

Processing and Application of In-Situ TiB_2 Reinforced Aluminium Matrix Composites

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Abstract: Aluminium matrix composites with TiB_2 reinforcements have several applications in aerospace and automobile industries due to their high specific strength, stiffness, hardness and wear resistance. TiB_2 reinforcements incorporated in the Al matrix via the in situ reaction has the advantage of delivering clean interface between the matrix and the particle, thermodynamic stability and finer distribution of the second phase particles. Fabrication methods of Al- TiB_2 in situ composites include both liquid state and solid state processing. In this paper we provide the highlights of the development, properties and applications of in-situ Al- TiB_2 metal matrix composites in the industries.

Keywords: Aluminium; Metal Matrix Composites; TiB_2 ; Mechanical Properties; In-situ.

1. Introduction

Composite materials are increasingly replacing metallic materials in various applications because of the desired combination of properties offered by these materials which are otherwise unavailable from a single metal. The composites are increasingly being used in automobile, aerospace, sports goods, electrical applications and constructions amongst others. Metal matrix composites (MMC) are materials that have metallic

matrix and a metal or ceramic or organic material as the reinforcement. They have several characteristics like high strength and specific modulus, thermal stability, better wear resistance and lower coefficient of thermal expansion, making them the potential candidate materials for use in the manufacturing aerospace and automotive components. The properties of the metallic matrix (ductility and toughness) are combined with the properties of the reinforcement (high strength and high modulus in the case of ceramic reinforcements) to obtain a material with the desired characteristics. Various metals that are being used as matrix materials include Aluminium, Titanium, Magnesium and some other light metals. Aluminium remains the most utilized matrix material in the development¹ of MMCs. Aluminium based metal matrix composites (AMMCs) have been the dominant engineering materials because they meet most of the stringent specifications in applications where light-weight, high stiffness and other favourable properties are desirable.

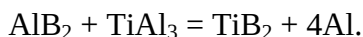
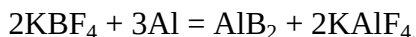
Ceramic particulate reinforcements (CPRs) like TiB_2 , Al_2O_3 , B_4C and SiC are widely used as a second phase in AMMC because they improve the specific strength and modulus of the composite. Among the CPRs, TiB_2 has attracted special attention because it exhibits high melting point, high elastic modulus, high hardness and do not form brittle phases at the reinforcement-matrix interfaces. TiB_2 can be added to the Al matrix externally (ex-situ composites) or it can be generated within the matrix itself by initiating chemical reactions during processing (in-situ composites).

Fabrication techniques of Al- TiB_2 MMCs can be broadly classified into two categories: (1) liquid state processing (casting) and (2) solid state processing (powder metallurgy). In case of powder processing technique like mechanical alloying, uniform particle distribution in the matrix can be achieved. Also the processing temperature is low and there is a greater control on the final microstructure. The liquid processing route, from the practical perspective is favoured for its simplicity and lower cost in manufacturing bulk components with complex geometry.

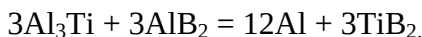
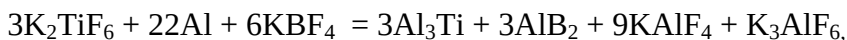
In-situ process of manufacturing has the advantage of delivering clean interface between the matrix and the particle, thermodynamic stability and finer distribution of second phase particles. This paper attempts to review the processing techniques, properties and improvements in terms of both processing and properties of Al- TiB_2 MMCs for the last 10 years.

2. Liquid State Processing

London and Scandinavian Metallurgical Co. Ltd. in 1993 patented² a liquid state processing technique of in situ TiB₂ reinforcement in Al alloys using K₂TiF₆ and KBF₄ salt reaction in molten Al. Till date it is one of the most widely used techniques for processing Al-TiB₂ MMCs³⁻⁹. According to some of the researchers, the reactions between K₂TiF₆ and KBF₄ in molten Al proceed by the following stages¹⁰



However, Christy et al.¹¹ proposed that the reaction between K₂TiF₆ and KBF₄ in molten Al occurred in the following manner :



These authors¹¹ also examined the microstructure and mechanical properties of the composite developed by the above salt-metal in situ reaction and compared the same with base metal ie. Al 6061 alloy. In addition to TiB₂, the authors also reported the formation of TiAl₃, TiB and TiSi₂. Uniformly small and irregularly shaped particles were found to be present along with larger TiB₂. An Agglomeration of TiB₂ particles has been observed by the investigators¹¹. Nevertheless, the manufactured Al-TiB₂ composite exhibited improvement in hardness, tensile strength and Young's modulus when compared to the base alloy. However, the developed composite unveiled lower ductility than that of the aluminium 6061 alloy.

2.1 Role of mechanical stirring: Chen et al.¹² fabricated TiB₂ reinforced in situ Al based MMCs using the conventional halide salt route. The authors used a device for stirring at the salts/aluminum interface. Schematic diagram of the experimental set-up has been illustrated in Fig. 1 below.

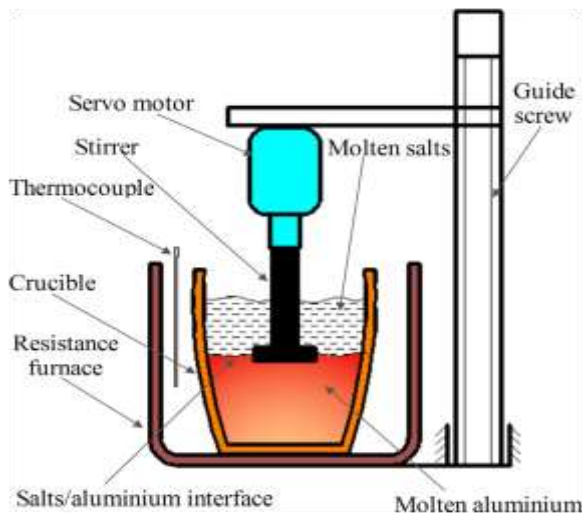


Figure 1. Schematic of the experimental set-up for fabricating Al-TiB₂ MMCs

The effects of processing parameters, i.e. stirring speed, duration, and time on the microstructure and mechanical properties of the final composite products were examined by the authors. The authors also used Synchrotron Radiation X-ray Computed Tomography (SR-CT) to study the particle distribution of Al-TiB₂ composites from three dimensional images. It has been observed that with increase in stirring intensities, the distribution of TiB₂ in Al improved. 3D structures of the composites without and with the interface stirring by SR-CT technique is shown in Fig. 2.

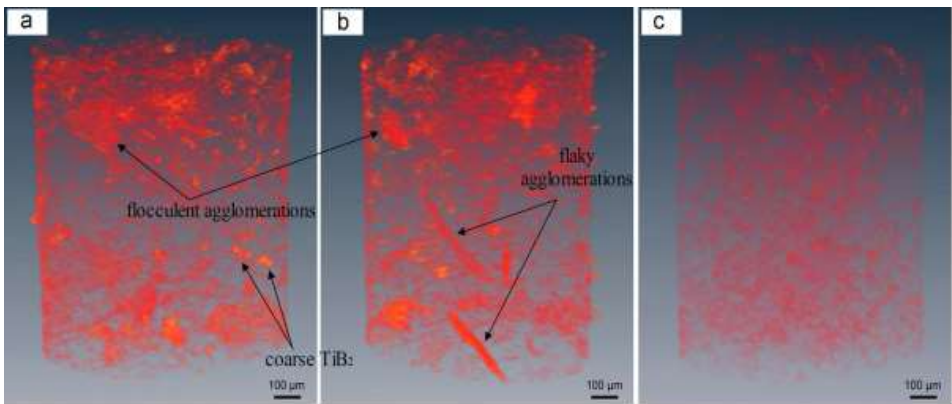


Figure 2. SR-CT images of the Al-7% TiB₂ composites: (a) and (b) without stirring; (c) with the technique developed by the author

3D images revealed that the TiB_2 particles formed by the developed technique¹² are distributed more uniformly in the aluminum matrix compared to the flocculent and flaky-shape particle agglomerates which developed without optimized conditions of stirring.

The authors attributed the uniform distribution of the TiB_2 particles to the mechanical stirring, which improves TiB_2 particle distribution by favouring diffusion at the salts/aluminum interface. The velocity gradient, which exists in the flowing melt causes engulfment and increased rate of particle diffusion. Also improved distribution of TiB_2 particles resulted in improved tensile properties. The authors¹² attributed this improvement in mechanical properties to various strengthening mechanisms like grain refinement strengthening, Orowan strengthening and dislocation strengthening etc. Yadav et al.¹³ investigated the effect of Friction Stir Processing (FSP) on the particle distribution, microstructure and mechanical properties of as cast Al- TiB_2 in situ MMC processed by halide salt route. Scanning electron microscope (SEM) backscattered electron (BSE) image of the as-cast composite revealed that the in-situ formed TiB_2 particles are agglomerated along the grain boundaries. But the distribution of the particles improved after FSP was carried out. This uniform distribution can be observed in Fig. 3 which depicts the SEM image of the interface between as cast and the friction stir-processed (FSPed) region¹³. A clear demarcation was observed to be present between the as-cast region and the FSPed zone. After the second pass of FSP, casting defects were also removed.

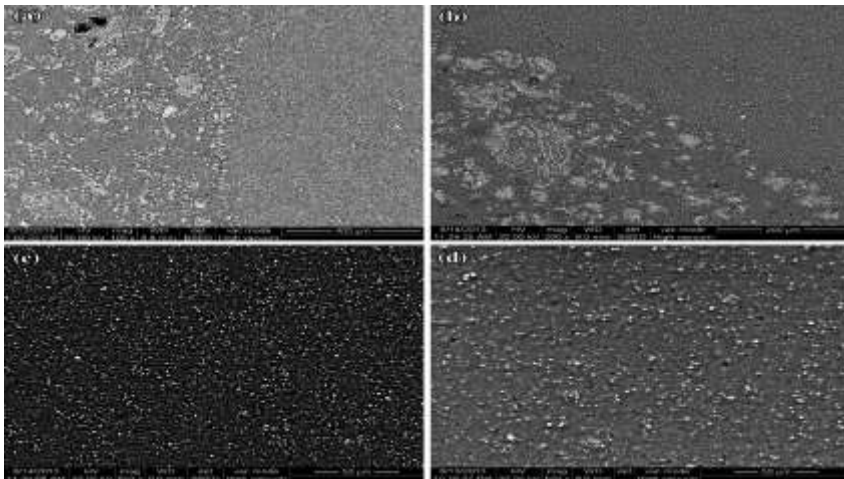


Figure 3. SEM images of the interface between as cast and FSPed region on (a) surface, (b) cross section, (c) and (d) FSPed region

Gao et al.¹⁴ synthesized in-situ 5vol% TiB₂ particulate reinforced Al–4.5Cu alloy matrix composites by the salt-metal reactions assisted by improved mechanical stirring. The mechanical stirring reduced the large agglomerations of TiB₂ particles and resulted in grain refinement. Distribution of TiB₂ particles also became more uniform with increasing stirring speed. All of these contributed to the improvement in yield stress and UTS of the final composites to a great extent.

Gao et al.¹⁵ studied the effect of ultrasonic vibration treatment (UVT) on the particle distribution of in-situ 5 vol% TiB₂ reinforced Al–4.5Cu alloy matrix composites. It was observed that the distribution of TiB₂ particles improved after UVT. During solidification, the TiB₂ particles were pushed by advancing solidification front leading to the distribution of the particulates along the grain boundaries. Formation of large agglomerates were eliminated by UVT and the grains of the composites were also effectively refined. With the increase in UVT durations, further reduction in agglomerations took place. The authors explained that cavitation bubbles generated by ultrasonic vibrations and whirlpools caused by acoustic streaming created shock waves which broke the large agglomerations leading to the formation of small agglomerations and finally dispersed particles. Grain refinement took place due to the hindrance in grain growth by dispersed particles. Also cavitation bubbles promoted nucleation. Similar phenomena were observed by Nampoothiri et al.¹⁶ where the formation of Al–4.4Cu/2TiB₂ nanocomposite took place from microcomposite by ultrasonic treatment.

2.2 Effect of heat treatment: Wang et al.³ investigated the mechanical properties of in-situ TiB₂/A356 composites developed by conventional halide salt route in the cast and T6 condition. The authors noted that the experimental values of Young's modulus for TiB₂/A356 composites and A356 alloys in both as cast and T6 states can be well fitted by Tsai-Halpin equation. The authors discussed about various strengthening mechanisms e.g. mismatch of thermal expansion coefficient, Orowan strengthening, load-bearing effect of the reinforcement and particulate assisted precipitation strengthening responsible for improving the strength properties of the composites. Similar improvement of mechanical properties have been observed by Ramesh et al.¹⁷. These authors¹⁷ synthesized in situ TiB₂ reinforced Al 6063 composites by melting Al–10%Ti and Al–3%B master alloys with Al 6063 alloy using the liquid metallurgy route. The authors proposed that the formation of TiB₂ took place in five steps, including migration of B atoms towards Al₃Ti particles

followed by formation of TiB_2 particles, diffusion of B atoms, fragmentation and dissolution of Al_3Ti particles and formation of ring like TiB_2 .

Microstructural stability of the in-situ Al- TiB_2 composite during solution treatment at T4 state was investigated by Geng et al.¹⁸. The authors fabricated the composite by the conventional halide salt route and the as-cast ingots were first extruded followed by T4 heat treatment. High temperature solution treatment (ST) was carried out, followed by natural aging at room temperature. Hardness of the composite was found to be decreasing with increasing ST time due to the coarsening of microstructure and recrystallization. EBSD maps and grain size (GS) distributions from the materials exhibited fine grain size along with more uniform distribution of the second phase in the composite compared to the alloy.

2.3 Effect of forming processes: Mathew et al.¹⁹ examined the effect of semi-solid forging on the microstructure and mechanical properties of Al-4.5Cu alloy and Al-4.5Cu-5 TiB_2 in-situ composite. The composite, prepared by flux assisted synthesis route and subsequently forged to 30% and 50% reduction in size in the semisolid state with 0.3 volume fraction of liquid. It was observed that the semisolid forging lead to the breaking of agglomerated particles and uniform distribution of the second phase particles throughout the matrix. The grains were observed to be elongated in the normal direction to forging. The as cast composite exhibited mostly high angle boundaries, while higher amount of low angle boundaries was displayed by semisolid forged composite. During hot deformation, migration of grain boundaries occurs which instigated the recrystallization process. Some of the boundaries are of mixed character and the mixed nature of the boundaries is due to the continuous type recrystallization. This dynamic recrystallization in the forged composite resulted in the formation of finer grains in the composite. Nanoindentation tests of the alloy and the composites in the as cast and forged state revealed that both the hardness and elastic moduli of the forged materials are of higher value and this has been attributed to the cluster size reduction, better distribution of TiB_2 particles and dynamic recrystallization caused by forging operation.

Dan et al.³ studied the microstructure evolution and particle behaviour of Al based TiB_2 nanocomposites cold rolled at various amounts of strain. 5 wt% in situ Al- TiB_2 composites were synthesized and cold rolled to obtain true strain ϵ of 0.9, 1.4, 2.3 and 3.0. SEM images of the composite at strain 0.9 showed the presence of TiB_2 particle clusters and fine TiB_2 particles.

Electron backscatter diffraction (EBSD) maps of the composites at different strain states are shown in Fig. 4. It was observed that the large grains got elongated along the rolling direction and compressed along the normal direction. Deformation bands were observed. Formation of fine grains was observed around the TiB_2 particle clusters. The authors explained that during the deformation process, rotation of Al matrix occurred, but the region within particle clusters remained undeformed which finally led to orientation differences. Generation of a large number of high angle grain boundaries around the TiB_2 particle clusters was observed from the distribution of these grain boundaries in EBSD maps. The rate of generation was inhibited by dispersed TiB_2 particles. The authors also studied the cold rolling texture evolution in Al- TiB_2 composites by neutron diffraction and EBSD analysis⁴. Neutron diffraction was used to analyse texture development in the sample as a function of strain. Copper, S, Brass and Goss orientations were observed at various strains.

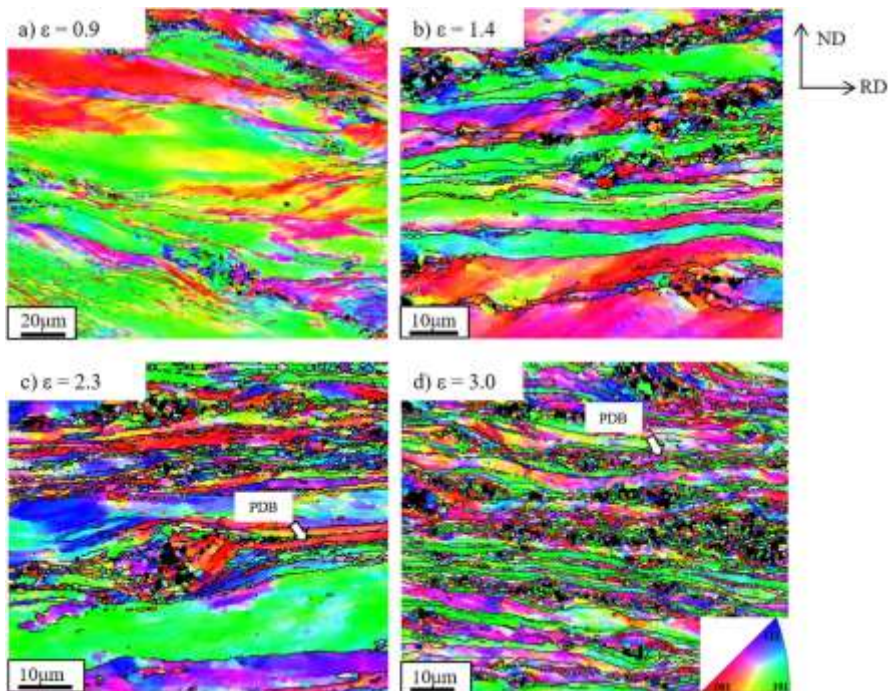


Figure 4. EBSD maps of the composite at different strain states (a) $\epsilon = 0.9$, (b) $\epsilon = 1.4$, (c) $\epsilon = 2.3$, (d) $\epsilon = 3.0$.

Atturan et al.²⁰ studied the deformation behaviour of in-situ Al- TiB_2 composite foams. The authors processed the composite through halide salt route followed by blowing with TiH_2 . Two composites with 5 wt% and 10 wt% TiB_2 were prepared. The relative density of the foams was calculated. Compression test and impact test were carried out after electrical discharge machining of the samples. Stress-strain diagrams of the composite foams exhibited three distinct regions which were due to the elastic deflection of cell walls, onset of cell damage and collapse of cells respectively. It was observed that the plateau stress values of the composite foams were independent of the wt% of TiB_2 .

Wang et al.⁵ studied ductility and fracture behaviours at a high temperature for a particle reinforced in-situ Al- TiB_2 composites. Al-6 wt% TiB_2 in-situ composites were used for the investigation. The specimen was extruded and subjected to stress-relieving annealing. The samples then underwent tensile test at around 350°C-450°C. The composites exhibited good ductility at higher temperatures. However, the strength of the composites exhibited decreasing trend with the increase in temperature and decrease in the strain rate. SEM images of the fracture surfaces of the composite test specimens were observed in order to understand the fracture behaviour. All the samples exhibited equiaxial dimples and cavities characteristic to the dimple fracture.

Su et al.⁸ studied and compared the mechanical properties of 2024-T4 alloy with those of in-situ TiB_2 particle reinforced 2024-T4 alloy matrix composite. They combined conventional test methods like metallography and nanoindentation tests with finite element (FE) analysis. The in-situ composite was synthesized by the conventional halide salt route. The as cast ingot after homogenization was subjected to hot extrusion process and finally T4 heat treatment. Presence of TiB_2 particle segregation zones in the Al matrix was revealed in the SEM images. Presence of dislocations was observed in TEM images around the dispersed particles which finally gave rise to Orowan strengthening. Dislocations were generated during the hot extrusion process and also due to the mismatch in coefficients of thermal expansion between the dispersed TiB_2 particles and the matrix. The Young's modulus, 0.2% yield strength and ultimate tensile strength of 2024-T4 alloy were found to be less than those of the in-situ TiB_2 /2024-T4 composite because of the various strengthening mechanisms in the composite material. However, the ductility of the composite was less than that of the 2024-T4 alloy. Nanoindentation tests were conducted on the composite sample and indentation load-depth curves were recorded.

Indentation modulus and hardness were obtained by Oliver-Pharr (OP) method.

There is a lack of availability of experimental load-depth curves for the 2024-T4 alloy under 20 mN. Hence, finite element (FE) simulation of the nanoindentation test results for the alloy was carried out by the authors. It was observed that the indentation modulus of the matrix Al alloy obtained from tensile test was close to that obtained by FE simulation. The Young's modulus of the composite calculated from Tsai-Halpin equation was found to be in close agreement with that of the composite determined by the uniaxial tension test. The authors attributed the increase in this elastic modulus value to the high stiffness of the TiB_2 particles in the segregation zones. Indentation hardness of the Al matrix was found to be higher than that of 2024-T4 alloy due to the microstructural strengthening of dispersed nanoscale TiB_2 particles in the Al matrix. The indentation moduli and hardnesses of TiB_2 particles segregation zones showed different values due to the inhomogeneity of the segregation zones.

3. Liquid-Solid Techniques

TiB_2 microcrystals with different morphologies was fabricated by Li et al.²¹. Al-3 TiB_2 composites were prepared by aluminium melt reaction method and growth mechanisms were discussed. The investigated composites were processed under different conditions by reacting pure aluminium with Al-3B master alloy and Ti sponge at two different temperatures (850°C and 1200°C). Field emission scanning electron microscope (FESEM) images of the TiB_2 microcrystals of the samples revealed that most of the TiB_2 microcrystals exhibited hexagonal plate-like morphology. Some of the TiB_2 microcrystals existed in the form of agglomeration. Also hierarchical tower-like and dendritic morphologies of TiB_2 microcrystals were observed in some samples. The hierarchical TiB_2 microcrystals were composed of multiple thin platelets the displacements of which formed layered steps along a certain direction. Typical faceted growth mode was exhibited by TiB_2 microcrystals due to their high entropy of fusion and large Jackson alpha factor (as suggested by the authors). The authors also indicated that the growth of the microcrystals was controlled by two-dimensional nucleation and this was vetted by the presence of growth steps on the {0001} facets of the TiB_2 microcrystals. Equilibrium crystal morphology of TiB_2 was predicted to be hexagonal platelet. However, at higher temperature, hierarchical tower-like and dendritic morphologies were observed due to the accelerated growth rate along a

particular direction caused by the higher atomic concentration, reaction rate and the atomic diffusion rate at that temperature. This growth was a two-step process: In step 1, intermittent two-dimensional nucleation took place, followed by continuous lateral spreading of layers in step 2.

Zhang et al.²² studied the microstructure and mechanical properties of TiB_2 /6063Al matrix composites. The composites were prepared by high energy ball-milling of Al, TiO_2 and B_2O_3 powders. SEM images confirmed the presence of TiB_2 particle clusters in the matrix. The authors explained that the solidification process of the alloys and density difference between the matrix and second phase particles exert a dominant influence on the nature of distribution of the TiB_2 particles. SEM images and EDS patterns of the composites processed with and without high energy ball milling were studied by the authors. It was observed that during milling, the in-situ reaction was completed, leading to the formation of TiB_2 particles whereas the intermediate phase Al_3Ti was formed without the assistance of milling. It was suggested that during high energy milling, the particles repeatedly collided and broke resulting in the formation of lattice distortion and defects. The activation energy, decreased during the ball milling because of the formation of these defects. TiB_2 particles formed because of the increase in numerous reaction sites for the in situ process as there was an increase in specific surface area and contact area between composite powder and liquid aluminum. The authors also studied the tensile properties and tensile fracture surfaces of both the as cast TiB_2 /Al matrix composites and composites formed with the assistance of high energy ball milling. Tensile strength and yield strength were found to be more and percentage elongation is less in the samples formed with high energy ball milling. Improvement in tensile strength and yield strength has been attributed to the dislocations formed as a consequence of CTE mismatch strengthening between the matrix and TiB_2 particles. Orowan strengthening and grain refinement also contributed to the improvement of mechanical properties. SEM images of the tensile fracture surface of the samples with and without ball milling revealed that the fracture surface in the first case was of a mixed character with quasi-cleavage fracture and some small part of dimple fractures. In the later case, more numbers of dimples were observed to decrease in the brittle plane areas.

4. Solid State Processing

Sadeghian et al.⁶ processed Al- TiB_2 nanocomposites by two-step mechanical alloying. Starting materials were Al, Ti and B powders. At first, milling of Al powder (10 wt%) was carried out with a mixture of 62 wt%

Ti-28 wt% B for 20 h. In order to achieve Al-20 wt% TiB_2 , the mixture was again milled for 20 h with additional aluminum powder. X ray diffraction (XRD) analysis of the resulting mixture confirmed the formation of TiB_2 alongwith Al after the total 40 hours duration of ball milling. Uniform distribution of TiB_2 particles in the Al matrix were exhibited by the SEM images of the composite. Scanning transmission electron microscope (STEM) analysis confirmed that most of the TiB_2 particles were in the nanometer size range. TEM images of the sample are shown in Fig. 5. Nanocrystalline characteristics of the microstructure was confirmed by the dark field image as well as selected area diffraction pattern (SADP) which showed a continuous ring. The size of the grains as obtained from the dark field image was in the range of 2-110 nm. High resolution transmission electron microscope (HRTEM) observation further established the nano scale size range of TiB_2 particles. Differential Scanning Calorimetry (DSC) of the sample was carried out and no exothermic peak was obtained up to 550°C. XRD patterns taken after DSC revealed no undesirable phases like Al_3Ti . Also the resulting nanocomposite exhibited good thermal stability even after annealing in DSC.

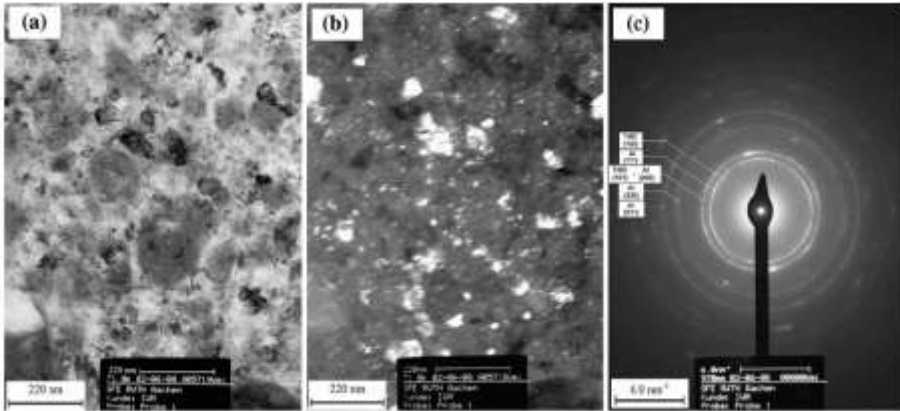


Figure 5. TEM images of the composite (a) bright field image (b) dark field image (c) SADP pattern

The authors also studied the microstructure and mechanical properties of the Al- TiB_2 nanocomposites developed by two-step mechanical alloying process⁷. Al- TiB_2 powders were subjected to spark plasma sintering (SPS) and after that the sintered samples were hot-extruded. Energy Filtered Transmission Electron Microscopy (EFTEM) image of the extruded sample

confirmed that the particle size of TiB₂ was smaller than 100 nm. Hardness of the sintered composite sample was found to be lesser than that of the as milled powder. The authors attributed this to the elimination of the effects of cold work on high temperature.

5. Conclusions

Processing and properties of Al-TiB₂ in-situ Metal Matrix Composites were discussed in detail. Most of the investigations carried out by researchers involved production of these composites by liquid state processing. A wide range of properties were studied starting from the morphology of TiB₂ particles to the mechanical properties like hardness, yield strength, tensile strength. Efforts have also been made to study the microstructure evolution during cold rolling of the composites. Texture evolution of the composites was also reported. However, the problems encountered by the researchers during processing of the Al-TiB₂ MMCs is the poor distribution of the second phase particles. Therefore, attempts have been made to study the effect of ultrasonic treatment and mechanical stirring on the distribution of second phase particles and thereby improving the properties. Halide salt route is still considered to be the most popular route adopted by the researchers in processing of the Al-TiB₂ in-situ composites, although new methods like remelting of master alloys have been introduced by some researchers. Overall, liquid state processing is the major processing technique selected by the majority of the researchers till date.

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