ TiF_{4\,(g)}$ (5)
$9KBF_4 + 5Al \leftrightarrow 9(KF.AlF_3) + 9\underline{B}$ (6)
$KBF_4 \leftrightarrow KF + BF_{3\,(g)}$ (7)

Lee et. all. [11-12] examined the interfacial phenomena of the reactions between Al and KBF_4 + K_2TiF_6 mixture of salts. When Al powder is mixed with

KBF_4, K_2TiF_6 and eutectic mixture (KF – AlF_3) (flux), the TiB_2 agglomerates to long stringers, indicating that particle bonding occur with KF – AlF_3 flux present.

After the start of the reaction, cracks and voids initiate from the external surface of the $TiAl_3$ particles (Fig. 2) can propagate into the bulk; the number of sites for reaction is increased so that the rate of the process is raised with the resulting formation of finer TiB_2 particles.

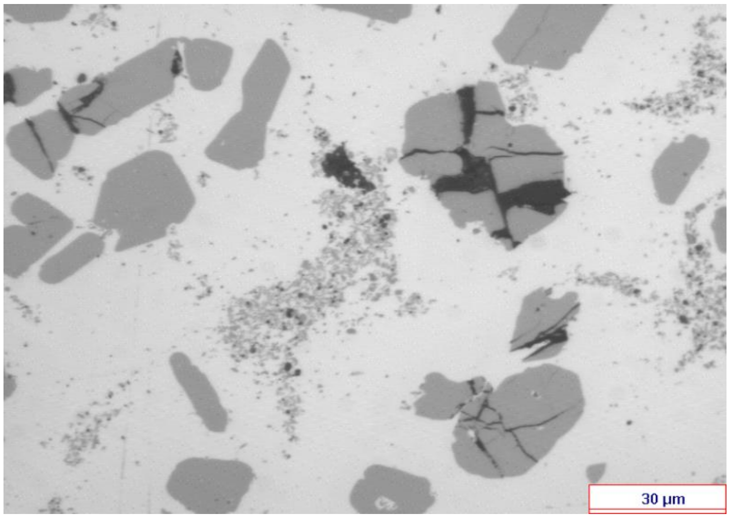


Fig. 2. Optical micrograph of $TiAl_3$ cracked particles during the synthesis process of Al/TiB_2 composite

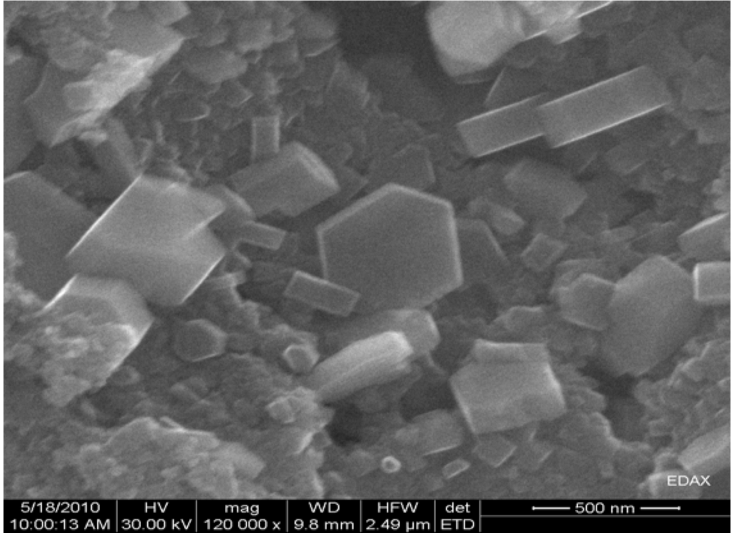


Fig.3. SEM micrograph of the TiB_2 particles extracted from Al/TiB_2 composite

On the Fig. 2 we can observe the $TiAl_3$ cracked particles.

Titanium boride particles are hexagonal in shape, with average size of 50nm (Fig. 3) [17].

Fig. 4 shows the TiB$_2$ particles size distribution by volume.

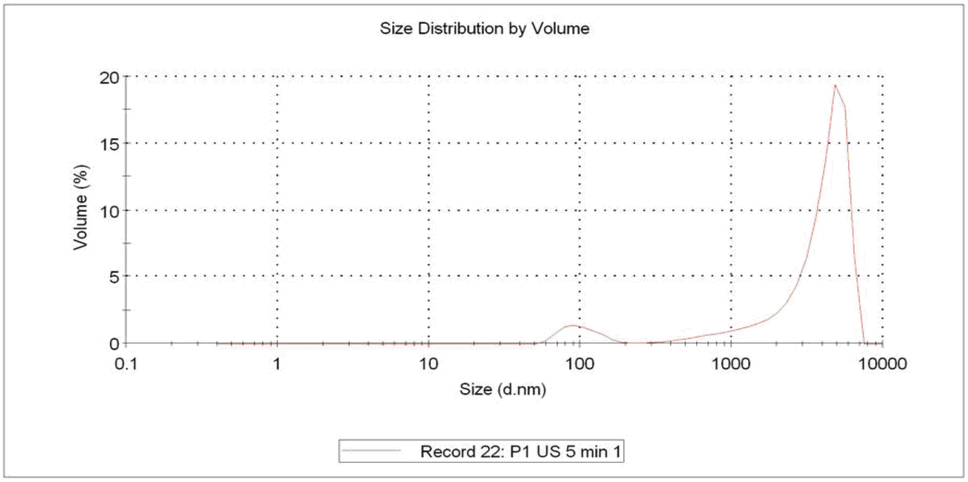


Fig. 4. Fig. 4. TiB$_2$ particles size distribution by volume

Fig. 5 shows an X-ray diffraction (XRD) pattern of the Al/TiB$_2$ composite which reveals the presence of TiAl$_3$, AlB$_2$, TiB$_2$ and Al peaks, after the beginning of reaction, and Fig. 6 shows the presence of TiB$_2$ peaks, only.

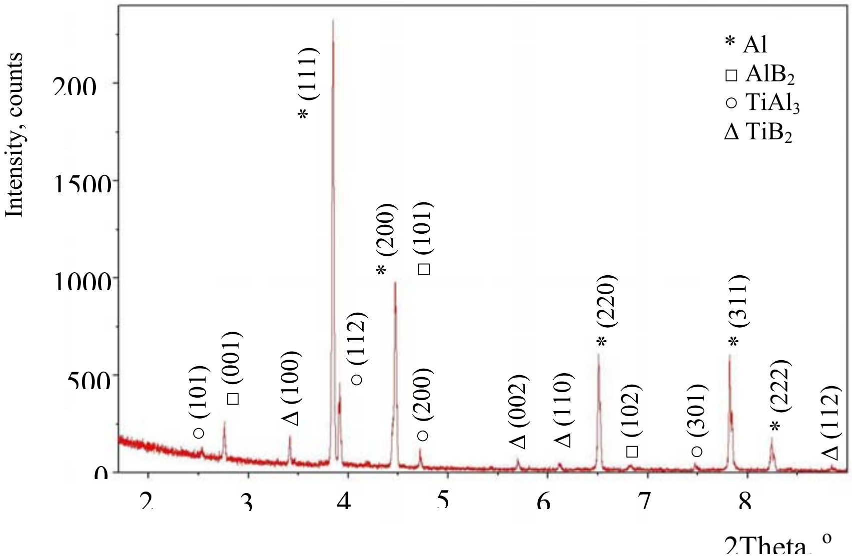


Fig. 5. XRD pattern of the composite at the beginning of reaction

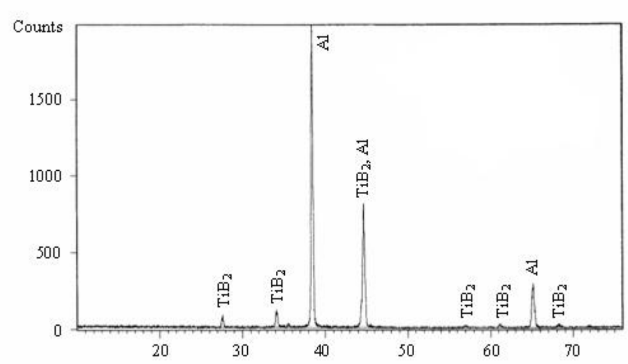
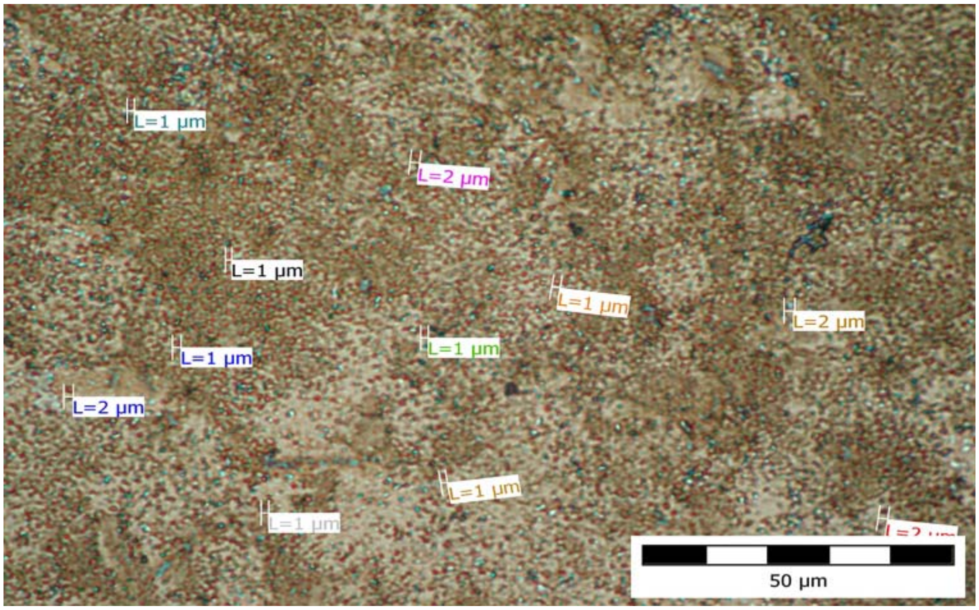
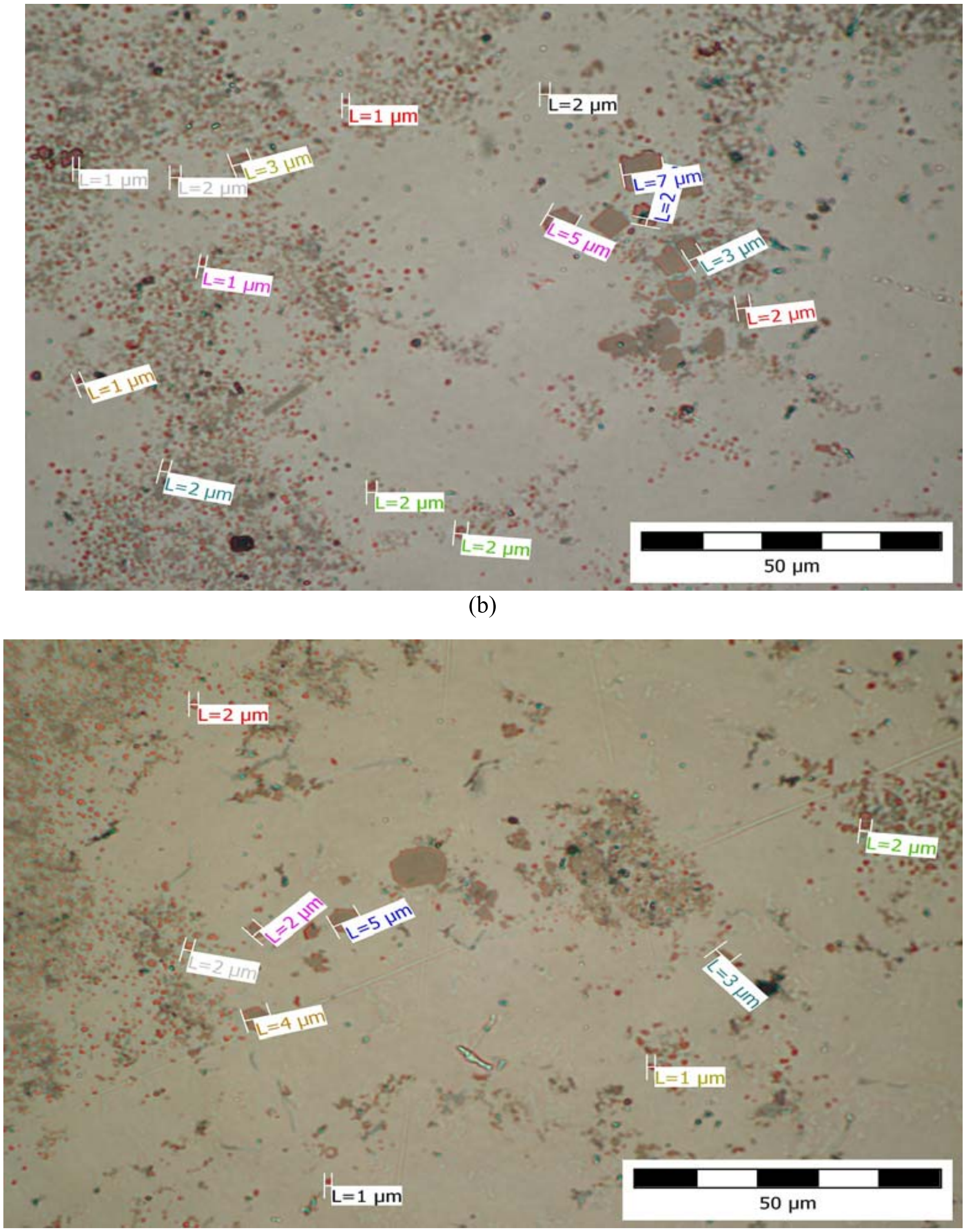


Fig. 6. XRD pattern of AA6063/TiB_2 composite at the end of reaction

TiB_2 particles size increase with time of reaction was observed; in Fig. 7 is done the evolution of TiB_2 particles dimensions after 60, 90, 120 minutes.



(a)



(b)

(c)

Fig. 7. Evolution of TiB$_2$ particle size vs reaction time: (a) 60 min; (b) 90 min; (c) 120 min.

The sequence of TiB_2 particle formation can be proposed in the following steps:

(a) transport of boron atoms presented from reaction (6) toward $TiAl_3$ particles resulted from reaction (2);

(b) natural cracks on the surface of $TiAl_3$ particles and also further fragmentation of $TiAl_3$ that enhances dissolution of $TiAl_3$ particles, increasing the rate of TiB_2 formation;

(c) reaction between titanium and boron resulted from reactions (4) and (6) respectively with formation of TiB_2 particles.

A similar mechanism of formation of TiB_2 particles was proposed by Emamy et all [13] by mixing two molten master alloys Al-Ti and Al-B respectively.

3.2. Thermodynamics

In the flux-assisted synthesis of Al-Mg-Si/TiB_2 in situ composites, the effect of alloying element additions are not fully understood.

The aluminothermic reduction of potassium hexafluorotitanate (K_2TiF_6) and potassium tetrafluoroborate (KBF_4) take place according to reaction:

$$K_2TiF_6 + 2KBF_4 + 3.333Al = 4KF + 3.333AlF_3 + TiB_2 \tag{8}$$

Calculated thermodynamic data of reaction (8) in the temperature range of 1100 K to 1300 K using the HSC Chemistry 6.0 program are presented in Table I.

Table 1

Thermodynamic data for reaction (8)

	T	Cp	H	S	G	Reference
1	**K2TiF6+2KBF4+3.333Al=4KF+3.333AlF3+TiB2**					
2	**T**	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
3	**K**	**kJ**	**J/K**	**kJ**		
4	1100,000	-829,170	-6,956	-821,518	1,033E+039	39,014
5	1200,000	-695,839	110,654	-828,624	1,181E+036	36,072
6	1300,000	-670,373	131,035	-840,719	6,072E+033	33,783
7						
8	K2TiF6		Extrapolated form		398.000	K

The magnesiothermic reduction of mixed K_2TiF_6 and KBF_4 occured via the reaction:

$$K_2TiF_6 + 2KBF_4 + 5Mg = 4KF + 5MgF_2 + TiB_2 \tag{9}$$

Thermodynamic data of the reaction (9) are given in the Table 2 in the same temperature range.

Table 2

Thermodynamic data for reaction (9)

	T	**Cp**	**H**	**S**	**G**	**Reference**
1	**K2TiF6+2KBF4+5Mg=4KF+5MgF2+TiB2**					
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	K2TiF6		Extrapolated form		398.000	K

From calculated data one can observe that reaction (9) is more probable than reaction (8), because of high negative values of ΔG^0_T.

When we have used an Al-Mg-Si alloy (0.61 wt.% Mg, 0.47 wt.% Si) magnesium dissolved in aluminum doesn't play an important role in changing the component activity and hence can affect the reaction in the melt because of very low concentration of Mg.

By proposing an extended Miedema model with the Wilson equation, T. Fan et all [14], the thermodynamic effect on the alloying element additions (M) on the stability of precipitated phases in the quaternary Al-Ti-B-M alloy was evaluated during the fabrication of in situ reinforced Al/TiB$_2$ composites.

Wilson equation for the calculation of the activity coefficient γ_i in the multicomponent metallic solutions, is expressed as:

$$\ln\gamma_i = -\ln\left(1-\sum_j x_j A_{j/i}\right) + 1 - \sum_j \left[\frac{x_j\left(1 - A_{i/j}\right)}{1 - \sum_k x_k A_{k/j}}\right] \tag{10}$$

where x_i is the molar fraction of component i and $A_{i/j}$ and $A_{j/i}$ are adjustable parameters.

In a quaternary system, the Wilson equation can be simplified, considering the very low solution of Ti and B in the melt, $x_{Ti}\to 0$ and $x_B\to 0$, for the activity coefficients of Ti and B as:

$$\ln\gamma_B^{xT_i\to 0 xB\to 0} = 1 - \ln(1 - x_{Al}A_{Al/T_i} - x_M A_{M/T_i}) - \frac{x_{Al}(1-A_{Ti/Al})}{1-x_M A_{M/Al}} - \frac{x_{Al}(1-A_{Ti/M})}{1-x_{Al}A_{Al/M}} \tag{11}$$

$$\ln \gamma_{\beta}^{xT_i \to 0 xB \to 0} = 1 - \ln(1 - x_{Al}A_{Al/B} - x_M A_{M/B}) - \frac{x_{Al}(1 - A_{B/Al})}{1 - x_M A_{M/Al}} - \frac{x_M(1 - A_{B/M})}{1 - x_{Al}A_{Al/M}} \quad (12)$$

When the solutes Ti and B in liquid aluminium reach saturation, they will be separated out as the intermetallic compound TiB_2 according to equation:

$$[Ti]_{Al} + 2[B]_{Al} \rightarrow TiB_2 \quad (13)$$

In order to evaluate the stability of the TiB_2 precipitated phase, it is necessary to calculate the excess free energy of reaction (13) as:

$$\Delta G_{TiB2} = \Delta G^0_{TiB2} - 2RT \ln a_B - RT \ln a_{Ti} \quad (14)$$

where ΔG^0 is the standard Gibbs free energy of formation, a_i represent the activity of component in the composite melt.

From Fig. 8. it can be seen that, except silicon, all alloying elements (Mg, Cu, Fe, V, Ni, La, Zr) can decrease the excess energy of TiB_2 formation. This indicates that these elements can promote TiB_2 phase formation at 1000 K.

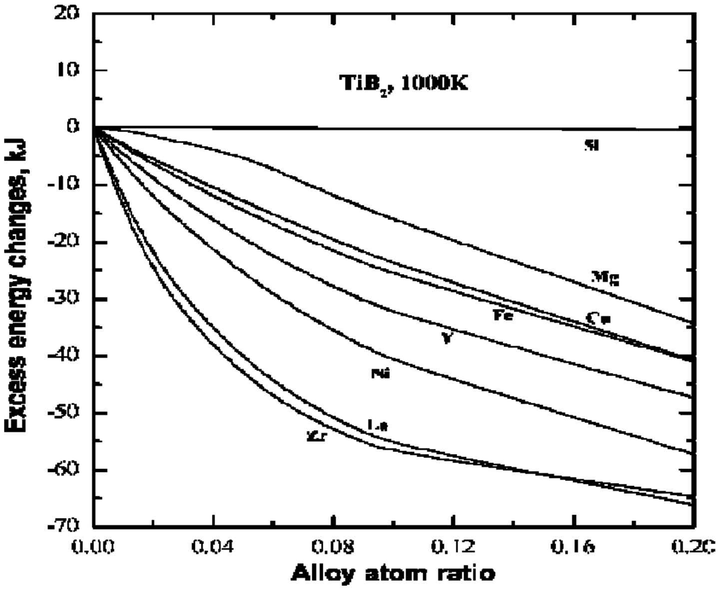


Fig. 8. Changes of the excess free energy of TiB_2 at 1000 K with different alloys [14]

The addition of Zr can promote the formation of TiB_2, but zirconium can, also, react with boron for formation ZrB_2 particles because of the very high values of Gibss free energy of formation (Fig. 9).

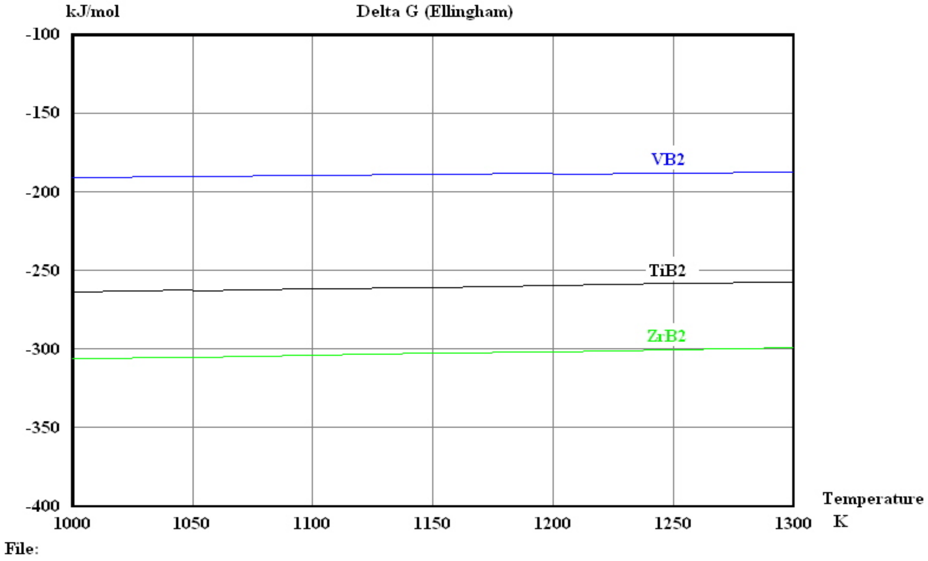


Fig. 9. Ellingham diagram $\Delta G^0_T = f(T)$, at the formation of ZrB_2, TiB_2 and VB_2

Particulate reinforced in situ TiB_2 and ZrB_2 via the potassium fluoride were synthesized successfully through the mixing salts reaction among the KBF_4, K_2TiF_6, K_2ZrF_6 and Al at 1000 K [15].

4. Conclusions

AA6063/TiB_2 in situ composite was successfully produced by reaction between KBF_4 and K_2TiF_6 in molten aluminum alloy.

After the start of the reaction, cracks and voids formed on the external surface of the $TiAl_3$ that particles can increase the rate of the dissolution of $TiAl_3$ particles in the melt, increasing the rate of nanoparticles and microparticles of TiB_2.

From the thermodynamic data calculated by HSC Chemistry 6.0 it results that magnesiothermic reduction of mixed K_2TiF_6 and KBF_4 is more probable than aluminothermic reduction of the salts, because of high negative values of ΔG^0_T in the temperature range of 1100-1300K.

Magnesium dissolved in AA6063 alloy (0.61 wt.%Mg) doesn’t play an important role in changing the component activity and affecting the stability of TiB_2 particles in the composite.

The thermodynamic effect of the alloying elements in the aluminum matrix can be evaluated by Wilson equation (by proposing an extended Miedema model) in the quaternary system Al-Ti-B-Mg. The thermodynamic stability of the TiB_2 phase can be evaluated by the value of excess free energy of TiB_2 formation.

Magnesium, at high concentration, in Al-Ti-B-Mg system, can decrease the excess free energy of TiB_2, thus promoting TiB_2 phase formation. The same role can be attributed to other solutes as V and Zr.

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REFERENCES

[1]. *S.Lakshmi, L.Lu and M.Supta,* In situ preparation of TiB_2 reinforced aluminum based composites, Jourmal of Materials Processing Technology, 1998, **Vol. 73**, pp. 160-166.
[2]. *P.Moldovan,* Compozite cu matrice metalică (Metal Matrix Composite), 2008, Editura Printech, Bucureşti.
[3]. *S.C.Tjang, Z.Y.Ma*, Mater.Sci.Eng. **B 29** (2000) pp.49-113.
[4]. *D.Lewis,* In situ Reinforcements of metal matrix composites, Metal matrix composites: Processing at interface, Academic Press, London, pp. 121-150.
[5]. *K.L.Tee, L.Lu, M.O.Lai*, Compos. Str. **47** (1999) pp. 589-593.
[6]. *J.Fiellstedt, A.E.W.Jarfors*, On the precipitation of TiB_2, Materials Science and Engineering **A 413-414**, 2005, pp. 527-532.
[7]. *P.Davies, J.L.F.Kellie, J.V.Wood*, Key Eng. Matern. **77-78**, 1993 pp. 357-362.
[8]. *G.P.Jones, I.Pearson*, Metall. Trans. **B. 73**, 1976, p. 223.
[9]. *J.D.Donaldson, C.P.Squire, F.E.Stokes*, J. Mater.Sci. **13**, 1978, pp. 421-426.
[10]. *M.S.Lee, B.S.Terry, P.Grieveson*, Metall.Trans**. B.24**, 1993, pp. 955-961.
[11]. *M.S.Lee, B.S.Terry, P.Grieveson*, Metall.Trans. **B.24**, 1993, pp. 947-953.
[12]. *M.S.Lee, B.S.Terry, P.Grieveson*, Metall.Trans. **B.30**, 2001, pp. 256-262.
[13]. *M.Emamy, M.Mahta, J.Rasizadeh*, Formation of TiB_2 particles during dissolution of $TiAl_3$ in Al-TiB_2 metal matrix composite using an in situ technique, Composites Science and Technology, **66**, 2006, pp. 1063-1066.
[14]. *Tongxiang Fan, Guang Yang, and Di Zhang*, Thermodynamic effect of alloying addition an in situ reinforced TiB_2/Al composites, Metallurgical and Materials Transactions A, **Volume 36A**, January 2005, 225-233.
[15]. *Degang Zhao, Xiangfa Liu, Yuxian Liu, Xiufang Bian*, In situ preparation of Al matrix composites reinforced by TiB_2 particles and sub-micron ZrB_2, Journal of Materials Science, **40**(2005), pp. 4365-4368.
[16]. *P.Moldovan, M.Butu, G.Popescu, M.Buzatu, E.Usurelu, V.Soare, D.Mitrica*, Therodynamics of interactions of Al-K_2TiF_6-KBF_4 system, Revista de Chimie, **Vol. 61**, nr. 9, 2010, pp. 828-832.
[17]. *M. Buţu, E. Uşurelu, P. Moldovan, A. Hadăr, A. Berbecaru*, Growth of TiB_2 nano and microstructural particles using in-situ reaction, 4th International Conference “Biomaterials, Tissue Engineering & Medical Devices” BiomMedD'2010, p.237.