Thermodynamics and Mechanism of Metalothermic Reduction of Molten Salts

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The objective of this paper is to present the differences which appear in terms of thermodynamics and structure in the elaboration process of two composite materials produced through an aluminothermic reduction of molten salts. There were conducted two sets of experiments of reduction of liquid Potassium Fluoroborate (KBF_4) and the mix of salts ($KBF_4 + K_2TiF_6$) with aluminium. In order to indentify the formed compounds there were carried out XRD analysis, electronic microscopy analysis (SEM+EDS) and optical microscopy analysis.

Keywords: potassium tetrafluoroborate, aluminium diboride, titanium diboride, potassium fluorotitanate

In recent years, aluminum matrix composites reinforced with ceramic particles represent a significant area in the research of structural composites. For the study of MMCs (metal matrix composites) there has been developed a large variety in the fabrication procedures. Thus, the composite materials have been obtained by different techniques like powder metallurgy, sputter deposition and casting methods.[5]

The in-situ composites occured in the mid '80s, offers a termodynamic stability to fine and dispersed particles into the metal matrix due to the growth and germination of the reinforcement particles which takes place into the matrix alloy, assuring a strong link at the particle – matrix interface [6-8]. The purpose of this paper is to make a paralel between the thermodynamics and mechanism of the forming reactions of borides (TiB_2 and AlB_2) by an aluminothermic reduction of fluorides.

A1-B System

It is agreed that an eutectic exists at low boron contents, and that boron has a low solubility (< 100 ppm) in the solid. However, there is disagreement on the boron solubility in the liquid. The older data, when extrapolated to 660 °C give an eutectic composition of 0.09 wt [1]. More recent studies show the eutectic to be at 0.022 wt and 659.7°C and give higher boron solubilities at temperatures higher than 900 °C.

The boron composition of the hypoeutectic liquid is given by the relation

$$X_B^l = \frac{-\Delta H_f \Delta T}{RTT_f(1-K_B)} \quad (1)$$

X_B^l is the mole fraction of boron in the liquid; ΔH_f is the latent heat of fusion; ΔT is the change in freezing point cause by the presence of boron; R is the molar gas constant; T is the absolute temperature (Kelvin); T_f is the melting point of pure aluminium (Kelvin); and K_B is the distribution coefficient of boron between liquid and solid phases ($K_B = X_B^s / X_B^l$). The boron composition in the solid is much less than in the liquid, so $K_B \approx 0$. ΔH_f. is 2580 cal./mole and T_f is 933.25 K.

Equation [1] at the eutectic becomes

$$X_B^l = \frac{-2580 \times -0.4}{1.986 \times 933.25 \times 932.85} = 5.97 \times 10^{-4} \quad (2)$$

which corresponds to 0.024 wt pct.B. This theoretical eutectic composition is in excellent agreement with the most recent data (0.022 wt pct.B), so these are felt to be more accurate than the earlier result and are used in this study.

The hypereutectic solubility of AlB_2 in weight percent can be represented by the equation

$$log_{10}\ pct\ B = -\frac{5255}{T} + 3.975 \quad (3)$$

where T is the absolute temperature (°K).[1]

Ti-B system

There is a disagreement about the congruent melting temperature of TiB_2. These data are listed in table 1. The highest reported congruent temperature 3498 K is chosen in the assessed phase diagram as reported in [7]. By metallographic studies, a homogeneity range of TiB_2 was also observed by different measurements. The small varieties of lattice parameters correspond to the narrow homogeneity range. In the assessed phase diagram, the range is taken from 65 to 67.6 at.% B , table 6 [6].

Experimental part

There were produced two aluminium metal matrix composites by using pure aluminium and also aluminium alloys (6xxx and 5xxx series) as matrix.

In order to obtain the composite materials reinforced with TiB_2 and AlB_2 particles there were used the following salts: Potassium Hexafluorotitanate (K_2TiF_6 with the melting point of 780°C and molecular mass of 240.09 g/mol) and Potassium Fluoroborate (KBF_4 with the melting point of 530°C and molecular mass of 125.91g/mol). Also cryolite (Na_3AlF_6 with the melting temperature at 1027 °C and molecular mass 209.94 g/mol) was used for the metal bath protection and disolution of the formed oxides [4].

The two types of composites have been produced in an electric furnace in a graphite crucible, with mechanical stirring at a speed of 200 rot./min.

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Type of data	Method	Value
Solubility of B in (αTi)	Metallography	1155 K< 1.7 at%B
Solubility of B in (βTi)	Metallography	1813 ± 10K <1 at%B
Melting point of TiB	Metallography	2463 ±25K
		2333
		2173 ± 50 K
Homogeneity of TiB	Metallography	45.8-49.3 at.%B
Melting point of TiB2	Metallography	>3153 K
		3498 ± 25 K
		3173 ± 80 K
		3498 K
Homogeneity of TiB2	Metallography	65.2-66.3 at.%B
Eutectic reaction, liquid ↔TiB2 +(βB)	Metallography	2353 ± 20K > 98 at.%B

Table 1
EXPERIMENTAL PHASE DIAGRAM DATA OF THE TI-B SYSTEM

Mechanism and termodynamics of the reactions

When KBF_4 is added into molten aluminium, it is reduced by Al and forms $KAlF_4$. It can be seen from reactions that the formation of one mol AlB_{12} produces a larger quantity of $KAlF_4$ than the formation of one mol of AlB_2. $KAlF_4$ is lighter in weight than aluminium and floats on to the surface of the aluminium melt. This makes the build up of boron inside the aluminium melt difficult. However, the exotermic reaction is vigorous and the build up of boron still happens. As a result the concentration of boron at the flux/melt interface may exceed 44.5 wt.% locally and results in the formation of AlB_{12} at a temperature lower than 975 °C. During the reactions AlB_{12} moves into the aluminium melt away from the flux/melt interface and causes a reduction in local boron concentration.[3]

For the synthesis of Al/AlB_2 composites the following reactions were considered [3] :

$$3Al + 2KBF_4 \rightarrow 2\,KAlF_4 + AlB_2 \quad (4)$$

$$12KBF_4 + 13Al \rightarrow AlB_{12} + 12\,KAlF_4 \rightarrow AlB_{12} + 12KF + 12AlF_3 \quad (5)$$

$$2KBF_4 + 3Al \rightarrow AlB_2 + 2KAlF_4 \rightarrow AlB_2 + 2KF + 2AlF_3 \quad (6)$$

Figure 1 shows the graphic scheme of the forming mechanism for AlB_2 particles.

For the synthesis of Al/TiB_2 composites the following reactions were considered [4] :

$$3K_2TiF_6 + 6KBF_4 + 10Al \rightarrow 3TiB_2 + 12KF + 10\,AlF_3 \quad (7)$$

$$3K_2TiF_6 + 13Al \rightarrow 3Al_3Ti + 6KF + 4AlF_3 \quad (8)$$

$$6KBF_4 + 9Al \rightarrow 3AlB_2 + 6KF + 6AlF_3 \quad (9)$$

$$AlB_2 + Al_3Ti \rightarrow TiB_2 + 4Al \quad (10)$$

The mechanism of the TiB_2 particles formation is presented in figure 2.

Results and discussions

The sequence of TiB_2 particle formation consists in:

- boron atoms transport toward Al_3Ti particles resulting from reaction as described by different authors [2, 6];
- natural craks on the surface of Al_3Ti particles and also further fragmentation of Al_3Ti that enhances dissolution of Al_3Ti particles, increasing the rate of TiB_2 formation;
- reaction between titanium and boron with formation of TiB_2 particles.

The thermodynamic data have been calculated using the program HSC Chemistry 6 (table 2,3). They show that between 750-950 °C the reactions are possible, due to the fact that ΔG_T^0 has a negative value. From reactions results

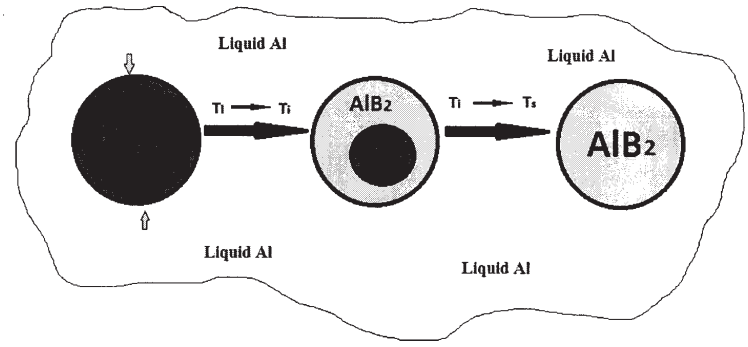

Fig. 1. Graphic representation of the forming mechanism for AlB_2 particles which takes place through a peritectic reaction : L + AlB_{12}→ AlB_2.T_l = liquid temperature, Ti = 975 °C, Ts = solidus temperature

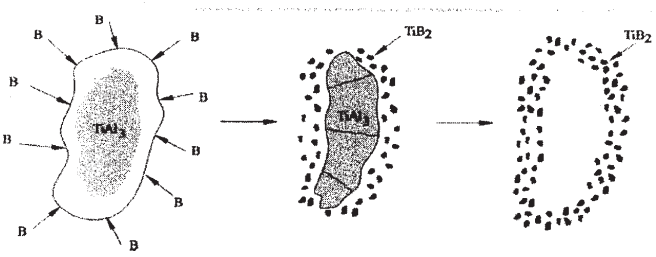

Fig. 2. Graphic representation of the forming mechanism for TiB_2 particles

T,°C	deltaH kJ	delta S J/K	delta G kJ	K	Log(K)
650	-605.259	-156.612	-460.683	1.172E+026	26.069
700	-639.012	-192.753	-451.434	1.711E+024	24.233
750	-640.340	-194.085	-441.762	3.590E+022	22.555
800	-641.441	-195.137	-432.030	1.073E+021	21.030
850	-642.317	-195.935	-422.253	4.360E+019	19.639
900	-588.369	-148.190	-414.520	2.871E+018	18.458
950	-588.646	-148.422	-407.104	2.437E+017	17.387
1000	-588.797	-148.543	-399.680	2.508E+016	16.399
Formula	FM	Conc.	Amount	Amount	Volume
	g/mol	wt-%	mol	g	l or ml
Al	26.982	24.326	3.000	80.945	29.979
KBF4	125.902	75.674	2.000	251.804	100.520
	g/mol	wt-%	mol	g	l or ml
KF	58.097	34.919	2.000	116.193	46.852
AlF3	83.977	50.475	2.000	167.953	54.179
AlB2	48.602	14.606	1.000	48.602	15.236

Table 2
THERMODYNAMICAL VALUES OF REACTION (4) CALCULATED WITH HSC CHEMISTRY 6.0

T, °C	ΔH, kJ	ΔS, J/K	ΔG, kJ	K	Log(K)
750	-254.47	-70.2158	-2469.63	1.2E+126	126.0921
800	-2507.59	-37.8843	-2466.93	1.2E+120	120.0858
850	-2472.7	-6.11292	-2465.83	4.9E+114	114.6888
900	-2109.22	315.024	-2478.79	2.4E+110	110.3775
950	-2071.43	346.5618	-2495.33	3.7E+106	106.572
Formula	FM	Conc.	Amount	Amount	Volume
	g/mol	wt-%	mol	g	l or ml
Al	26.982	15.458	10.000	269.815	99.932
K2TiF6	240.087	41.264	3.000	720.261	0.000
KBF4	125.902	43.278	6.000	755.411	301.561
	g/mol	wt-%	mol	g	l or ml
TiB2	69.520	11.949	3.000	208.560	47.616
KF	58.097	39.941	12.000	697.160	281.113
AlF3	83.977	48.111	10.000	839.767	270.893

Table 3
THERMODYNAMICAL VALUES OF REACTION (7) CALCULATED WITH HSC CHEMISTRY 6.0

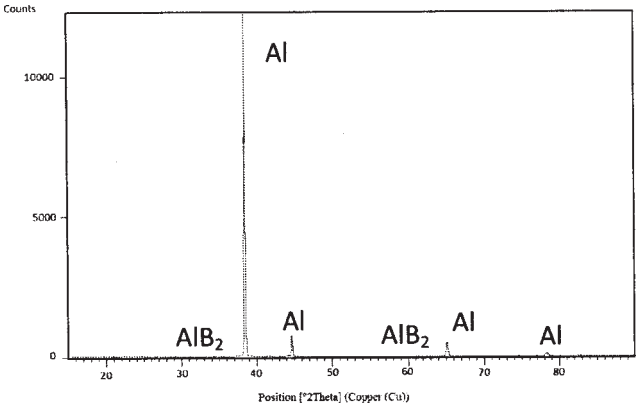

Fig. 3. XRD Patten showing ALB_2 formation

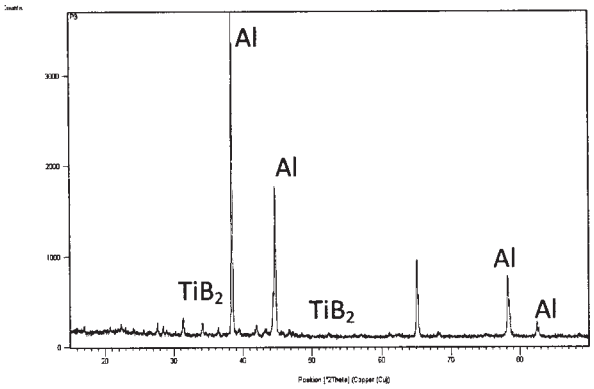

Fig. 4. XRD Patten showing TIB_2 formation

T, °C	deltaH, kJ	deltaS, J/K	deltaG kJ	K	Log(K)
650,000	-931,786	-196,507	-750,381	2,900E+042	42,462
700,000	-933,763	-198,593	-740,502	5,628E+039	39,750
750,000	-935,521	-200,356	-730,527	1,989E+037	37,299
800,000	-937,066	-201,831	-720,471	1,178E+035	35,071
850,000	-938,403	-203,049	-710,348	1,094E+033	33,039
900,000	-884,934	-155,721	-702,249	1,864E+031	31,270
950,000	-885,711	-156,370	-694,447	4,558E+029	29,659
1000,000	-886,385	-156,910	-686,614	1,488E+028	28,173

Table 4
THERMODYNAMICAL VALUES OF REACTION (11) CALCULATED WITH HSC CHEMISTRY 6.0

the forming of Al_3Ti and AlB_2 and from reaction (4) the formation of AlB_2.

From thermodynamical values results that TiB_2 is more stable than AlB_2.

The X-ray diffraction analysis (fig.3,4) confirms AlB_2 and TiB_2 particles formation.

In order to determine the purpose of Magnesium from the Al alloys an experiment was conducted using AA5083 alloy (4.0 and 4.4%) as a matrix.

Figure 3 shows that no Mg compounds formed, thus Mg does not influence AlB_2 formation. From the thermodynamic data for reaction (11) it can be observed

that is possible MgB_2 compound formation. After calculating the thermodynamic data results that the value of ΔG is -702.249 KJ at 900 °C. Regarding the fact that ΔG of reaction (7) at 900 °C is -1243.56 KJ, the MgB_2 compound has a reduced chance of forming.

$$2KBF_4 + 4Mg \rightarrow 2KF + MgB_2 + 3MgF_2 \quad (11)$$

Conclusions

In terms of thermodynamic data the stability of TiB_2 compounds resulting from the aluminothermic reaction is higher than that of AlB_2 compounds.

The in-situ forming mechanism of the AlB_2 compound is in tight relation with the peritectic reaction at 975°C up to the solidus line (659 °C) of the Al-B binary phase diagram.

The in-situ forming mechanism of the TiB_2 particles is restricted to the reaction $Al_3Ti + AlB_2$ this mechanism being more complex than the AlB_2 mechanism.

Magnesium does not influence the aluminothermic reaction of the fluoride salts.

ACKNOWLEDGEMENTS: : Authors recognize financial support from the European Social Fund through POSDRU/89/1.5/S/54785 project: "Postdoctoral Program for Advanced Research in the field of nonomaterial" and POSDRU/88/1.5/S/60203 project : „Dezvoltarea de cariere stiintifice competitive prin programe de burse doctorale (COMPETE)".

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Manuscript received: 3.07.2012