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Effect of Cryolite on Microstructure of Insitu AlB_2 Aluminium Metal Matrix Composites

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ABSTRACT--- Todays composite material have gained more popularity due to their improved properties over the conventional materials. In the present paper, insitu composites were fabricated via chemical reaction between molten aluminium alloy and halide salt KBF4 with cryolite at 8000C by stir casting method. The microstructures of the composite containing 3 and 5 wt. % of AlB2 reinforcement phase have been compared with the unreinforced aluminium alloy. The microstructure analysis shows clean AlB2 particles uniformly distributed throughout the matrix. With the increase in the AlB2 reinforcement, insitu composite show less agglomeration and recovery of boron is more when compared to the unmixed halide salt in the fabrication of inistu composites.

Keywords — Aluminium diboride, Cryolite, Halide salt, Insitu

I. INTRODUCTION

In today's trend aluminum matrix composites were gaining more importance because of its high strength to weight ratio and excellent performance inorder to fulfill the needs and demands in the aviation and automobile industries. Various manufacturing techniques were adopted in AMC's with the various reinforcements [1-4] such as Al_2O_3, B_4C, TiC, graphite, TiB_2, fly ash, AlB_2, and $ZrB_2$for manufacturing of variety of components like brake drums, cylinder liners, connecting rods, bearings, gears, drum and rotors for the above industries[5-10].

For the production of insitu master alloys different halide salts have been extensively used. MMC have been drawn considerable attention through the world because of its excellent mechanical and tribiological properties. AMC with ultra-fined ceramic material or particles have been extensively used in aerospace and automotive application[11-13]. In the recent years more attention is paid to insitu composites mainly because of its clean interface formed in between the base matrix with reinforcement, good bonding strength, high interfacial integrity, clear uniform distribution in the matrix with high mechanical properties and low fabrication costs[14-19]. Owing to its uniform distribution in the matrix, the insitu AMC are widely used in the structural application, when high stiffness, more strength to weight ratio plays an important role in the aerospace and automotive industries [20-22].

Binary master alloys (Al-B) receiving very good response to replace the tertiary master alloys (Al-Ti-B) which fail to grain refine in Al foundry alloys [23]. Binary master alloys have recently become predominant role for grain refining in pure aluminum. For the production of master alloys in the industrial application involves addition of halide salt KBF_4 directly into the base matrix molten aluminum alloy at the required melting and reaction temperature. Exothermic reaction takes place between the halide salt and Al alloy, the presence of boron in the salt reduced and reacts with aluminum to form the aluminium diborides. Special care and measures is required for the formation and dispersion of aluminum diboride in the melt. Chemical reaction and stirring time plays the predominant role for the production of insitu AlB_2 particles. Alumnium boride thus formed in the melt are retained in the dross layer and mix with the remaining aluminum in the melt are in the form of clusters and contaminated with the salt residues[24-29]. Similar production technique is applied for the production of Al-TiB_2 composites and tertiary master alloys by using KBF_4 and K_2TiF_6 halide salts where TiB_2 particles are distributed uniformly and more easily [30-32].

There are various insitu processing techniques are employed to improve the interfacial capability and reduce the reinforcement sizes particle to produce the high performance insitu dispersoid. Aluminum diboride particles are produced by the exothermic chemical reaction between the aluminium and different ceramic compound or halide salt such as KBF_4. Literature survey on Al-AlB_2 composites reveals that very meager amount of work has been carried out in the field. In various insitu reinforcement AlB2 has emerged outstanding insitu reinforcement because of its excellent stiffness, hardness and wear resistances. Present paper Al-AlB_2 composites are prepared using halide salt to increase the boron recovery by adding cryolite with varying wt. % of reinforcement and to optimize the manufacturing process [33-36].

II. MATERIALS AND EXPERIMENTAL PROCEDURE

6061Al which is commercially available from PMC Corporation, Bengaluru was used as matrix material and halide salt KBF_4 of 99% from Madras Fluorine Private Ltd, Chennai, having PH value of 4.3, were used as starting materials for the formation of AlB_2 reinforcement during in situ reaction. Cryolite (SHWET MULTIMETALS, MUMBAI) is used during casting acts as an activator for the exothermic reaction (to accelerate the system and reduce energy) and solvent for Al_2O_3 formed during casting

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process. It is used in different ratio of the wt.%. with the reinforcement for the preparation of the insitu Al-AlB_2 composites. The chemical composition of the matrix and reinforcement material is as shown in Table 1.1, 1.2 and 1.3.

1.1 Cryolite (Na_3AlF_6)

Cryolite salt is in powder form and is used as a refining flux and accelerate the system reaction in the fabrication of inistu composites and master alloys for maximizing the boron recovery during the chemical reaction. Inorder to increase and maximize the boron recovery which is present in the melt and cleanliness of the salt cryolite Na_3AlF_6 is used in the exothermic reaction between the aluminum and the salt KBF_4.

Table:1.1 Shows Chemical Composition of Al6061

Elements	Si	Cu	Fe	Zn	Mn	Cr	Mg	Al
%	.76	.22	.28	.06	.04	.07	.92	Balance

Table:1.2 Shows Chemical Composition of KBF_4 halide salt

Elements	B	K_2SiF_6	Fe	Moisture	Assay
%	8.51%	0.84%	0.022%	0.06%	98.9%

Table:1.3 Chemical composition of Na_3AlF_6

Elements	F>	Na>	Al>	SiO_2<	Fe_2O_3<	SO_4<	Ignite<
%	53	32	13	0.25	0.05	0.7	2.5

Cryolite Na_3AlF_6 is highly surface active which breaks the oxide boride agglomerates or mushy parts which are glued together and recover the borides at the maximum extent during the chemical reaction between the Al-KBF_4 insitu processes, otherwise the boride particles would end up in the dross. Addition of cryolite Na_3AlF_6 in the preparation Al-AlB_2 composites impact was very remarkable [37-41].

1.2 Fabrication Process

Al6061/AlB_2 composites containing 3wt% and 5wt% of inistu AlB_2 dispersoid were fabricated by insitu chemical reaction involving exothermic dispersion in an electrical resistance furnace equipped with an automatic stirrer. Known quantity of base matrix material is loaded into a 5 Kg graphite crucible and heated to a temperature of 800^0C ±5˚C in a furnace. By using hexa chloro ethane tablets (C_2Cl_6) degasification process is carried out to expel gases absorbed during melting process. The KBF_4 halide salt and cryolite Na_3AlF_6 salt, was preheated to a temperature of 300^0C in a muffle furnace to remove the moisture present in the salt. A calculated quantity of premixed and pre heated KBF_4 halide salt and cryolite Na_3AlF_6 (0.5 wt. % of KBF_4) salt mixture is added to the melt with continues stirring at a speed of 150 rpm for 15-60 minutes using a zirconia coated stirrer. The premixed salt is fed into the molten aluminum either in the form of powder or tablet form was performed gradually, to avoid melt due to excessive cooling retain the temperature above 800^oC in the addition process. To monitor the progress of KBF_4-Al reaction melt temperatures has to be recorded and melt temperature is maintained at 800^oC upto 60 minutes[42-43]. After 60 minutes reaction time and a temperature of 800ºC, the slag was skimmed off before half of the melt and the remaining half was stirred manually with a preheated graphite rod. The melt was finally cast into a permanent mould. Fabricated castings of aluminium alloy and inistu composites specimens were machined and cut into pieces according to ASTM standards for microstructural studies. The samples of microstructural studies were then metallographically polished with different grades of silicon carbide papers, followed by surface finishing and chemical etching with kellers reagent to reveal microstructural details [44]. The prepared inistu composites were examined for microstructures using Scanning Electron Microscope to know the formation, distribution and morphology of inistu AlB_2 particle in the composites.

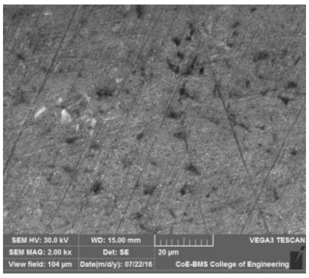
Reactions occurring during the process of interaction between aluminum and potassium fluoroborate are [45]

$$12KBF_4 + 13Al = AlB_{12} + 12KAlF_4 \ (1) = AlB_{12} + 12KF + 12AlF_3 \quad (1)$$

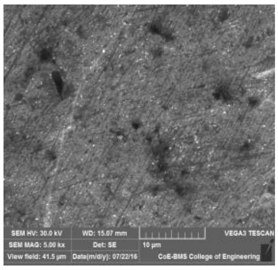
$$2KBF_4 + 3Al = AlB_2 + 2KAlF_4 = AlB_2 + 2KF + 2AlF \quad (2)$$

III. RESULTS AND DISCUSSIONS

3.1 Microstructural studies

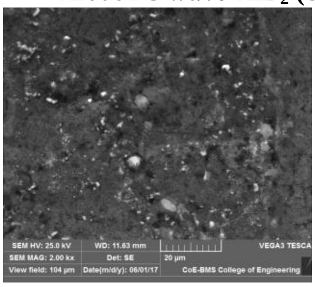


(a)

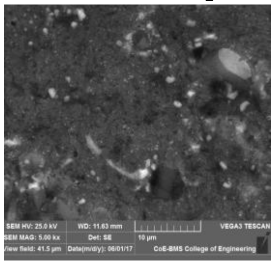


(b)

Fig 3.1(a)-(b) shows the micrograph without cryolite (a) Al6061-3 wt.% AlB_2 (b) Al6061-5 wt.% AlB_2

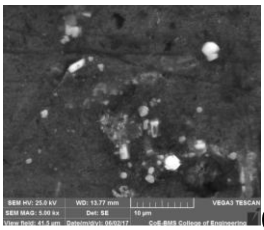


(c)

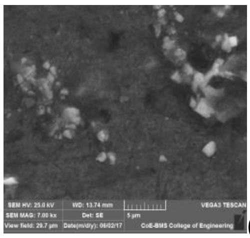


(d)

Fig 3.1(c)-(d) shows the micrograph with cryolite in the ratio 1:4 (a) Al6061-3 wt.% AlB_2 (b) Al6061-5 wt.% AlB_2



(e)



(f)

Fig 3.1 (e)-(f) shows the micrograph with cryolite in the ratio of 1:2 (e) Al6061-3 wt.% AlB_2(f) Al6061-5 wt.% AlB_2

Fig.3.1 (a)-(f) represents the micrograph of with and without cryolite using the formation of Al-AlB_2 insitu MMC's. Introducing of halide salt KBF_4 into the liquid molten alumnium has resulted in exothermic chemical reaction for developing AlB_2 insitu particle as clearly visible in SEM micrographs in Fig. 3.1 (a) and (b) as seen with dark colour AlB_2 particles. But the AlB_2 particles have not been distributed uniformly in the matrix. According to the Aluminum Binary phase diagram [46], peritectic type of reaction occurs to form the AlB_2 particles i.e, Al (liquid) + AlB_{12} → AlB_2 at 900^0C. Amid which the at first framed AlB_{12} phase responds with encompassing aluminum dissolve to shape AlB_2 amid cooling. The vast majority of the AlB_2 particulates formed amid the insitu chemical reaction have hexagonal shape with light dim/dull dark shading as plainly observed in SEM microphotographs. Fig.3.1(c) and (d), when KBF_4 salt is premixed with the cryolite in the ratio of 1:4 wt. % of the reinforcement. Genuinely uniform scattering of AlB_2 particles in Al6061 base matrix can be accomplished by stirring the melt persistently which helps in fracture of substantial agglomeration of boride particles into littler particles which can be consistently distributed in the matrix [47]. Figure .3.1 (e) and (f) pertain to micrograph when KBF_4 salt is premixed with the cryolite in the ratio of 1:2 wt.% of the reinforcement, fairly uniform dispersion of AlB_2 particles in Al6061 matrix can be achieved by stirring the melt continuously which helps in breakage of clustering of boride particles into smaller particles which can be uniformly distributed in matrix[48].It is also observed that low aspect ratio of AlB_2 particles distributed throughout the base matrix. For converting from low aspect ratio to high aspect ratio AlB_2 particles melt to be heated more than 950^0C and to be cooled according to the Al-Boron binary phase diagram. Even vigorous stirring is carried out during the chemical reaction in the melt, retaining of uniform distribution of AlB_2 particle is extremely impossible [49]. Depending upon the cooling rate, chemical reaction time and melt temperature reaction, the clustering of the inistu particles forms inside the matrix. The properties of Al-AlB_2 insitu composites profoundly relies on the resolution, distribution, shape and size of AlB_2particles.

Table 1.Recovery of boron (B) and cleanliness in Al–AlB_2 composites produced adding with and without cryolite[49]

Sl No	Salt used	Stirring	B recovery%	Cleanliness
1	KBF_4	With	40	Modesty
2	Halide salts KBF_4 + Na_3AlF_6 at ratio of 1 : 2	With	90	Rich

IV. CONCLUSIONS

The present work involving effect of cryolite on Al-AlB_2 insitu composite is fabricated by an exothermic chemical reaction between Al6061 with two different premixed halide salts KBF_4 and Na_3AlF_6 has leads to the following conclusions.

- Insitu composites having 3 and 5 wt. % of AlB_2 were successfully fabricated using 6061Al and premixed salts KBF_4 and Na_3AlF_6 halide salt in a electrical resistance furnace.
- The micrographs reveals there is no clustering or agglomeration and clear uniform distribution of insitu AlB_2 particles in Al6061 matrix.
- Addition of Cryolite (Na_3AlF_6) shows best results when premixed with the KBF_4halide salt to the melt in the form powder or pressed tablets.
- Na_3AlF_6 breaks up the mushy part, oxide-boride agglomerates and recover the borides which are glued together with the spent salt when vigorous stirring is employed.
- The minimum addition level required for a trouble free processing and full B recovery is possible in the ratio of 1:2 (Na_3AlF_6:KBF_4).

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