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On the role of process parameters of aluminothermic reaction synthesis of in-situ Al-TiB_2 composites: microstructure and mechanical properties

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This is an account of a process that has led to an application for a patent of relevance to the metal cutting industry and the paper examines the scientific aspects like the influence of process parameters of aluminothermic reaction synthesis of in-situ Al-TiB_2 metal matrix composites on their microstructure and mechanical properties. The reaction between the salts potassium fluoborate (KBF_4) and Potassium hexafluorotitanite (K_2TiF_6) in the aluminium melt leads to the formation of TiB_2 particles. The process parameters of reaction time (Rh), reaction temperature (Rt) and weight percentage of precursors (W) were carefully controlled in order to regulate the volume fraction of TiB_2 formation in the aluminium melt. Detailed microstructure analysis at different processing conditions revealed that particle clustering was present in the reinforcement and that this changes the hardness and density of the resultant composites. Addition of cryolite, which is a surface-active salt, prevented agglomeration and emulsification at high temperatures and also facilitated the uniform distribution of the particles in the matrix. The prepared Al-TiB_2 composites were tested for their tensile properties, density and hardness. Both hardness and yield strength are found to increase with an increase in the percentage of reinforcement. The percentage elongation decreases due to an increase in TiB_2 ceramic particle content in the matrix. It is found that the reaction time plays a major role in TiB_2 growth and the distribution of TiB_2 particles within the matrix.

Keywords: in-situ composites, aluminothermic reaction, Al-TiB_2 composite, metal matrix composites, metal cutting.

1. Introduction

Aluminium-based metal matrix composites (MMC's) are widely used as structural materials owing to their superior mechanical properties such as high specific strength, high hardness, wear resistance etc. [1,2]. Use of MMCs in aerospace and automotive industries has been increasing in the past few decades. Conventional ex-situ methods have been successfully employed for the preparation of Al alloy-based composites which involve the addition of particles such as SiC, Al_2O_3 etc. to the aluminium melt followed by mechanical stirring or electromagnetic agitation which would distribute the reinforcement particles uniformly in the matrix melt. However, the ex-situ method of preparation of particle-reinforced MMCs have certain technological challenges, e.g., non-uniform particle distribution [1], formation of undesirable interfacial reaction products, inherent casting defects and poor bonding at the matrix/reinforcement interface [3]. To overcome these problems, in-situ preparation of composites has been considered [4]. Many researchers have adopted different fabrication techniques such as liquid metallurgy using a master alloy route, salt melt reaction, plasma deposition, self-propagating high temperature synthesis etc. for the in-situ preparation of composites. Among these, liquid metallurgy route based salt metal reaction has attracted many researchers [5-10]. The most important advantage of MMCs produced by the in-situ process is that the reinforcement particles possess high thermodynamic stability [11]. It is also known from published reports that the in-situ technique can be used to fabricate successfully composites with uniform distribution of particles that leads to a clean interface with the matrix material [11]. The formation of TiB_2 is not possible by reactions between salts alone. It needs a medium to generate the boride particles [13]. Moreover, dispersion of TiB_2 particles in Al is improved by adding Si to the matrix. Feng and Froyen [9,13] reported that a homogeneous distribution of TiB_2 was obtained when a eutectic Al-Si alloy was used. Erlin et al. [14] examined the microstructure and hardness of as cast TiB_2 reinforced Ti-6Al composites which were synthesized by ball milling high purity titanium powder, aluminum powder and boron powder for 24 hours, followed by uniaxial pressing and heating in vacuum. Basu et al. [15] fabricated successfully yttria-coated ZrO_2 powder composites with 30% TiB_2 particles by ball milling followed by hot isostatic pressing (HIP). It is also noted that the cooling rate has a considerable impact on the morphology and size of the in-situ particles. Chen et al. [8] studied the solidification process and interfacial structure of in-situ Al-4.5Cu/TiB_2 composite. The reinforcement phase was prepared by adding TiO_2, H_3BO_3 and Na_3AlF_6 powders into Al-4.5Cu alloy melt and the resulting composite had a clean and well bonded interface between TiB_2 particles and the matrix.

The effect of alloying elements on the reactive synthesis of in-situ Al/TiB_2 composites was studied by Brinkman et

al. [16]. They reported that the alloying elements in general do not exert a significant effect on the reaction mechanism and phase formation sequence in the Al-Ti-B system. However, the addition of Cu leads to an increase in the reaction rate during the formation of intermediate reaction products leading to a more complete conversion of the intermediate Al_3Ti in the final composite products. Bunin et al. [17] prepared a conductive TiB_2–AlN ceramic by self-propagating high-temperature synthesis in a filtration combustion chamber in nitrogen atmosphere. Microstructure, electrical conductivity, and mechanical strength were studied as a function of TiB_2 content. The resistivity of the materials was found to change sharply at 19vol % of TiB_2 content in the TiB_2-AlN system. This was attributed to the formation of fractal surfaces.

Though a significant amount of work is published on the in-situ processing of TiB_2 reinforced MMCs, studies pertaining to the influence of process parameters and their effect on the microstructure of in-situ composites are limited and these effects have not been discussed extensively. There is a need to understand the contribution of individual process parameters on the resulting characteristics such as microstructure, Young's modulus and hardness of these composites, often used in metal cutting applications. The present paper reports the method of preparing an Al-TiB_2 composite with enhanced mechanical properties and free of agglomeration and emulsification at elevated temperatures. Some applied aspects of this work have formed the basis of a recent patent application [18].

2. Experimental procedure

Aluminum reinforced with in-situ TiB_2 was produced through salt melt reaction or flux assisted synthesis [19]. Calculated amounts of KBF_4 and K_2TiF_6 powders are introduced into the aluminum melt and then subjected to stirring to facilitate the reaction in order to generate the required volume fraction, i.e., 2.5, 5, 7.5 vol. % of TiB_2 particles. The number of experiments were designed as per L_9 orthogonal array by considering three melt temperatures (700°C, 750°C and 800°C), reaction time (30, 45 and 60 min) and volume fraction of TiB_2 (2.5, 5 and 7.5%). The volume fraction of TiB_2 that is formed is controlled by adding weighted amount of KBF_4 and K_2TiF_6 according to stoichiometry. Calculated amount of potassium fluoborate (KBF_4) was added first and stirred. Since Potassium hexafluorotitanite (K_2TiF_6) reacts faster with aluminum it was added later into the melt followed by the addition of sodium cryolite, which prevents particles agglomeration and helps to achieve uniform distribution of the TiB_2 particles within the aluminium matrix. The interaction of two halide salts with the aluminium melt yields TiB_2 particles through the following reactions. First KBF_4 and K_2TiF_6 in the Al melt decompose according to [19]

$$KBF_{4(l)} \rightarrow KF_{(l)} + BF_{3(g)} \quad \text{----------} \quad [1]$$

$$K_2TiF_{6(l)} \rightarrow 2KF_{(l)} + TiF_{4(g)} \quad \text{----------} \quad [2]$$

The formed TiF_4 and BF_3 gases diffuse into the liquid Al and the following aluminothermic reaction results.

$$BF_{3(g)} + [Al] \rightarrow [B]_{Al} + AlF_{3(l)} \quad \text{----------} [3]$$

$$TiF_{4(g)} + [Al] \rightarrow [Ti]_{Al} + AlF_{3(l)} \quad \text{----------} [4]$$

The Ti and B act as solutes in the Al melt and when the concentration of Ti and B reach saturation in the Al melt, they form intermediate compounds according to the following reactions.

$$[Ti]_{Al} + 3[Al] \rightarrow Al_3Ti \quad \text{----------} \quad [5]$$

$$2[B]_{Al} + [Al] \rightarrow AlB_2 \quad \text{----------} \quad [6]$$

$$[Ti]_{Al} + 2[B]_{Al} \rightarrow TiB_2 \quad \text{----------} \quad [7]$$

Since aluminum produces a significant amount of dross and oxide during melting, degassing was employed by bubbling argon through the melt to absorb hydrogen and other impurities. After allowing sufficient time for the aluminothermic reaction to take place, the melt was allowed to solidify in a die, which was preheated to 400 °C. Another set of experiments was tried by using scrap Al as the matrix material. However, for the present discussion, the mechanical properties are reported for the composites prepared using primary aluminum. Besides, from the XRD results it was found that the particles are free from contamination, regardless of whether primary Al or scrap Al was used. So the same properties are expected even when Al scrap is used. Cylindrical tensile specimens (Gauge diameter 0.160 and length 0.640 in.) were prepared from the cast specimens based on ASTM B557-M standards. To characterize the in-situ TiB_2 particles the composites were dissolved in NaOH solution and the extracted particles were analysed by SEM EDS and X-ray diffraction using Cu-Kα radiation.

3. Results and discussion

Microstructural characterisation

(a) TiB_2 particles

Mechanical properties of composites generally depend on particle size, shape etc. Hence, it is necessary to understand the characteristics of in-situ TiB_2 powders.

Figure 1a shows the SEM micrograph of extracted in-situ TiB_2 particles produced at 750 °C in 30 minutes with the

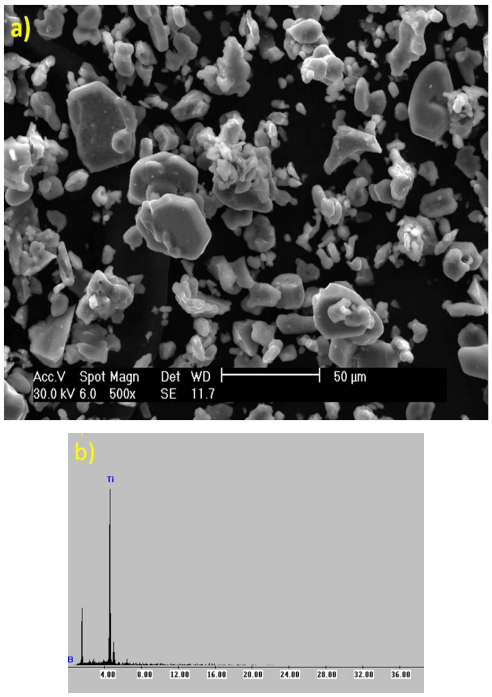

Fig. 1. (a) SEM micrograph of extracted TiB2 particles, (b) EDS Spectrum

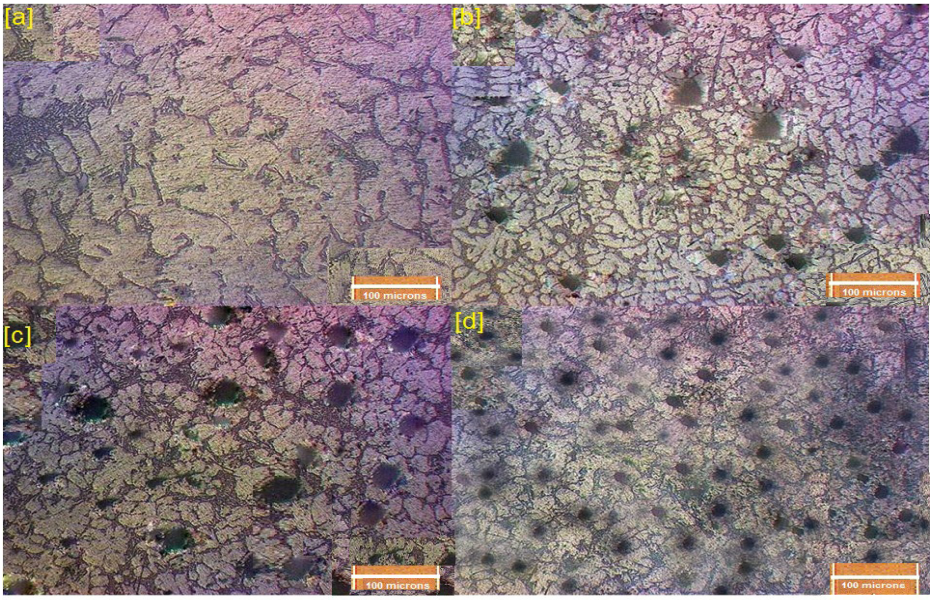

Fig. 2. Optical micrographs of Al-TiB_2 composites produced at different processing conditions: (a) Primary Al alloy; ambient condition, (b) 750°C for 30 min, (c) 750°C for 45 min, (d) 750°C for 60 min.

addition of calculated amounts of K_2TiF_6 and KBF_4 to yield 2.5, 5, 7.5% of TiB_2 in the aluminium melt. The EDS spectrum shown in fig.1b confirms that the particles are indeed TiB_2. As the reaction time increases, particles are found to be much finer due to formation of more nucleis.

(b) Al-TiB_2 composite

Figure 2a shows the microstructure of the matrix material, which is an LM25 (cast) alloy. The microstructure shows grains of Al-Si eutectic with particles of Mg_2Si, which are present as fine particles and segregated into the grain boundaries. Figure 2b shows the microstructure of Al-2.5% TiB_2 produced at 750°C following 30 minutes reaction of the halide salts. It is clear from the microstructure that the particles are distributed well in the matrix. The reaction of the two salts, which finally produces TiB_2, has modified the solidification process. The nucleation and growth of matrix material is controlled by the kinetics of the TiB_2 reaction. The dendrite size of aluminum matrix is finer which is due to the kinetics associated with the formation of TiB_2. The Si morphology seems to be free from spike or script-like details. TiB_2 is in the form of spherical particles of uniform distribution with almost equal distance between them. Higher particle nucleation was observed in composites processed at 750°C for 60 min: increase in the percentage of TiB_2 particles produces finer and spherule particles. TiB_2 particles not only act as a grain refiner, but also change the eutectic Si morphology.

The average grain size of the specimens processed at 750˚C for 30 min was 35μm. Increase in the reaction time to 45 and 60 min leads to 5 and 7.5% TiB_2 formation and average grain sizes of 30 (standard deviation: +/- 15.5μm) and 20 μm (+/- 6.3 μm) respectively were obtained.

XRD Analysis

A typical XRD powder pattern of the in-situ TiB_2 particles synthesized at 750 °C using primary aluminum is shown in fig.3a. Figure 3b shows the XRD pattern of the in-situ TiB_2 particles obtained using aluminum scrap. The results are satisfactory, since the TiB_2 particles are found to be free of contamination, though it is obtained from scrap Al. There is no evidence for other brittle intermetallic phases such as Al_3Ti in either sample. This is achieved by a careful control of the process parameters such as reaction temperature, time and regular stirring of the melt.

Hardness of Al-TiB_2 composite

The hardness were recorded on the cast specimen from the bottom of the casting to the top with a distance between the readings of 1 cm to know the uniformity of hardness. The variation in hardness can be directly related with the amount of TiB_2 formed and the distribution of TiB_2 in the Al matrix corresponding to each condition and location. The effects of reaction temperature, reaction time and the particle volume fraction are well related with the hardness values. It is found that with an increase in the amount of TiB_2 the composite hardness increases considerably. Figure 4 shows the variation in hardness of Al-TiB_2 composite for all the experimental conditions. TiB_2 particles formed during an in-situ reaction in metal matrixes promote a strong particle-matrix bonding. Probably this can reduce debonding of particles in MMCs. For higher reinforcement of 7.5% and 60 min of holding time the grains of TiB_2 are equiaxed and much finer, whereas in the case of 5% TiB_2 the hardness is considerably lower due to somewhat coarser, less numerous and globular grains.

In material containing 2.5% of TiB_2 the particle distribution is found to be uniform for 750 °C and 45 min reaction time. At the same conditions the distribution of particles is found to be homogeneous for 5% TiB_2 reinforcement also. But in the case of 7.5% of TiB_2 reinforcement, the distribution is found to be uniform only at a reaction temperature of 750°C and a higher reaction time of 60 min. The average hardness recorded for 2.5% TiB_2 content is 57 BHN and increased for 5 and 7.5% to 67 and 81BHN, respectively.

The variation in hardness within a specimen reveals the non-uniformity in particles distribution. The regions, which had more number of particles, display higher hardness than the rest of the material. The hardness variation could also reflect a change in the local matrix grain size. Therefore, the measured values could be a reflection of the combined effects of these variables.

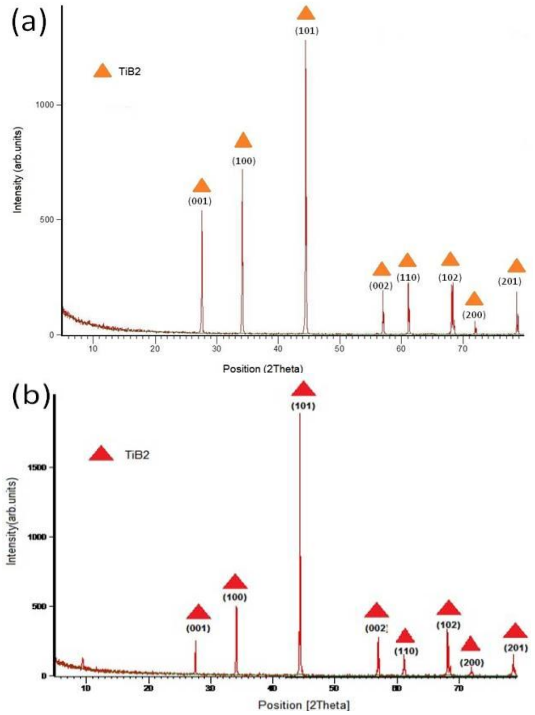

Fig. 3. XRD pattern of in-situ TiB_2 particles (a) produced using Primary Al alloy, (b) made from Al alloy scrap.

Tensile Strength

TiB_2 particles, when present in molten aluminium, readily agglomerate. A higher processing temperature released greater amounts of titanium into the matrix alloy for TiB_2 formation and this correlated well with the variation in the tensile properties of the as-cast Al alloy. Table 1 shows the tensile properties of the composite as a function of percentage of TiB_2. The yield strength calculated using the Rule of Mixtures (ROM) for isostrain condition also shows close agreement with the experimental values. Both the ultimate tensile strength and the yield stress increase with increasing TiB_2 content. Understandably, the elongation also decreases as a result of TiB_2 increasing being present in the matrix. The Young's moduli of the composites were calculated using the rule of mixtures for iso-strain and iso-stress conditions. The values predicted for iso-strain condition are closer to the experimental ones.

Fractography

Figure 5 suggests ductile fracture comprises fine shallow dimples containing small inclusions. There are considerable differences in fracture surfaces with amounts of TiB_2. This is not seen in the case of ex-situ materials. The important features of the fractures of the composites are flat facets with irregular profile. Besides, regions of cleavage fracture

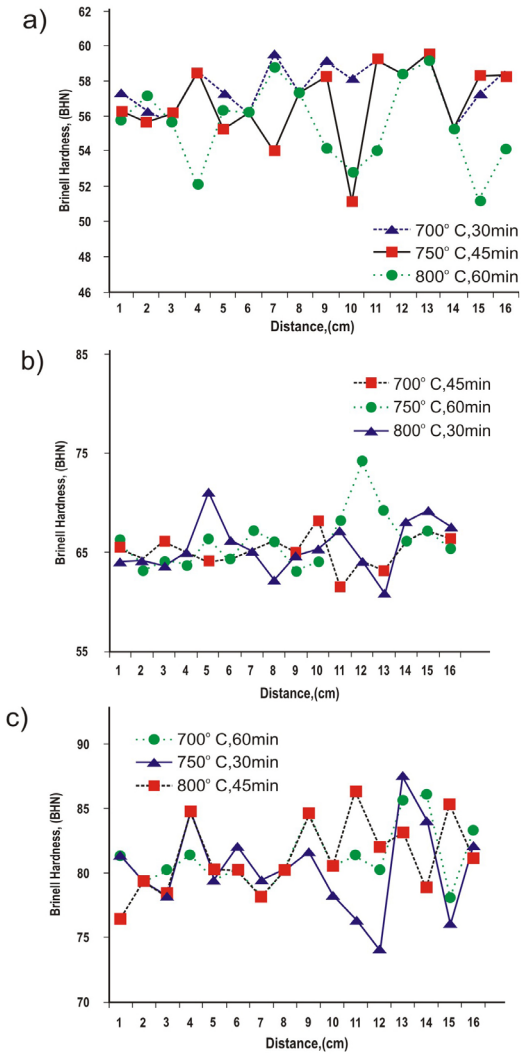

Fig. 4. Variation of hardness measured along the height from the bottom of the cast specimen: (a) Al-2.5%TiB_2, (b) Al-5%TiB_2, (c) Al-7.5%TiB_2.

are hardly seen. Thus, matrix yielding with rough fracture surfaces is dominant.

4. Conclusions

In-situ Al-TiB_2 composites are synthesized successfully through the aluminothermic reaction. It is found that the grain size and the TiB_2 content vary with reaction time and temperature. Even at a reaction temperature of 800 °C the hardness is high, which implies that there is no boron loss in the form of BF_3 and the TiB_2 content increases with reaction time right up to the highest temperature employed in the present tests.

Table 1

Tensile properties of as-cast in-situ Al-TiB_2 composites

Material	Al	Al-2.5%TiB_2	Al-5%TiB_2	Al-7.5%TiB_2
UTS (MPa)	115	164(42)*	182(58)*	202(76)*
0.2% YS (MPa)	82	98(19)*	136(65)*	164(100)*
YS (iso strain)**	-	110	141	171
E (GPa)	71	80.5	86	94
E (iso-strain)**	-	78.39	85.79	93.175
E (iso-stress)**	-	72.5	73.9	75.57
% Elongation	11.2	8.3	7.6	5.2

*( ) percentage increase in property with respect to matrix alloy,
** calculated using Rule of Mixtures.

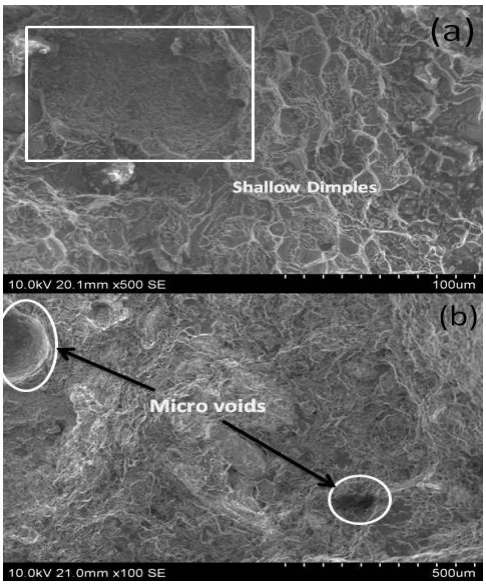

Fig. 5. SEM images of tensile fracture surface show (a) shallow dimples, (b) micro-voids in a composite obtained by processing at 700 °C for a reaction time of 30 min.

– It is evident from the microstructure and properties that the ability to achieve uniform particle distribution in the matrix is influenced by the reaction time and temperature.

– There is considerable improvement in the ultimate tensile strength and the yield stress with increasing amount of reinforcements, which mainly depends on the reaction time and temperature. The hardness of the in-situ composites specimen shows improvement due to the presence of finer and equiaxed particles with increasing temperature and reaction time of processing.

– The XRD results for the TiB_2 particles extracted from scrap Al is found to be satisfactory and similar to those of particles obtained using primary Al. So similar properties are expected for composites developed using the former at a significantly reduced cost.

– From the fracture surfaces of tensile tested specimens it is evident that matrix yielding, moderated by the presence of TiB_2 particles, is the dominant mechanism for initiating failure. The results also show that the in-situ particles have good bonding with the matrix (no evidence for delamination at the interfaces).

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