

Microstructure and mechanical characterization of in situ synthesized AA6061/(TiB₂+Al₂O₃) hybrid aluminum matrix composites

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Abstract

TiB₂ and Al₂O₃ particulates reinforced AA6061 aluminum matrix composites (AMCs) were synthesized by in-situ reaction of titanium (Ti) and boric acid (H₃BO₃) powders with molten aluminum. AMCs were fabricated using an electric stir casting furnace under a controlled environment. Heat flow curves of differential thermal analysis (DTA) showed that the synthesis temperature for the formation of TiB₂ and Al₂O₃ using Al-Ti-H₃BO₃ reaction system was 950°C. The in-situ synthesized composites were characterized using XRD, FESEM, TEM and EBSD. XRD results revealed the formation of TiB₂ and Al₂O₃ particulates in the composite. FESEM micrographs revealed a homogenous distribution of both the particulates with good interfacial bonding. EBSD maps showed that the in-situ formed TiB₂ and Al₂O₃ particulates refined the grains of the aluminum matrix from 103 μm at 0 wt.% to 14 μm at 15 wt.%. Al₂O₃ particles exhibited spherical shape while TiB₂ particles displayed hexagonal and cubic shapes. The formation of ultrafine and nano scale thermodynamically stable TiB₂ and Al₂O₃ particles enhanced the microhardness and the tensile strength of the

AMCs. The microhardness and the tensile strength were respectively 122 HV and 287 MPa at 15 wt.%.

Key words: Aluminum Matrix Composites; Casting; Microstructure; Tensile strength.

1. Introduction

Aluminum matrix composites (AMCs) were developed from the incessant requirement for lightweight materials with superior properties in structural, aerospace and automotive industries [1–4]. AMCs are increasingly replacing the conventional monolithic aluminum alloys due to their excellent properties such as high strength to weight ratio, good wear resistance and low thermal expansion coefficient [5]. The growth in manufacturing methods led to the reinforcement of variety of ceramic particles such as oxides (Al_2O_3 , SiO_2 , TiO_2), carbides (SiC , TiC , B_4C), borides (TiB_2 , ZrB_2) and nitrides (AlN , Si_3N_4) [6–14].

AMCs are currently manufactured by many methods such as powder metallurgy [15], stir casting [16], mechanical alloying [17] and squeeze casting [18]. Liquid metallurgy route is preferred for the manufacturing of AMCs owing to its ease of adaption, cost-effectiveness and mass production. The incorporation of ceramic particulates into molten metal can be classified as ex-situ and in-situ methods [19–20]. Ceramic particulates are externally fed to the molten metal in ex-situ method. Conversely, ceramic particulates are internally generated within the molten metal using in-situ methods. The major disadvantage of ex-situ method is the deprived ability for the molten metal to wet the ceramic particulates leading to a reduction in mechanical properties. In-situ methods results in numerous advantages which are not limited to sub-micron and nano level particulates, improved distribution, superior interfacial bonding, thermodynamic stable particulates and low cost of processing [21–25].

The in-situ fabrication of dual or multiple particulate reinforced AMCs were reported in some literatures as presented subsequently [26-31]. Zhao et al. [26] formed Al/(TiB₂ + ZrB₂) AMCs using in-situ reaction among KBF₄, K₂ZrF₆, K₂TiF₆ and molten aluminum and presented the morphology and size distribution of particulates. Li et al. [27] fabricated Al/(ZrB₂+Al₂O₃) AMCs using in-situ reaction among Zr(CO₃)₂, KBF₄ and molten aluminum and demonstrated enhanced mechanical properties. Zhao et al. [28] synthesized Al-10Cu/(TiB₂ + Al₂O₃) AMCs using in-situ reaction among K₂TiF₆, KBF₄, CuO and molten aluminum. They reported superior mechanical properties of the composites compared to aluminum matrix due to the formation of TiB₂ and Al₂O₃ particulates. Yutao et al. [29] developed Al/ (ZrB₂, Al₂O₃ and Al₃Zr) AMCs using in-situ reaction between Zr(CO₃)₂, B₂O₃ and molten aluminum. They observed a good distribution of particulates with a size ranging from 80 nm to 2 μm. Zhu et al. [30] synthesized Al/(α-Al₂O₃+ Al₃Zr) AMCs using in-situ reaction between ZrO₂ and molten aluminum and explained the reaction mechanism. Jing et al. [31] produced A356/(ZrB₂+Al₂O₃+Al₃Zr) AMCs using in-situ reaction between KBF₄, K₂ZrF₆, Na₂B₄O₇ and molten aluminum and studied the morphology of particles. Zhu et al. [32] prepared Al/(α-Al₂O₃+ ZrB₂) AMCs using in-situ reaction between ZrO₂, B₂O₃ and molten aluminum and elaborated the mechanism of chemical reaction.

Literature survey showed that various AMCs reinforced with multiple particulates were prepared using in-situ reaction of several elements. The present work is focused on preparing AA6061/(TiB₂ + Al₂O₃) AMCs using in-situ reaction between titanium (Ti), boric oxide (H₃BO₃) and molten aluminum. A detailed characterization of the prepared composites was reported.

2. Experimental procedure

Aluminum alloy AA6061 was used as matrix material in this investigation. Titanium (Ti) and boric oxide (H_3BO_3) powders were used for synthesizing TiB_2 and Al_2O_3 . AA6061 in the form of cylindrical rods was melted using an electrical resistance furnace as shown in Fig. 1. A graphite crucible was used for keeping the rods inside the furnace. The chemical composition of AA6061 is furnished in Table 1. The amount of Ti and H_3BO_3 powders fed to the molten aluminum is given in Table 2. The powders were initially dehydrated at a temperature of $400^\circ C$. The temperature of the furnace was maintained at $950^\circ C$ and the aluminum melt was stirred intermittently for 30 minutes. The composite melt was poured into a preheated die subsequent to the removal of dross. Castings were taken having different weight percentage of (0, 5, 10 and 15wt.%) of $TiB_2 + Al_2O_3$ particulates.

Differential thermal analysis (DTA, NETZSCH STA 449F3 STA449F3A-0843-M)) was performed to study the reaction system of Ti, H_3BO_3 and aluminum. The powders were heated in an alumina crucible under an inert environment from atmospheric temperature to $1200^\circ C$ at a heating rate of $10^\circ C$ per minute. Specimens for metallurgical and mechanical characterization were prepared from the castings. Small specimens were polished following standard metallographic procedure and etched using Keller's reagent. The etched specimens were examined using field emission scanning electron microscope (FESEM, CARL ZEISS-SIGMAHV), electron backscattered diagram (EBSD) and transmission electron microscopy (TEM, JEOL JEM 2100). EBSD was carried out in a FEI Quanta FEG SEM equipped with TSL-OIM software. X-ray diffraction patterns (XRD) were recorded using Shimadzu XRD - 6000. The microhardness was recorded using a microhardness tester at 500 g load applied for 15 s. The tensile specimens were prepared as per ASTM E8 M-04 standard having a gauge length of 40 mm, a gauge width of 7 mm and a thickness of 6 mm. The ultimate tensile strength (UTS) was measured using a computerized universal testing machine. The fracture

surface was recorded using FESEM. A portion of AA6061/15 wt.% (TiB₂ + Al₂O₃) casting was dissolved in 35% HCl solution and the particulates were filtered out. The extracted particulates were observed using FESEM.

3. Results and discussions

3.1. DTA Analysis

Fig. 2 depicts the DTA curve recorded during heating of the powders. DTA graph consists of three endothermic peaks formed at 148°C, 174°C and 672°C. The first two endothermic peaks belongs to the removal of moisture from H₃BO₃ and the third endothermic peak formed at 672°C due to melting of aluminum alloy AA6061 [33]. Further, raise in temperature increases the reaction between Ti, H₃BO₃ and aluminum. Three exothermic peaks with higher intensity show the occurrence of combustion. The in-situ reaction takes place at a temperature of 950°C. DTA graph records no further peaks which indicate that the reaction products are thermodynamically stable.

3.2 XRD analysis of AA6061/(TiB₂+Al₂O₃) AMCs

XRD patterns of the cast AMCs are presented in Fig. 3. XRD pattern reveals the diffraction peaks of TiB₂ and Al₂O₃ particle. XRD pattern confirms the formation of TiB₂ and Al₂O₃ due to the reaction between Ti, H₃BO₃ and Al. The height of peaks of TiB₂ and Al₂O₃ increases with an increase in weight percentage. XRD pattern does not show peaks of any other possible compounds such as Al₃Ti and AlB₂. This observation suggests that the reaction was complete and the synthesized in-situ particulates were thermodynamically stable. The formation of TiB₂ and Al₂O₃ particles takes place according to the following chemical equations. The addition of Ti reacts with molten aluminum to form Al₃Ti compound [34]. H₃BO₃ reacts with molten aluminum and produces Al₂O₃, AlB₂ and water vapor. Al₃Ti and

AlB₂ respectively act as sources for Ti and B atoms. They are attracted towards each other and combine to yield TiB₂ particulates. The escape of boron atoms above a temperature of 900°C is expected. Hence, H₃BO₃ was added slightly in excess of stoichiometric ratio to suppress the retention of Al₃Ti in the composite.



3.3. Microstructure of AA6061/(TiB₂+Al₂O₃) AMCs

FESEM micrographs of AA6061/(TiB₂+Al₂O₃) AMCs are shown in Fig. 4. Fig. 4a refers to the microstructure of the cast aluminum matrix. It is characterized by typical cast dendritic structure with long arms. The dendritic spaces are covered with coarse Mg₂Si particles which form due to the alloying elements of AA6061. Such a dendritic structure is not found in the composite micrographs (Fig. 4b–d). This can be correlated to the formation of in-situ TiB₂ and Al₂O₃ particulates. The synthesizing of particulates leads to changes in the solidification pattern resulting in the disappearance of dendritic structure. The particulates are scattered across the aluminum matrix. No portion of the micrograph is left particulate free. The distribution is roughly homogenous. The in-situ particulates are not aggregated. The particulates are mostly in sub-micron and nano level. Hence, they suspend in the molten aluminum melt for a long time overcoming the effect of density gradient. The tendency to sink to the bottom of the crucible is reduced due to smaller size particulates. The in-situ reaction and the release of water vapor agitate the molten aluminum which assists to break down clusters of particulates. Hence, a proper distribution of particulates is achieved.

FESEM micrographs of AA6061/15wt.% (TiB₂+Al₂O₃) AMC at higher magnification is shown in Fig. 5. The micrographs clearly reveal a finer interface and good bonding

between the aluminum matrix and the in-situ formed TiB_2 and Al_2O_3 particulates. The clear interface and good interfacial bonding are owing to the in-situ formation of particulates within the melt. The interface plays a major role in deciding the mechanical properties of the AMCs. Pores and reaction compounds at the interface reduces the load bearing capability. Since the particulates are synthesized within aluminum melt, the atmospheric contamination to form oxides on the surface of the particles is remote. The in-situ formed particles are oxide free. The local temperature raise due to exothermic reaction enhances the wettability of the particulates [21].

EBSD maps of AA6061/ $(\text{TiB}_2+\text{Al}_2\text{O}_3)$ AMCs are shown in Fig. 6. The maps reveal the grain structure and the effect of weight percentage of reinforcement particulates. In-situ synthesizing of TiB_2 and Al_2O_3 caused a change in grain structure. Grains become finer with increased weight percentage of particulates. This is reflected in the graph shown in Fig. 7. The average grain size of the composite was measured to be 103 μm and 14 μm respectively at 0 wt.% and 15 wt.% of TiB_2 and Al_2O_3 . The phenomenon of grain refinement is furnished as follows. The formation of TiB_2 and Al_2O_3 particulates changes the solidification pattern of the composite melt. The suspension of particulates in the aluminum melt causes them to act as nucleating sites for grains. The presence of reinforcement particulates makes it harder for the free growth of α -aluminum grains. Their growth is restricted and the size of the grains is reduced in the composite. This effect is multiplied with an increase in weight percentage. The number of nucleating sites increases and the growth of α -aluminum is further restricted. Hence, the grains size decreases with increased content of particulates.

TEM micrographs of AA6061/15wt.% $(\text{TiB}_2+\text{Al}_2\text{O}_3)$ AMC are shown in Fig. 8. A nano level TiB_2 particulate is visible in Fig. 8a. Few ultra-fine Al_2O_3 particulates are spotted in Fig. 8b. The interfacial feature is confirmed in those micrographs. There is no reaction

layer around the particulate. There are no features resembling a needle shape which confirms that the particulates are stable under the applied casting conditions. Huge number of dislocations is seen in Fig. 8c and d. The cause of dislocations is the difference in coefficient of thermal expansion of aluminum matrix and the reinforcement particulates. The aluminum matrix expands and contracts at a faster rate compared to TiB_2 and Al_2O_3 due to high coefficient of thermal expansion. Therefore, dislocations are generated during solidification and cooling to accommodate the thermal strain or misfit. Strain fields containing dislocations are beneficial to boost the mechanical properties of the composite.

FESEM micrographs of extracted particles of AA6061/15wt.% ($TiB_2+Al_2O_3$) AMC are shown in Fig. 9. Hexagonal, cubic, spherical and irregular shape particles are seen. Many investigators reported hexagonal shape TiB_2 particulates by in-situ synthesizing [35–37]. Some investigators who attempted to prepare mono Al_2O_3 particulates reinforced AMCs by in-situ synthesizing reported spherical shape [27–30]. It is documented in literature that a column of in-situ particulates form during chemical reaction. Subsequent fracture of the column results in different size particulates. The alloying elements of the aluminum matrix also may favor the formation of particular shape for the particulates. Studies on the shape of in-situ synthesized ceramic particulates are limited. Most of the particulates are categorized into sub-micron and nano level. Since in-situ reaction generates fine size particulates, the mechanical properties are superior to ex-situ composites. The fine size negates the effects of particulate shape.

3.4. Mechanical properties of AA6061/($TiB_2+Al_2O_3$) AMCs

The microhardness and tensile strength of AA6061/($TiB_2+Al_2O_3$) AMCs are graphically presented in Fig. 10. The graphs show that the mechanical properties of the composite improve with an increase in TiB_2 and Al_2O_3 particulates. The microhardness was

tested to be 60.1 HV at 0 wt.% and 122 HV at 15 wt.%. The UTS was estimated to be 160 MPa at 0 wt.% and 287 MPa at 15 wt.%. The incorporation of the in-situ formed TiB₂ and Al₂O₃ particulates strengthened the composite remarkably. TiB₂ and Al₂O₃ particulates are harder compared to the aluminum matrix. They impart the hard nature to the composite according to rule of mixtures [38]. The proper interfacial bonding assists to transfer the tensile load to the particulates effectively. The homogenous distribution of the particulates invokes Orowan strengthening mechanism into operation. The strain fields around the particulates due to difference in coefficient of thermal expansion resist the motion of dislocation. Therefore, the mechanical properties improve. The effect of the above discussed factors multiplies with increased weight percentage of particulates resulting in an enhanced performance of the composites.

The fracture morphology of AA6061/(TiB₂+Al₂O₃) AMCs is shown in Fig. 11. The fracture morphology suggests that the composite experienced brittle failure at macroscopic level and ductile failure at microscopic level. The flatness of the fractured surface increases with increased weight percentage. The dimples are finer in the composite due to grain refinement. Several TiB₂ and Al₂O₃ particulates are spotted on the fracture surface indicating good interfacial bonding.

4. Conclusions

AA6061/(TiB₂+Al₂O₃) AMCs were effectively synthesized using the reaction system Al-Ti-H₃BO₃. The reaction temperature was found to be 950°C using DTA. XRD pattern confirmed the formation of TiB₂ and Al₂O₃ particulates without any other undesirable compounds. There was proper distribution of both the particulates in the composite. The interface of the particulates was reaction free and exhibited good interfacial bonding. TiB₂ and Al₂O₃ particulates refined the grain structure of the composites by acting as grain

nucleating sites and restricting the growth of α -aluminum grains. The average grain size of the composite was measured to be 103 μm and 14 μm respectively at 0 wt.% and 15 wt.%. TiB_2 and Al_2O_3 particulates were characterized with hexagonal and spherical shape. Most of the particulates were observed to be sub-micron and nano level. The large difference in thermal expansion generated strain fields in the aluminum matrix and around the particulates. The formation of TiB_2 and Al_2O_3 significantly contributed to the enhancement of mechanical properties such as hardness and tensile strength. The microhardness was tested to be 60.1 HV at 0 wt.% and 122 HV at 15 wt.%. The UTS was estimated to be 160 MPa at 0 wt.% and 287 MPa at 15 wt.% .

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Table 1 Chemical composition of AA6061 aluminum alloy

Element	Mg	Si	Fe	Mn	Cu	Cr	Zn	Ni	Ti	Aluminum
wt. %	0.95	0.54	0.22	0.13	0.17	0.09	0.08	0.02	0.01	Balance

Table 2

The amount of chemical elements added to molten aluminum.

TiB ₂ + Al ₂ O ₃ (wt. %)	0	5	10	9
Ti (g)	0	13.75	26.91	39.84
H ₃ BO ₃ (g)	0	17.76	34.75	51.44