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IN SITU AA7XXX/TiB_2 COMPOSITES PRODUCED BY FLUX ASSISTED SYNTHESIS

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In situ aluminum alloys AA7050 and AA7075 reinforced with different amounts (2.5%, 5.0% and 7.5 % wt.%) TiB2 particulate composites were produced by flux-assisted synthesis using salts of K_2TiF_6 and KBF_4. Processing parameters in terms of salts quantities, and reaction time were optimized in order to form fine TiB_2 particles in matrix. The AA7050/TiB_2 and AA7075/TiB_2 composites were characterized by X-ray diffraction, optical microscopy (OM) and scanning electron microscopy (SEM, EDS). SEM analysis indicate that TiB_2 particles, formed in situ, have a hexagonal or spherical shape and sizes from 155 nm to 1.15 µm.

Keywords: in-situ composite, AA7XXX alloy, TiB_2.

1. Introduction

Particulate reinforced aluminium matrix composites have found extensive use in many applications due to their high specific modulus, strength, hardness and stiffness and excellent wear resistance [1-3]. The development of these materials has been driven by the aerospace and automotive industries.

To overcome inherent problems of traditional ex-situ methods of fabrication of MMCS and to improve the interfacial compatibility researchers are now focusing on in situ techniques. New in situ processing techniques like flux-assisted method have been reported in literatures [4-7].

Literatures reporting on AA7075 and AA7050 aluminium matrix reinforced with TiB_2 composites are limited compared to other matrix-alloys [8-9].

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In this work and attempt is made to produce AA7XXX aluminum alloys (AA7075 and AA7050) reinforced with TiB_2 particles by flux assisted synthesis and study the morphology and size of TiB_2 particles.

2. Experimental

The AA7050 or AA7075 rods were melted and overheated at 1000-1200K. The chemical composition of alloys is done in Table 1.

Composites were fabricated by mixing potassium tetrafluoroborate (KBF_4), potassium tetrafluorotitanate (K_2TiF_6) and cryolite (Na_3AlF_6), preheated at 250^{o}C for 3 hours, to remove humidity. The salt mixture was slowly added, and stirred by graphite rod. Slag formed during the reaction between aluminum and mixed salts were skimmed thoroughly before pouring the molten composite. The parameters of the process is shown in Table 2 and experimental details is shown in Table 3.

The in-situ composite was poured into preheated die. The specimens were polished using standard metallography technique.

The polished specimens were etched with Buswell's reagent (10 ml HNO_3, 1 ml HF, 89 ml H_2O and 0.1 ml $CuSO_4$•$5H_2O$). The specimens were observed using an optical microscope and scanning electron microscope(SEM).

Table 1

Chemical composition of alloys

Alloy	Element, wt %									
	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr	Al
AlZn6CuMgZr AA7050	0.065	0.11	2.20	0.021	2.28	0.0025	5.95	0.035	0.09	bal.
AlZn5.5Mg Cu AA7075	0.14	0.23	1.52	0.13	2.45	0.20	5.47	0.043	0.01	bal.

Table 2

Parameters of the manufacturing process of composites

Process phase	Parameter	
	Temperature, ^{o}C	Duration, min
Load crucible	20	2
Melting and overheating	750-950	30
Introduction of mixture of salts	750-950	5
Na_3AlF_6 addition	750-950	1
Stirring the melt	740-940	60-120
Slagging	740-790	3
Casting	750-760	4

Table 3

Experimental details

Matrix	KBF_4	K_2TiF_6	Notation	Reaction time, min
AA7050 200g	20g	20g	C1	60
	40g	40g	C2	60
	40g	40g	C22	90
	40g	40g	C23	120
	60g	60g	C3	60
AA7075 200g	20g	20g	D1	60
	40g	40g	D2	60
	60g	60g	D3	60

3. Results and Discussions

In the flux assisted synthesis of AA7050/TiB_2 and AA7075/TiB_2 in-situ composites, the formation of TiB_2 particles is carried out by reaction between the salts mixture (K_2TiF_6 and KBF_4) and the molten aluminum.

$$3K_2TiF_6 + 6KBF_4 + 10Al = 3TiB_2 + 12KF + 10AlF_3 \quad (1)$$

Calculated thermodynamic data of reaction (1) in the temperature range of 750°C and 950°C, using the HCS Chemistry 6.0 program, is done in Table 4.

Table 4

Thermodynamic values calculated with HCS Chemistry 6.0

$3K_2TiF_6 + 6KBF_4 + 10Al = 3TiB_2 + 12KF + 10AlF_3$					
T, °C	ΔH, kj	ΔS, J/K	ΔG, KJ	K	Log (K)
750	-2541.47	-70.2158	-2469.63	1.2E+126	126.0921
800	-2507.59	-37.8843	-2466.93	1.2E+120	120.0858
850	-2472.7	-6.11262	-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

The SEM micrograph and the EDS microanalysis of the TiB_2 particles is presented in Fig. 1. The in-situ formed TiB_2 particles exhibit hexagonal and spherical shapes [3, 4]. The average size of TiB_2 particles was measured to be between 155 nm and 1.15 μm.

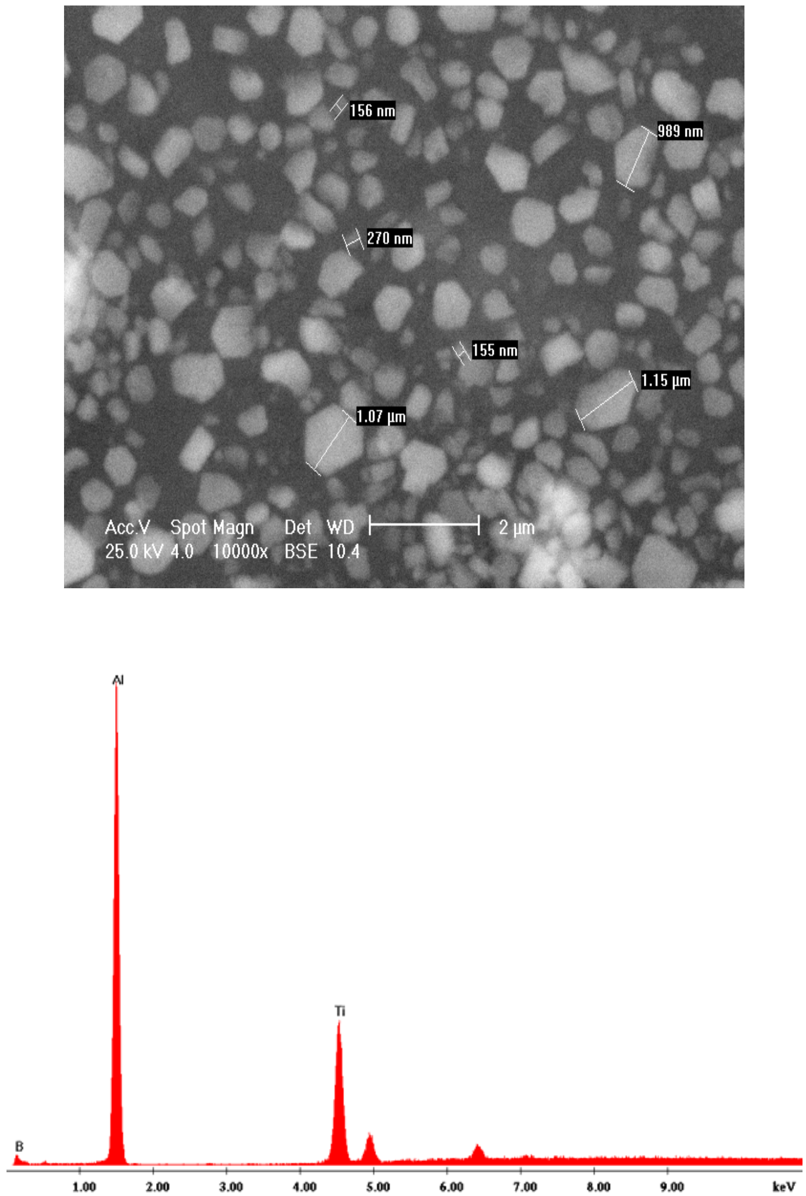
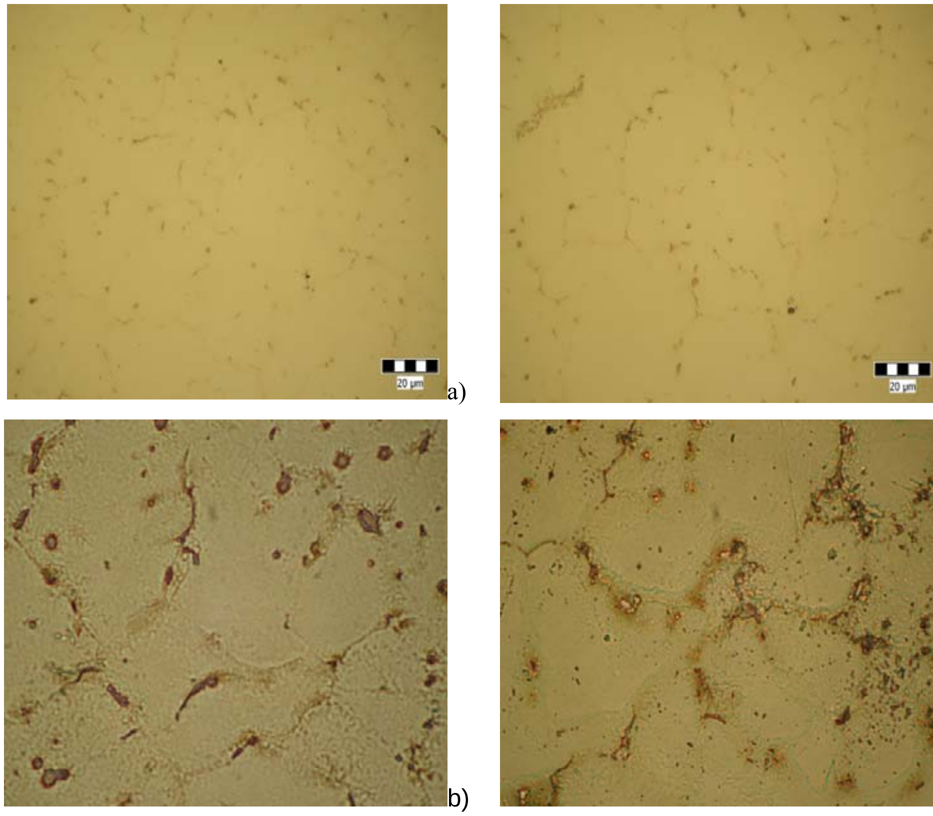


Fig.1. SEM micrograph (a) and EDS microanalysis of TiB_2 particles

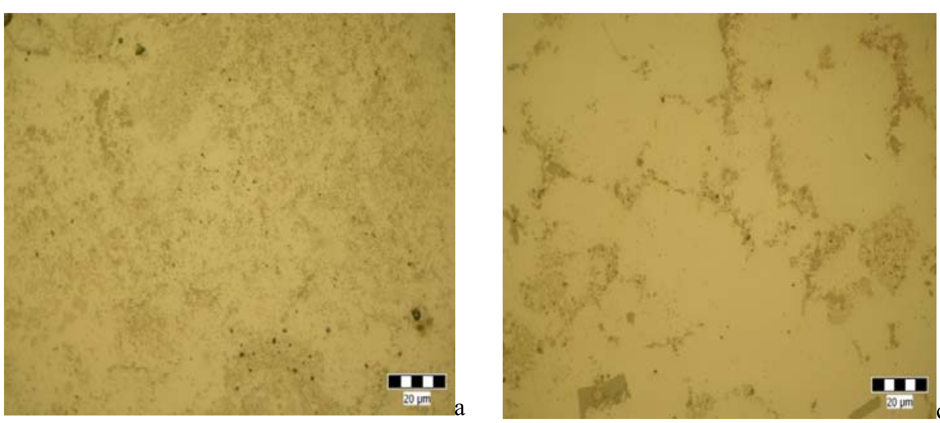
The optical micrographs of the AA7050/TiB_2 (C) and AA7075/TiB_2 (D) in situ-composites are shown in Fig. 2, 3, 4 and 5.



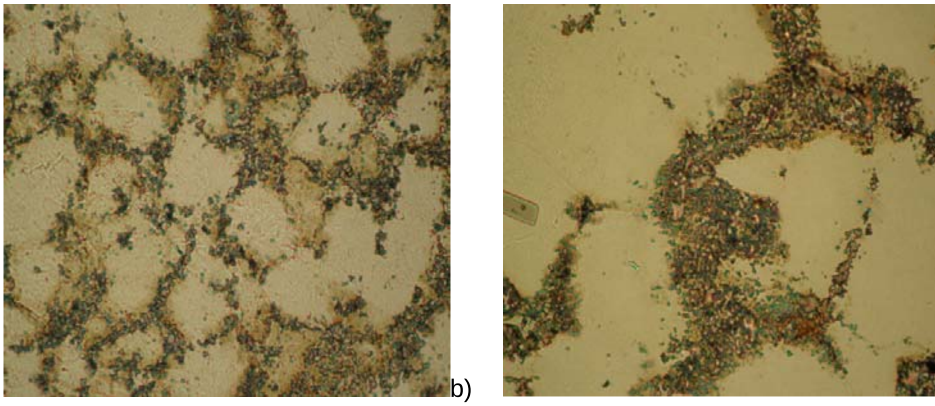
a) c) b) d)

a, b) C1 x500 c, d) D1 x500

Fig. 2. Microstructures of the AA7050/TiB_2 (a, b) and AA7075/TiB_2 composites (c, d) at a concentration of 2.5% TiB_2 particles, reaction time 60 minutes (b, d – etched)

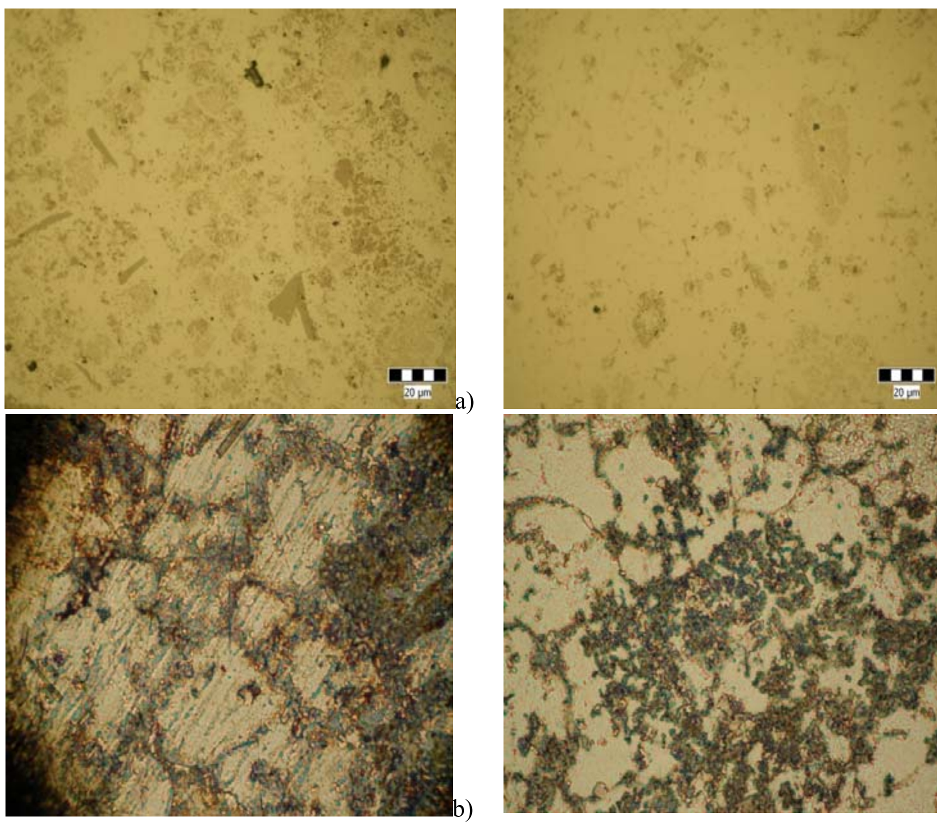


a) c)



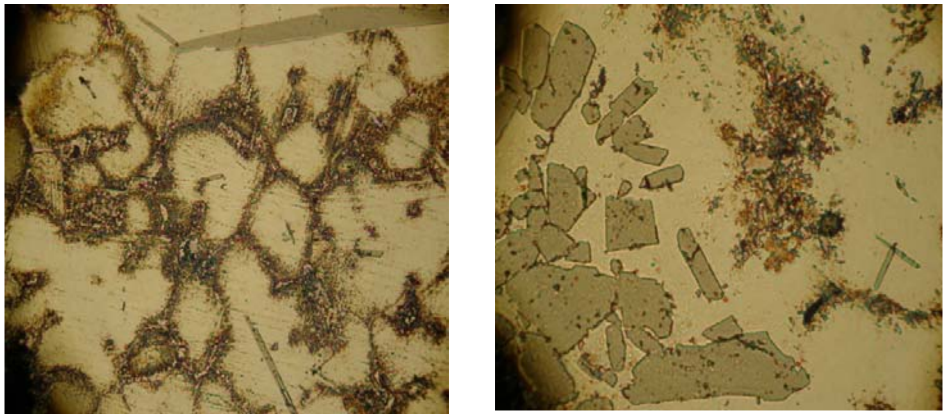
a, b) C2 x500 c, d) D2 x500

Fig. 3. Microstructures of the AA7050/TiB_2 (a, b) and AA7075/TiB_2 (c, d) composites at a concentration of 5% TiB_2 particles, reaction time 60 minutes (b, d – etched)



a, b) C3 x500 c, d) D3 x500

Fig. 4. Microstructures of the AA7050/TiB_2 (a, b) and AA7075/TiB_2 (c, d) composites at a concentration of 7.5% TiB_2 particles, reaction time 60 minutes (b, d – etched)



a) C22 x500 b) C22 x500

Fig. 5. Microstructures of the AA7050/TiB_2 composites at a concentration of 5% TiB_2 particles, reaction time 90 minutes (a, b)

In the Figs. 6 and 7 there have been presented the results of the analysis, with X-ray diffraction, of the AA7050/TiB_2 and AA7075/TiB_2 composites samples. There had been highlighted the compounds formed in the quaternary systems Al-Cu-Mg-Zn at the grain boundary.

As it can be seen from the C22 microstructures, at longer times of reaction we get TiB_2 but also $TiA1_3$ as reaction products (Fig. 6 a). This has been put in evidence by the XRD analysis in Fig. 6 (b).

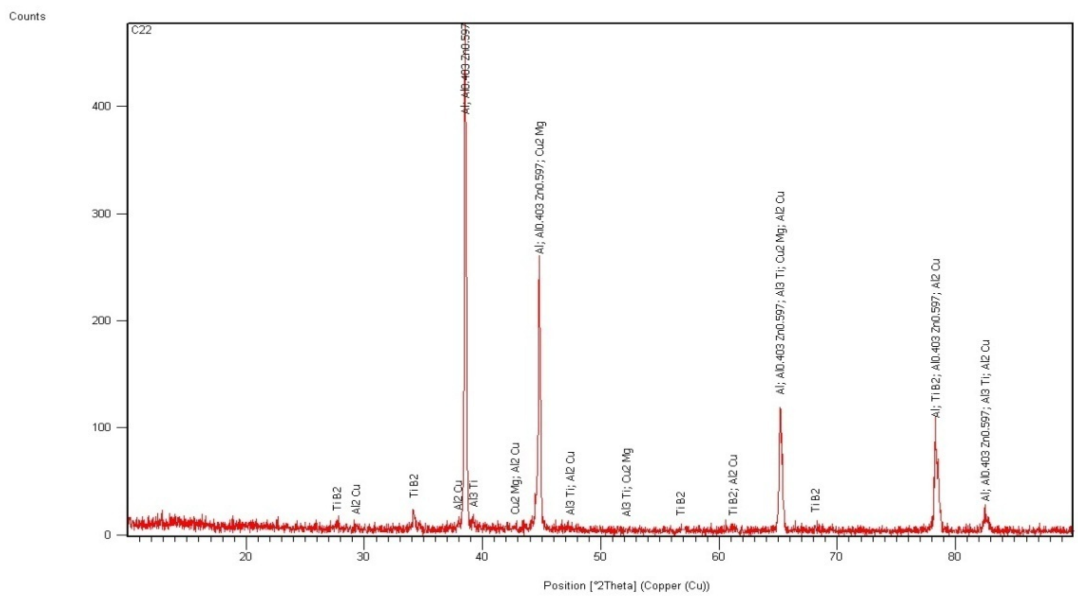
As it was expected, the particles concentration increases with the increase of salts quantities used to develop AA7xxx/TiB_2 composites. Relative uniform distribution of TiB_2 particles in the matrix-alloys AA7050 can be seen, while in the AA7075 alloy shows segregation at the grain boundary.

Increasing the reaction time from 60 to 120 minutes leads to agglomeration of the TiB_2 particles, emphasized by the microstructures shown in Fig. 5(b). Likewise, increasing the concentration of salts rich in Ti and B leads to an uncompleted reaction of converting $TiAl_3$ in TiB_2, Figs. 5(a) showing very obvious the needle particles of $TiAl_3$.

The grain refining action of TiB_2 particles is clearly seen; with addition of in the presence of TiB_2, the morphology of the matrix has turned from the dendritic feature to equiaxed grains, the grain size reduces when the amount of TiB_2 increases .

No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale ...	SemiQua
1	☐	01-089-3657	Aluminum, syn	Al	52	0.684	-
2	☐	01-071-5368	Titanium Bor...	Ti B2	18	0.042	-
3	☐	00-052-0856	Aluminum Zinc	Al0.403 Zn0.597	32	0.457	-
4	☐	03-065-7847	Aluminum Ti...	Al3 Ti	7	0.044	-
5	☐	03-065-9042	Copper Magnes	Cu2 Mg	0	0.079	-
6	☐	01-089-1981	Khatyrkite, s...	Al2 Cu	4	0.011	-

a)

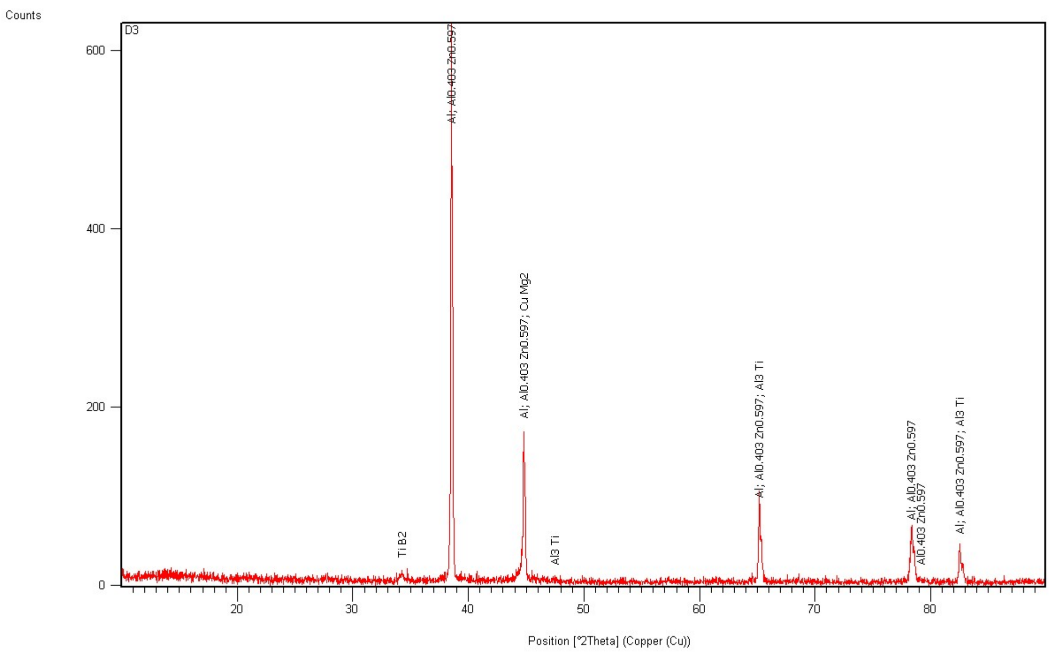


b)

Fig. 6. XRD pattern of AA7050/TiB_2 (C22) composite (a – compound list, b – compound diffraction)

No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale ...	SemiQua
1	☐	01-071-3760	Aluminum	Al	73	0.381	-
2	☐	00-052-0856	Aluminum Zinc	Al0.403 Zn0.597	27	0.385	-
3	☐	00-008-0121	Boron Titani...	Ti B2	9	0.025	-
4	☐	03-065-4505	Aluminum Ti...	Al3 Ti	2	0.238	-
5	☐	00-013-0504	Copper Magnes	Cu Mg2	2	0.053	-

a)



b)

Fig. 7. XRD pattern of AA7075/TiB_2 (D3) composite (a – compound list, b – compound diffraction)

4. Conclusions

Following the experiments we can draw some conclusions about both the effect of grain refining effect of TiB_2 particles and the influence of operating parameters on the final resulting compounds.

As expected, in the AA7XXX/TiB_2 composites, the intermetallic compounds found correspond to that formed in AA7XXX alloys but also TiB_2 and $TiAl_3$ compounds were in situ formed. TiB_2 and $TiAl_3$ particles are widely recognized as nucleating substrates for the solidification of aluminum alloys.

The concentration of the TiB_2 particles is subject to the initial amounts of salt used - in the case of composites with higher concentrations and higher reaction times (90, 120 minutes) is greater but also appear needle compounds of $TiAl_3$.

For the production of TiB_2 particles uniformly distributed in the matrix of the 7xxx series aluminum alloy is sufficient reaction time of 60 minutes, the increase of reaction time leading to a particle agglomeration.

R E F E R E N C E S

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