CHARACTERIZATION OF IN-SITU AA 6060/AlB_2 METAL MATRIX COMPOSITE

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Obiectivul prezentei lucrări îl constituie caracterizarea unui material compozit cu matrice din aliajul de aluminiu deformabil AA6060 armat cu particule de AlB_2. Pentru sinteza compozitului s-a utilizat reacția aluminotermică dintre aluminiul prezent în aliajul AA6060 şi KBF_4 . S-au efectuat analize prin microscopie optică, microscopie electronică (SEM +EDS) şi prin difracție de raze X. Compozitul conține particule cu morfologia caracteristică diborurii de aluminiu.

The objective of this paper is the characterization of a metal matrix composite material based on a deformable aluminum alloy AA 6060 reinforced with AlB_2 particles. An aluminothermic reaction between the aluminum AA 6060 alloy and KBF_4 was used for the synthesis of the composite. Analyses were performed by optical microscopy, electron microscopy (SEM + EDS) and X-ray diffraction. The composite contains particles with the characteristic morphology of the aluminium diboride.

Keywords: in-situ composite, AA6060 alloy, AlB_2

1. Introduction

Aluminum matrix composites (AMCs) have found extensive use in many engineering applications because of their high specific modulus, strength, hardness and stiffness, excellent wear resistance, low-heat expansion coefficient, stability of properties at elevated temperature, reduced density and competitive fabrication cost. The development of these materials has been driven by the aerospace and automotive industries for both nonstructural and structural applications [1].

Metal matrix composites (MMCs) reinforced with ceramic or metallic particles are widely used owing to their higher specific modulus, strength and

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wear resistance. MMCs have been considered as alternatives to monolithic metallic materials or conventional alloys in a number of specialized application areas. Aluminum matrix composites (AMCs) have been reported to possess higher wear resistance and lower friction coefficient with an increasing volume fraction of reinforcement particles, compared to aluminum alloys without reinforcement. AMCs also combine the low density of the matrix with the high hardness of the reinforcements[11].

To improve the interfacial compatibility and reduce the reinforcement size various new processing techniques are being employed to produce the high performance in situ composites. Ultrafine ceramic particles (TiB_2, AlB_2) are produced in situ by the exothermic reaction between aluminium and the ceramic compounds [2]. The literature on the in situ AlB_2 particle composites is very limited [7].

Al–B system (Fig. 1) is well known because Al-B master alloys are widely used in the production of electrical conductive grade aluminium to remove transition metal impurities, such as titanium, vanadium, chromium and zirconium.

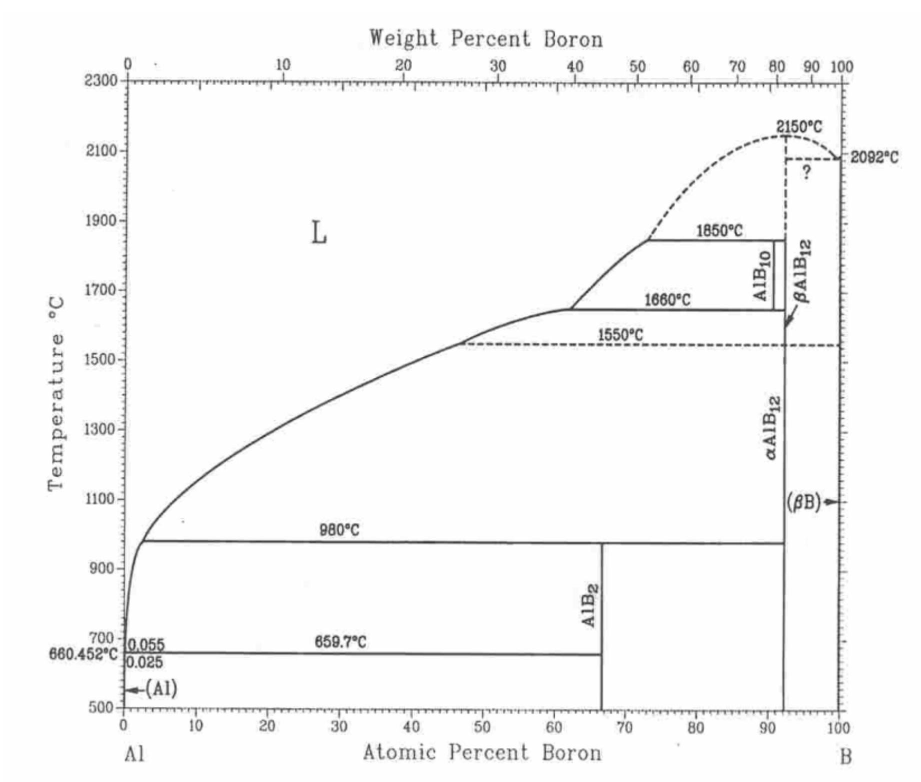


Fig.1. The aluminium-boron binary phase diagram

These elements are brought into aluminium as impurities with bauxite or from scraps. The contents of these elements are merely higher than several tens ppm. However, as solutes, the transition elements reduce the electrical conductivity of aluminium dramatically. To overcome this problem, boron is used to precipitate these impurities by forming borides of transition metals in aluminium which do not contribute to a major reduction in the electrical conductivity. Al–B master alloys are also used in the in-situ fabrication of aluminium matrix composites. One example is the in-situ fabrication of AlB_2 fibre reinforced aluminium metal matrix composites using an Al–B master alloy [3].

AlB_2 has a hexagonal close packed (HCP) crystal structure with lattice parameters: a = 0.3000 nm and c = 0.3245 nm, whereas AlB_{12} has a tetragonal crystal structure with a = 1.0161 nm and b = 1.4238 nm. Boron and aluminium occupy alternative layers in the HCP AlB_2 crystals. The melting points of AlB_2 and AlB_{12} were reported as 1655±50ºC and 2163±50ºC, respectively. Other Al–B compounds, such as AlB_{12} and AlB_{10}, were also reported. These compounds were later proved to be metastable or ternary compounds that are stabilized by small amount of impurities [3]. Also the elementary cell is an rhombic prism. Fig. 2 provides an image of the crystal lattice of AlB_2 while table 1 presents the distances between aluminium and boron atoms.

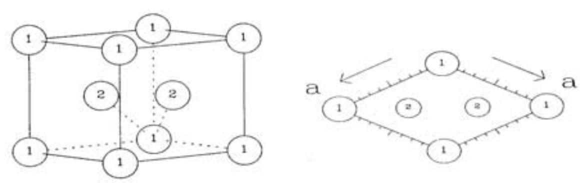


Fig. 2. Graphical representation of AlB_2 crystal atomic lattice

Table 1

Distances between the atoms in the AlB_2 crystallin structure

Reference atom: Al (1)			Coordonates		
			x	y	z
			0	0	0
Distance, [nm]	Mark	Type of atom	Coordonates		
			x	y	z
0,2373	2	B	1/3	-1/3	1/2
0,2373	2	B	-1/3	-2/3	1/2
0,2373	2	B	1/3	-1/3	-1/2
0,2373	2	B	-1/3	-2/3	-1/2
0,2373	2	B	-1/3	1/3	1/2
0,2373	2	B	-2/3	-1/3	1/2
0,2373	2	B	2/3	1/3	1/2

0,2373	2	B	1/3	2/3	1/2
0,2373	2	B	2/3	1/3	-1/2
0,2373	2	B	1/3	2/3	-1/2
0,2373	2	B	-1/3	-1/3	-1/2
0,2373	2	B	-2/3	1/3	-1/2
0,3000	1	Al	1	0	0
0,3000	1	Al	-1	0	0
0,3000	1	Al	0	-1	0
0,3000	1	Al	0	1	0
0,3000	1	Al	1	1	0
0,3000	1	Al	-1	-1	0
0,3245	1	Al	0	0	-1
0,3245	1	Al	0	0	1

2. Experimental materials and methods

The Al/AlB_2 in situ composite was produced via chemical reactions between KBF_4 (of analytical purity) and AA6060 aluminium alloy (0.44 wt% Mg, 0.48wt% Si) at 850ºC in an electrical furnace (Fig. 3). A small quantity of Na_3AlF_6 was also added as activator of the reaction (to reduce energy and accelerate the system). KBF_4 powder was continuously manually fed, and incorporated in the molten aluminium alloy during the stirring with an graphite rod. After 60 minutes reaction time at 850ºC the melt was cast into a steel mould. The cast ingot was sectioned into small pieces for microstructural analysis. The samples were polished to 1000 mesh grade with SiC paper, followed by surface finishing to 1µm. After polishing, the samples were subjected to chemical etching (0.5% HF) and afterwards microscopically analized.

Table 2 presents the thermodynamical propreties of the exothermic equilibrium equation of the in situ formation of AlB_2 particles in the melt:

$$3Al + 2KBF_4 = 2KF + 2AlF_3 + AlB_2 \tag{1}$$

The temperature in the furnace rised to about 900 - 950ºC and was measured by a thermocouple.

Table 2

Thermodinamical values of the reaction calculated with HSC Chemistry 6.0

	T	Cp	H	S	G	Reference	
1	**3Al + 2 KBF4 = 2KF + 2AlF3 + AlB2**						
2	**T**	**deltaH**	**delta S**	**delta G**	**K**	**Log(K)**	
3	**C**	**kJ**	**J/K**	**kJ**			
4	650.000	-605.259	-156.612	-460.683	1.172E+026	26.069	
5	700.000	-639.012	-192.753	-451.434	1.711E+024	24.233	
6	750.000	-640.340	-194.085	-441.762	3.590E+022	22.555	

7	800.000	-641.441	-195.137	-432.030	1.073E+021	21.030	
8	850.000	-642.317	-195.935	-422.253	4.360E+019	19.639	
9	900.000	-588.369	-148.190	-414.520	2.871E+018	18.458	
10	950.000	-588.646	-148.422	-407.104	2.437E+017	17.387	
11	1000.000	-588.797	-148.543	-399.680	2.508E+016	16.399	
12	**Formula**	**FM**	**Conc.**	**Amount**	**Amount**	**Volume**	
13		**g/mol**	**wt-%**	**mol**	**g**	**l or ml**	
14	Al	26.982	24.326	3.000	80.945	29.979	ml
15	KBF4	125.902	75.674	2.000	251.804	100.520	ml
16		**g/mol**	**wt-%**	**mol**	**g**	**l or ml**	
17	KF	58.097	34.919	2.000	116.193	46.852	ml
18	AlF3	83.977	50.475	2.000	167.953	54.179	ml
19	AlB2	48.602	14.606	1.000	48.602	15.236	ml

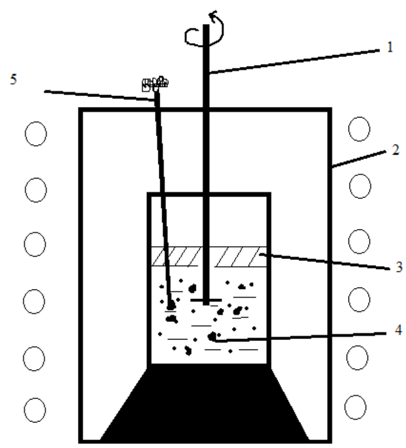


Fig. 3. Schematic of the furnace: 1 –graphite stirrer, 2 - electric resistance furnace, 3- flux K_2TiF_6 + Na_3AlF_6, 4 – Al_xB_y particles, 5 – termocouple

3. Results and Discussion

The cristalographic structures of the compounds that could appear in the microstructure of the composite are: hexagonal (AlB_2) and tetragonal (AlB_{12}). (Fig. 4)

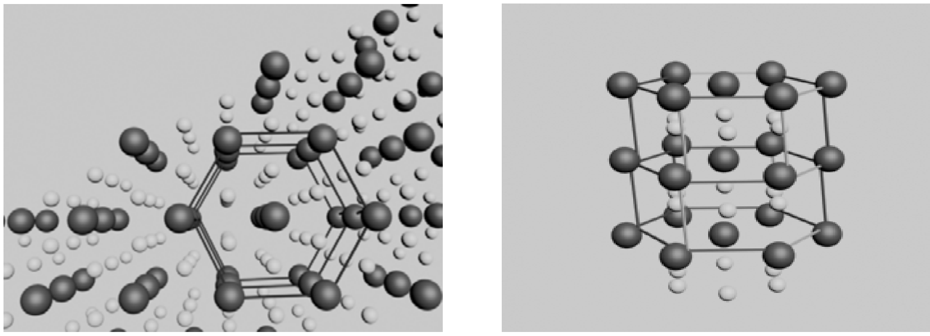


Fig. 4. The 3d structure of AlB_2: represents the aluminium atoms, and the boron atom

In Fig. 5 are presented the results of the optical analysis of the in situ obtained AA6060/AlB_2 composite. It can be noted that AlB_2 type structure formed, the hexagonal form of the particles beeing clearely noticeable. Since the exothermic reaction between aluminium (AA6060 alloy) and KBF_4 took place entirely in the molten alloy, no oxidation layer on the surface of the AlB_2 particles could be formed.

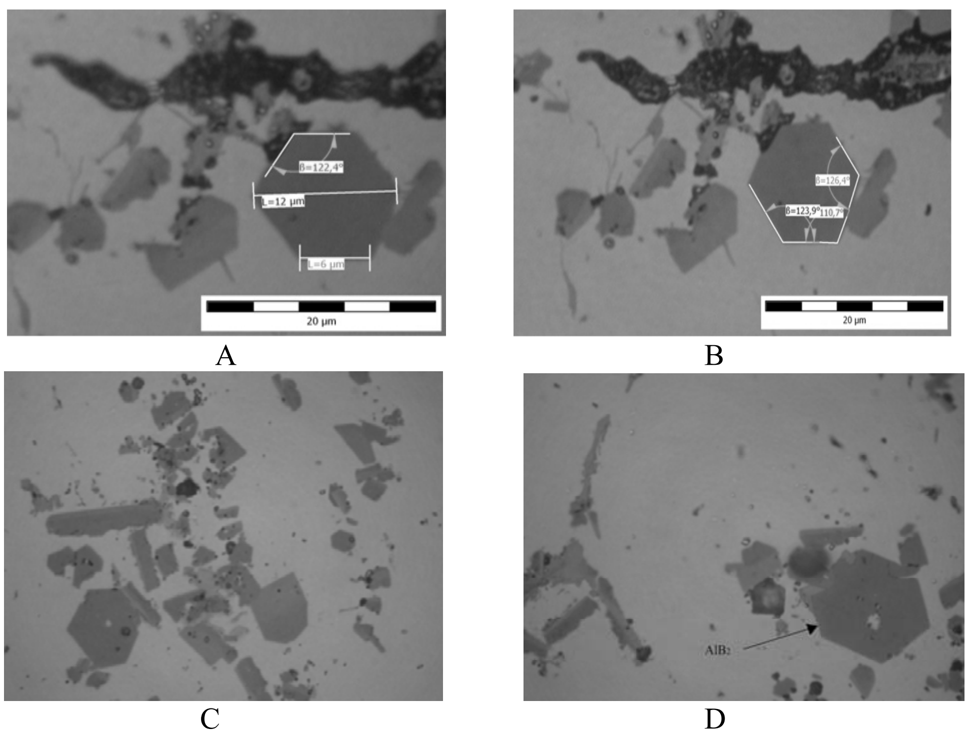


Fig. 5. The morphology of AlB_2 particles in AA6060/AlB_2 in situ composite

A representative sample was examined by X-ray diffraction methods using a nickel filtered Cu radiation (Fig. 6). For the measuring of the two specimens the measuring parameters were the same. The analysis was performed using a Philips diffractometer and the data were recorded using specialized software X 'Pert Data Collector. The pattern reveals the presence of Al and AlB_2 peaks, indicating that AlB_2 is formed in the composite, at high cooling rate. As it is known the adhesion mechanical work of the in situ composites is higher than of the ex situ composites, this fact presenting an advantage of the in situ composites.

The adhesion energy can be calculated from surface energies γ_{SV} and γ_{PV} using the following relation:

$$W_{AD} = 2\varphi\,(\gamma_{SV} \cdot \gamma_{PV})^{1/2} \quad (2)$$

where: $\varphi = 0.25$, s – solid metal, v – vapor, p – AlB_2 particles.

$\gamma_{SV} = 1.2(\gamma_{LV})_m + 0.45\,(T_m\text{-}T)$, where T_m is the melting temperature, K.

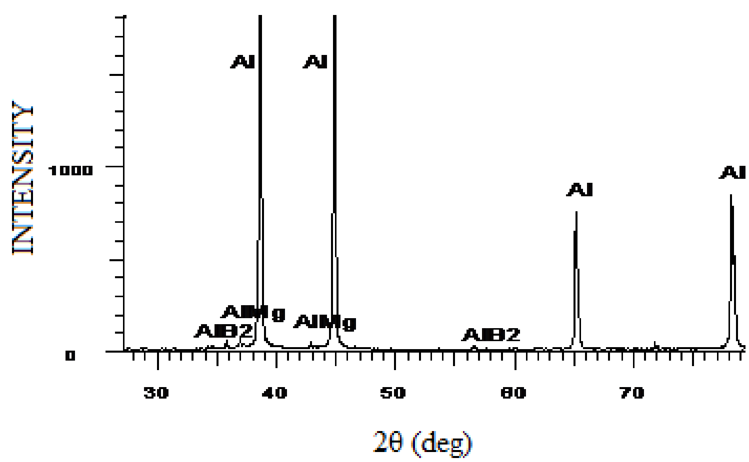
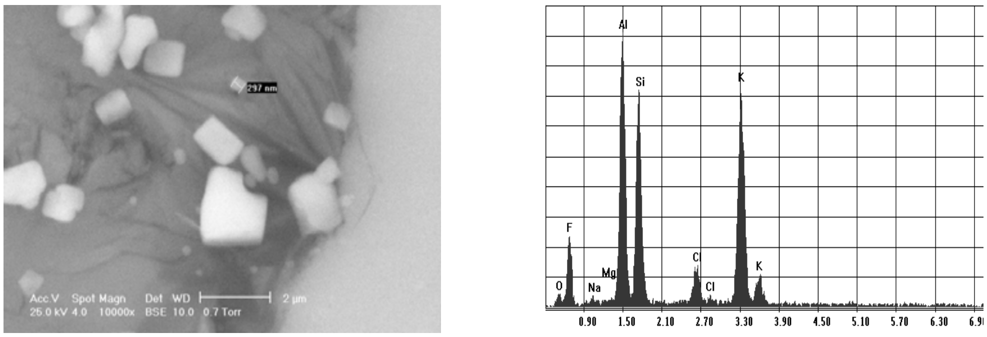


Fig. 6. XRD image of the representative sample of AA6060/AlB_2 composite

The morphology and the chemical composition of the composite samples have been investigated by Scanning Electron Microscopy (Fig. 7 a, b). The analysis was performed using an XL-30-ESEM TMP Electronic Microscope.

The SEM analysis revealed the morphology of the AlB_2 particles (white poliedric particles).

The EDS of the surface of the composite specimen indicate the presence of Si and Mg from the aluminium matrix and the presence of K, Na, F and Cl from salts.



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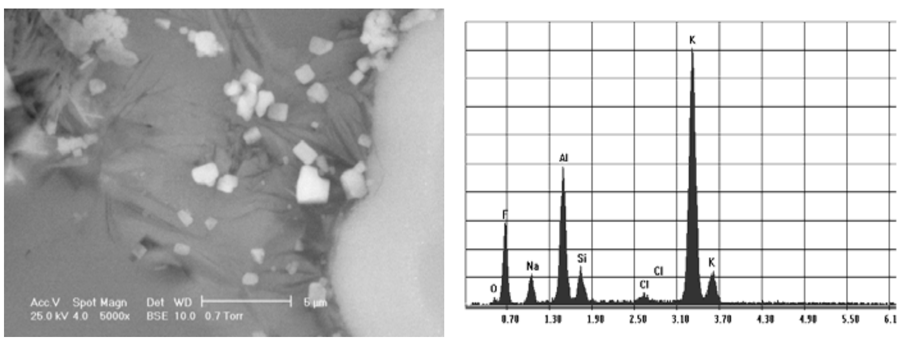

b

Fig. 7. SEM and EDS images of the samples

The mechanism of the interaction between Al and KBF_4 was explained by Wang[2]. When KBF_4 is added into molten aluminium, it is reduced by Al with $KAlF_4$ formation. It can be seen from reaction (1) that the formation of one mole of AlB_2 produces a larger quantity of $KAlF_4$ than the formation of one mole 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 reaction is vigorous and the build up of boron still happens.

$$12KBF_4 + 13Al = AlB_{12} + 12KAlF_4 = AlB_{12} + 12KF + 12AlF_3 \tag{3}$$

$$2KBF_4 + 3Al = AlB_2 + 2KAlF_4 = AlB_2 + 2KF + 2AlF_3 \tag{4}$$

The reactions (3) and (4) represent the explicit chemical processes which occur during the process of preparation in situ Al/AlB_2 (Na_3AlF_6 can cause slags to eliminate Al_2O_3) [6].

$$2Al_2O_3 + 2\ Na_3AlF_6 = 4AlF_3 + Na_2Al_2O_4 + 2Na_2O \qquad (5)$$

or by solving Al_2O_3 after the rise of temperature.

4. Conclusions

The Al/AlB_2 in situ composite was produced via exothermic chemical reaction between KBF_4 and liquid AA6060 aluminium alloy at 850ºC.

The thermodynamics and the mechanisms of the interaction between Al and KBF_4 in the presence of cryolite (as activator and solvent for Al_2O_3) was investigated.

The XRD analysis revealed the formation of AlB_2 poliedric compounds dispersed in the matrix and an interface Al/AlB_2 very clean and with a high adhesion energy generally observed.

The microstructures (Optical Microscopy, SEM/EDS) confirms the presence of AlB_2 compounds in the condition of high cooling rate of the composite material.

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