Synthesis, Characterisation and Mechanical Behaviour of In-situ Al7SiMg/TiB₂ Composites Prepared by Salt-Metal Reaction

Niranjan Oommen¹, Sanjay Ajayan¹, Chellam Sundaraman¹ and S Sasikumar¹
¹Department of Mechanical Engineering, SRM IST, Kattankulathur, Chennai, TN, India
E-mail: sasikumar.scholar@gmail.com

Abstract. Aluminium based lightweight-high strength metal matrix composites are widely used in applications such as automotive, military, and aerospace because of their improved physical, thermal and mechanical properties. In this work, the synthesis, structural and mechanical characterisation of Al7SiMg/TiB₂ composites prepared by the in-situ route was studied. The composites with different amounts (4 and 9 wt. %) of TiB₂ particles were developed as a result of the reaction between the molten alloy and the K₂TiF₆ and KBF₄ salts at 810 °C. These composites were examined by XRD and SEM/EDS. The elemental phases present in the composite and presence of TiB₂ were confirmed by XRD results. SEM micrographs showed the formation and distribution of micron-sized TiB₂ particles mostly along the grain boundary of the alloy matrix. The structure of TiB₂ particles was hexagonal. The effect of TiB₂ content on the hardness and wear resistance was investigated by using Vickers hardness tester and Pin-on Disc apparatus at room temperature. Increased hardness indicated increased wt. % of TiB₂ particles in the composites. The wear data indicated the amount of TiB₂ particles influence wear rate and mass loss values, while wear rate and mass loss of material increase with applied normal load and sliding distance.

1. Introduction
Aluminium alloys are extensively used materials in structural, automobile and aerospace applications to reduce the weight and save fuel, due to its outstanding properties such as lightweight, high specific strength, better wear, and corrosion resistance [1-3]. Nevertheless, the main drawback of Al alloys is their lower hardness compared with ferrous alloys. Besides, the lower wear resistance of aluminium alloys has limited their potential tribological applications in automotive parts like engine blocks, cylinder liners, pistons, and brake discs. The resistance to wear and hardness of Al alloys can be improved by the addition of ceramic reinforcements into the Al matrix leading to the production of metal matrix composites (MMCs). Ceramic reinforcements are available in different forms based on their morphology [4, 5]. Among them, particle–type contributes more to the strengthening of metals and alloys. Particle reinforced MMCs (PMMC) have become an interesting candidate for high strength applications because they can be made in lower production costs with ease in processing [5]. PMMCs can be synthesized in various ways which include solid, semi-solid, and liquid state processing techniques. The composites produced using these processes suffer from poor interfacial bonding between matrix and reinforcement, poor wettability, and thermodynamically unstable. Thus, deteriorating their mechanical properties. To overcome these issues, already a new process in-situ route has been developed where the reinforcement is created in the melt internally as a result of the
chemical reaction between the reactants and the matrix. The reinforcements formed by this route possess better homogeneity in particle sizes and distribution in the matrix, good mechanical properties, and high melting point [6].

The reinforcements are ceramic particles commonly used to produce Al-based MMCs include Al2O3, SiC, TiB2, and TiC [7-10]. Of them, TiB2 is considered as a better reinforcement as it possesses qualities like completely wetted and being stable in Al melts. Moreover, TiB2 acts as a heterogeneous nucleating agent, and a grain refiner in Al melts. Hence, TiB2 is recommended as a promising reinforcement for Al-based alloys. The effect of TiB2 on the mechanical properties of Al-Cu and Al-Si alloys has been already investigated [9, 11]. Liu et al. have reported that a problem is associated with achieving the dispersion of TiB2 homogeneously in the Al melt due to particle pushing during solidification [12]. By optimizing the stoichiometric ratio of Ti and B, a controlled amount of TiB2 and Al/Ti particles can be produced. Al/Ti is a brittle intermetallic compound which deteriorates the mechanical properties. However, a small amount of Al/Ti is beneficial for a dispersion of the in-situ TiB2 particles homogeneously through promoting the nucleation of α-Al grains [12, 13]. Mandal et al. also reported Al/Ti can be eliminated by optimizing the process parameters [11]. They have investigated furthermore the effect of TiB2 on the wear behavior of Al-Cu, Al-7Si, and A356 alloy systems [9,11]. Most of the studies reported so far are related to the fabrication and the mechanical properties of TiB2 composites [9, 11, 12, 14]. However, the testing parameters for wear test used in this work differs from the previous studies.

Thus, the current study highlights the synthesis of in-situ Al7SiMg composite and the influence of weight fraction of TiB2 on the resistance to indentation and wear property. Further, this paper also reports the formation and dispersion of in-situ TiB2 particles in the Al7SiMg system. The formation of TiB2 has been discussed in the viewpoint of morphological size in the Al matrix.

2. Materials and Experimental details

2.1. Raw materials

The base alloy, Al7SiMg alloy was first prepared by melting commercial pure aluminium ingots (Al, 99.6% purity) along with 7 wt.% of silicon rocks (Si, 99.6% purity), and 0.6 wt.% of Magnesium ingots (Mg, 99.7% purity) in a resistive electric furnace at 700 oC. The molten alloy was then cast in a steel mould. These materials were supplied by Vaishnavi Metals, Chennai, India. The composition of cast alloy was tested by spark spectroscopy technique (OES, Foundry master, Germany) and it is given in Table 1. Two salts, namely Potassium hexafluorotitanate (K2TiF6) and Potassium tetrafluoroborate (KBF4) were supplied by MFPL Pvt. Ltd, Chennai, India.

| Table 1. Composition of Al7SiMg alloy. |
| Si | Mg | Fe | Cu | Mn | Zn | Pb | Sn | Cr | Al |
|----|----|----|----|----|----|----|----|----|----|
| 6.5 | 0.5 | 0.12 | <0.01 | 0.01 | 0.12 | 0.07 | 0.11 | 0.03 | Rem. |

2.2. Preparation of the composite – Al7SiMg/TiB2

In this present work, Al7SiMg- x wt. % TiB2 (x =4, 9) in-situ composites were prepared via the exothermic salt-metal reaction according to the procedure used by Mandal et al. [9]. The fabrication process is illustrated in figure 1. First, the base alloy was melted using a graphite crucible in a resistive electric furnace at 700 °C. Secondly, the salts K2TiF6 and KBF4 were measured carefully and blended as per the stoichiometric ratio of Ti: B = 1:2. To remove moisture present in the blended salts, they were wrapped in Al foil and preheated at 150 °C for 3 h in a hot air oven. The batches of salt packs were poured into the melt maintained at 810±10 °C. The molten mixture was stirred for every 10 min using a cylindrical graphite rod (ø = 25 mm) coated with boron nitride paste for 60 min reaction time.
During this period, the chemical reaction between the melt and the salts takes place to form micron-sized TiB$_2$ particles in the melt. By the end of the reaction, the crucible was taken out from the furnace and the dross floating on the melt was decanted. Further, the melt was degassed with hexachloroethane tablets, and the melt was poured into the preheated steel mould. The equations (1-3) provided in Section 3.1 indicates the sequence of chemical reactions occurred during the in-situ method.

2.3 Structural characterisation
Samples were machined from the casted ingots and then ground by SiC emery sheets of grit sizes ranging from 800, 1200, 1500, and 2000. Polishing was performed on the samples for microscopy and hardness studies using the diamond paste of sizes 3 and 1 µm along with diamond spray as a lubricant. To reveal the microstructure, the samples were etched with Keller's reagent for 5-10 s. The etched samples were characterized by scanning electron microscope (SEM, FEI Quanta FEG 200) equipped with energy-dispersive spectroscopy (EDS). For phase analysis, the samples were tested using an X-ray diffractometer (XRD, PANalytical X’Pert Pro) operated with Cu Kα radiation (1.54 Å) at 40 kV, and a current of 15 mA.

2.4 Mechanical characterization: Hardness and Wear tests
The polished samples of both alloy and composites were subjected to the plastic indentation process to measure hardness according to the ASTM E92 Standard using Vickers hardness tester (Matuzawa, Japan) at 5 kg load with a dwell time of 10 s. Each hardness value presented is an average of at least ten observations. The wear tests at dry condition (without lubrication) were conducted using pin-on-disc apparatus (TR-20, DUCOM) as per ASTM G99-04 Standard. The cylindrical rods (diameter = 8 mm, height= 25 mm) of the alloy and composite were prepared as test samples. The hardened steel (diameter = 50 mm, 60 HRC) was used as the disc material. These samples were subjected under dry sliding at different loads (10, 30, 60, and 90 N) with a sliding speed of 2 ms$^{-1}$ and a sliding distance of 500 and 1000 m. The sliding point of rod samples on the disc was kept fixed at 60 mm. The height loss of rod samples was measured using vernier caliper manually. The wear loss was calculated by multiplying the height loss data with the area of cross-section of the rod samples.

3. Results and discussion

3.1 Fabrication of in situ TiB$_2$ particles
Al7SiMg with 4 and 9 wt. % of TiB2 composites were fabricated by the in-situ route. During the fabrication process, an exothermic reaction takes place between salts and Al which leads to the formation of TiB2 particles in the melt [9], according to the following sequence:

\[
\begin{align*}
    3K_2TiF_6 + 13 Al & \rightarrow 3Al_3Ti + 3KAlF_4 + K_3AlF_6 \\
    2KBF_4 + 3 Al & \rightarrow AlB_2 + 2KAlF_4 \\
    Al_3Ti + AlB_2 & \rightarrow TiB_2 + 4Al
\end{align*}
\]

XRD patterns of both alloy and composites are shown in figure 2. The presence of TiB2 particles has been identified by the peaks and angles corresponding to the TiB2 phase. The peak intensity of TiB2 in composite samples increases from lower TiB2 content to higher TiB2 content. This implies the number of TiB2 particles increased with increasing wt. % of TiB2 in the composite. This finding agrees well with the observation of Mondal et al. [9]. Moreover, figure 2 shows no evidence for Al3Ti and AlB2 peaks, therefore it is confirmed that Al3Ti and AlB2 particles were not formed in either of the composites. This is attributed to the process parameters such as reaction temperature, time, and stirring period maintained during the fabrication process [11].

**Figure 2.** Stacks of XRD patterns showing the phases present in the Al7SiMg - x % (0, 4, and 9) TiB2 composite. The JSPDS file number for the phases Al, Si, and TiB2 is mentioned inside the parenthesis.

3.2 Microstructural characterization

Figure 3 (a-d) show the SEM micrographs and EDS graphs of the Al7SiMg composites containing 4 and 9 wt. % of TiB2. The microstructure consists of fine TiB2 particles having a size of 1-4 µ dispersed in the Al matrix. The distribution of TiB2 particles is near homogenous in 9 wt. % TiB2 and also the number of particles is greater than 4 wt. % TiB2. It can be seen in figures 3(a) and 3(c) that the distribution of TiB2 particles is clustered in both composites. It is evident that the TiB2 particles formed in the matrix having a hexagonal morphology as shown in the insert of figures 3 (a) and 3 (c). This The TiB2 particles are located along the grain boundary region and the interdendritic region of the Al matrix. The Si and TiB2 are appeared as darker in the white region of α-Al. So, the final microstructure of composite contains pockets of a soft matrix (α-Al) surrounded by hard phases (Si and TiB2). Furthermore, the approximate chemical composition of all the elements present in the
composites was studied with the EDS. Figure 3 (b and d) show the EDS graphs of composites, which confirm the presence of elements like Al, Si, Ti, and B in the composites.

Figure 3. (a) and (c) SEM images, (b) and (d) EDS patterns of the Al7SiMg containing 4% and 9% TiB$_2$ particles respectively. The inserts contain circled marks indicating the hexagonal morphology of TiB$_2$ particle.

3.3 Mechanical characterization: Hardness

Figure 4 presents the influence of TiB$_2$ particles on the hardness value. It is observed that the hardness of the composites increased gradually with a weight fraction of TiB$_2$ particles in the alloy. The 9 and 4 wt. % TiB$_2$ achieved 38.21 % and 25.10 % of increase in hardness value than the alloy. This is because of the tendency of TiB$_2$ – a harder phase particle embedded in the matrix resist the plastic deformation.
3.4 Mechanical characterization: Wear Behaviour

Figures 5 and 6 present the graphs of wear rate and wear loss of Al7SiMg /TiB₂ (4, 9 wt. %) samples as a function of different loads and wt. % of TiB₂. For a fixed sliding speed and load, the wear rate decreases as a function of TiB₂. From figures 5 (a) and 6 (a), it is observed that the wear rate increases gradually with increasing load, and the wear rate reduces as the wt. % of TiB₂ increases. This is attributed to the resistance of TiB₂ particles against shear deformation experienced by the rod samples while sliding on the disc. Lim addressed that wear is not only influenced by hardness but also influence by microstructure, method of processing, thermal and mechanical properties of sliding material [15]. Kumar et al. reported that TiB₂ also acts as a load-bearing element in the matrix [14]. On the other hand, the wear loss increases gradually with increasing load, and the wear loss reduces as the wt. % of TiB₂ increases as shown in figures 5 (b) and 6 (b). Wear rates of composites are lower than the alloy at all the load conditions, due to the composite’s higher hardness.

Figure 5. (a) Wear rate vs. Load and (b) Wear loss vs. Load curves obtained after sliding distance of 500 m for Al7SiMg – x % (0, 4, & 9 ) TiB₂.
4. Conclusion
In this work, Al7SiMg/TiB$_2$ composite has been developed with different weight percentages (4 and 9) of TiB$_2$ particles by the in-situ salt-metal reaction. Microstructural and mechanical characteristics and the effect of TiB$_2$ on these characteristics were studied. The important conclusions are drawn as follows:

- Micron sized TiB$_2$ particles having regular hexagonal structure were produced successfully and their presence and distribution in the Al matrix were examined by XRD and SEM with EDS techniques.
- The in-situ composites exhibited better resistance to indentation and wear compared to unreinforced Al7SiMg alloy.
- The value of hardness increases linearly with wt. % of TiB$_2$ particles in the composites.
- Wear rate and wear loss decreases with increasing TiB$_2$ content.

5. References
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Figure 6. (a) Wear rate vs. Load and (b) Wear loss vs. Load curves obtained after sliding distance of 1000 m for Al7SiMg –x % (0.4, & 9 ) TiB$_2$. 

![Figure 6](image-url)