ON THE MECHANISM AND THERMODYNAMICS OF THE PRECIPITATION OF TiB₂ PARTICLES IN 6063 MATRIX ALUMINUM ALLOY

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S-au adus contribuții la mecanismul și termodinamica precipitării nanoparticulelor și microparticulelor de TiB₂ în aliajul matrice AA6063(AlMgSi), la fabricarea compozitului in situ Al/TiB₂. Evoluția formării particulelor de TiB₂ din reacția aluminotermică în sistemul Al-KBF₄-K₂TiF₆ a fost analizată prin microscopie optică și electronică și de asemenea prin difracție cu raze X. De asemenea, a fost examinat rolul adaosului de magneziu în sistemul Al-Ti-B-Mg, asupra stabilității particulelor de TiB₂ (entalpia liberă de exces).

Contributions to the mechanism and thermodynamics of the precipitation of the TiB₂ nanoparticles and microparticles in AA6063(AlMgSi) matrix alloy at the Al/TiB₂ in situ composite fabrication were proposed. The evolution of TiB₂ particles formation from aluminothermic reaction in the Al-KBF₄-K₂TiF₆ system was analyzed 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 TiB₂ particles (excess free energy) was also examined.

Keywords: TiB₂ 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].
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 TiB₂ 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 TiB₂ particles during aluminothermic process between aluminum alloys and KBF₄ and K₂TiF₆ salts.

2. Experimental

The composites were fabricated by mixing potassium tetrafluoroborate (KBF₄), potassium hexafluorotitanate (K₂TiF₆) and cryolite (Na₃AlF₆), 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 acting as activator, decreasing activation energy and accelerating the reaction, the other is reacting with Al₂O₃ 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 HNO₃, 1 ml HF, 89 ml H₂O, 0.1 ml CuSO₄·5H₂O) [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:

\[ 2\text{KBF}_4 + 3\text{Al} = \text{AlB}_2 + 2\text{KAlF}_4 \]  
(1)

\[ 3\text{K}_2\text{TiF}_6 + 13\text{Al} = 3\text{TiAl}_3 + \text{K}_3\text{AlF}_6 + 3\text{KAlF}_4 \]  
(2)

\[ \text{AlB}_2 + \text{TiAl}_3 = \text{TiB}_2 + 4\text{Al} \]  
(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$_3$Ti compound (Fig. 1).

![Fig. 1. Aluminum corner of the A-Ti-B ternary system \([8]\) at 1000K](image)

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:

\[ 9\text{K}_2\text{TiF}_6 + 12\text{Al} \leftrightarrow 9(\text{KF}.\text{AlF}_3) + 3(3\text{KF}.\text{AlF}_3) + 9\text{Ti} \]  
(4)

\[ 2\text{K}_2\text{TiF}_6 \leftrightarrow 4\text{KF} + 2\text{TiF}_4(\text{g}) \]  
(5)

\[ 9\text{KBF}_4 + 5\text{Al} \leftrightarrow 9(\text{KF}.\text{AlF}_3) + 9\text{B} \]  
(6)

\[ \text{KBF}_4 \leftrightarrow \text{KF} + \text{BF}_3(\text{g}) \]  
(7)

Lee et. al. \([11-12]\) examined the interfacial phenomena of the reactions between Al and KBF$_4$ + K$_2$TiF$_6$ mixture of salts. When Al powder is mixed with
KBF₄, K₂TiF₆ and eutectic mixture (KF – AlF₃) (flux), the TiB₂ agglomerates to long stringers, indicating that particle bonding occur with KF – AlF₃ flux present.

After the start of the reaction, cracks and voids initiate from the external surface of the TiAl₃ 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 TiB₂ particles.

Fig. 2. Optical micrograph of TiAl₃ cracked particles during the synthesis process of Al/TiB₂ composite

On the Fig. 2 we can observe the TiAl₃ cracked particles.

Fig. 3. SEM micrograph of the TiB₂ particles extracted from Al/TiB₂ composite
Titanium boride particles are hexagonal in shape, with average size of 50nm (Fig. 3) [17]. Fig. 4 shows the TiB₂ particles size distribution by volume.

![Size Distribution by Volume](image)

**Fig. 4. TiB₂ particles size distribution by volume**

Fig. 5 shows an X-ray diffraction (XRD) pattern of the Al/TiB₂ composite which reveals the presence of TiAl₃, AlB₂, TiB₂ and Al peaks, after the beginning of reaction, and Fig. 6 shows the presence of TiB₂ peaks, only.

![XRD pattern](image)

**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.
Fig. 7. Evolution of TiB₂ particle size vs reaction time: (a) 60 min; (b) 90 min; (c) 120 min.
The sequence of TiB₂ particle formation can be proposed in the following steps:

(a) transport of boron atoms presented from reaction (6) toward TiAl₃ particles resulted from reaction (2);
(b) natural cracks on the surface of TiAl₃ particles and also further fragmentation of TiAl₃ that enhances dissolution of TiAl₃ particles, increasing the rate of TiB₂ formation;
(c) reaction between titanium and boron resulted from reactions (4) and (6) respectively with formation of TiB₂ particles.

A similar mechanism of formation of TiB₂ particles was proposed by Emamy et al. [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/TiB₂ in situ composites, the effect of alloying element additions are not fully understood.

The aluminothermic reduction of potassium hexafluorotitanate (K₂TiF₆) and potassium tetrafluoroborate (KBF₄) take place according to reaction:

$$K₂TiF₆ + 2KBF₄ + 3.333Al = 4KF + 3.333AlF₃ + TiB₂$$  \hspace{1cm} (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>
<thead>
<tr>
<th>T</th>
<th>Cp H</th>
<th>S</th>
<th>G</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1100,000</td>
<td>-829,170</td>
<td>-6,956</td>
<td>1,033E+039</td>
</tr>
<tr>
<td>5</td>
<td>1200,000</td>
<td>-695,839</td>
<td>110,654</td>
<td>1,181E+036</td>
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<tr>
<td>6</td>
<td>1300,000</td>
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<td>131,035</td>
<td>6,072E+033</td>
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</tbody>
</table>

The magnesiothermic reduction of mixed K₂TiF₆ and KBF₄ occurred via the reaction:

$$K₂TiF₆ + 2KBF₄ + 5Mg = 4KF + 5MgF₂ + TiB₂$$  \hspace{1cm} (9)
Thermodynamic data of the reaction (9) are given in the Table 2 in the same temperature range.

<table>
<thead>
<tr>
<th>T</th>
<th>Cp</th>
<th>H</th>
<th>S</th>
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<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>K2TiF6+2KBF4+5Mg =4KF+5MgF2+TiB2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>deltaH</td>
<td>deltaS</td>
<td>deltaG</td>
<td>K</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>1100,000</td>
<td>-1419,562</td>
<td>-11,494</td>
<td>-1406,919</td>
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<tr>
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<td>106,186</td>
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<tr>
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<td></td>
<td>1300,000</td>
<td>-1260,637</td>
<td>126,606</td>
<td>-1425,225</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>8</td>
<td></td>
<td>K2TiF6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

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/TiB2 composites.

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

$$\ln \gamma_i = -\ln\left(1 - \sum_j x_j A_{ij}\right) + 1 - \sum_j \left[ \frac{x_j \left(1 - A_{ij}\right)}{1 - \sum_k x_k A_{kj}} \right]$$

(10)

where $x_i$ is the molar fraction of component $i$ and $A_{ij}$ and $A_{ji}$ 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, $x_{Ti} \rightarrow 0$ and $x_{B} \rightarrow 0$, for the activity coefficients of Ti and B as:

$$\ln \gamma_{Ti}^{x_{Ti} \rightarrow 0} = 1 - \ln(1 - x_{Al}A_{Al/Ti} - x_{M}A_{M/Ti} - x_{Al}(1 - A_{Al/Ti}) - x_{Al}(1 - A_{Al/M}))$$

(11)
When the solutes Ti and B in liquid aluminium reach saturation, they will be separated out as the intermetallic compound TiB₂ according to equation:

\[
[Ti]_{Al} + 2[B]_{Al} \rightarrow TiB_2
\]  

(13)

In order to evaluate the stability of the TiB₂ precipitated phase, it is necessary to calculate the excess free energy of reaction (13) as:

\[
\Delta G_{TiB2} = \Delta G^0_{TiB2} - 2RT \ln a_B - RT \ln a_{Ti}
\]  

(14)

where \( \Delta G^0 \) 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 TiB₂ formation. This indicates that these elements can promote TiB₂ phase formation at 1000 K.

Fig. 8. Changes of the excess free energy of TiB₂ at 1000 K with different alloys [14]
The addition of Zr can promote the formation of TiB₂, but zirconium can, also, react with boron for formation ZrB₂ particles because of the very high values of Gibss free energy of formation (Fig. 9).

Particulate reinforced in situ TiB₂ and ZrB₂ via the potassium fluoride were synthesized successfully through the mixing salts reaction among the KBF₄, K₂TiF₆, K₂ZrF₆ and Al at 1000 K [15].

4. Conclusions

AA6063/TiB₂ in situ composite was successfully produced by reaction between KBF₄ and K₂TiF₆ in molten aluminum alloy.

After the start of the reaction, cracks and voids formed on the external surface of the TiAl₃ that particles can increase the rate of the dissolution of TiAl₃ particles in the melt, increasing the rate of nanoparticles and microparticles of TiB₂.

From the thermodynamic data calculated by HSC Chemistry 6.0 it results that magnesiothermic reduction of mixed K₂TiF₆ and KBF₄ 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 TiB₂ 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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