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Development of TiB_2 reinforced aluminum foundry alloy based in situ composites – Part I: An improved halide salt route to fabricate Al–5 wt%TiB_2 master composite

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ABSTRACT

In Part I of the two part study, an improved halide salt route was developed to fabricate in situ TiB_2 particulate reinforced aluminum matrix master composites based on the well-established flux assisted synthesis (FAS) method using mechanical stirring. By microstructural and element-recovery analysis, we show how the simple but effective "improved method" – leaving the reactant molten salt on the surface of aluminum melt without introducing any stirring during holding – influences the mechanical performance of the final composites. Processing parameters in terms of holding duration, reaction temperature and stirring speed before casting were optimized to produce Al–5 wt% TiB_2 composite with consistent and sound quality. The experimental Al–5TiB_2 composite, prepared under the improved halide salt route condition, has achieved a 140% improvement in the UTS without compromising its ductility with respect to the Al matrix. The experimental validation of using the developed Al–5TiB_2 composite as a master composite to reinforce aluminum foundry alloys will be presented in Part II.

1. Introduction

Particulate reinforced aluminum matrix composites (AMCs) have found numerous commercial applications due to their excellent specific strength, low thermal expansion coefficient as well as lower cost and ease of fabrication [1–5]. Among various ceramic particulates such as Al_2O_3 [6,7], Si_3N_4 [8–10], SiC [11,12], B_4C [13] and TiC [14–16], TiB_2 is portrayed to be an outstanding reinforcement in aluminum matrix because it exhibits good features such as high melting point, hardness, modulus and does not react with most metallic elements at the interface between reinforcements and Al matrix [17–20].

For preparing AMCs, traditional ex situ approach involves addition of externally synthesized reinforcements into the molten matrix. Inherent problems, for instance, poor bonding, particulate agglomeration, formation of interfacial reaction products and unavoidable casting defects are posed by this ex situ process due to surface contamination of the reinforcements. To overcome these deficiencies, researchers are now focusing on in situ techniques. A number of in situ fabrication methods like self-propagating high-temperature synthesis (SHS) [21], exothermic dispersion (XD^{TM}) [22], reactive hot pressing (RHP) [23], flux-assisted synthesis (FAS) [24,25] and liquid metallurgy using master alloys [20,26] have been developed to fabricate in situ AMCs. The technique halide salt route, also known as the FAS method [1], is an attractive in situ approach developed by Davies et al. [24,27] who used K_2TiF_6 and KBF_4 salts as the starting Ti and B resources to form a dispersion of in situ TiB_2 particles in the Al matrix. This process is based on the well-developed technology for producing Al–Ti–B master alloys [28]. The major advantage of this process is that the Al/TiB_2 composites thus produced would be competitive both technically and economically with existing casting technologies [29]. However, the mechanical properties of the Al/TiB_2 composites produced by the halide salt route differ appreciably since the microstructure of the final composite is highly sensitive to the processing parameters employed in the preparation [30]. Efforts were made to obtain better and consistent mechanical properties of in situ Al/TiB_2 composites [5,25,31,32].

The present work, as Part I of the two part study, was undertaken to explore an improved halide salt route for the production of in situ Al/TiB_2 composites with consistent and good tensile properties. More recently, it has been studied that leaving the residual salt of the reaction on the melt surface until before casting helps to avoid oxidation of the molten alloy during holding [33,34]. This method was used to improve the Ti and B recoveries in the final composites. The effects of processing parameters, i.e. holding duration, reaction temperature, stirring during

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holding and stirring speed on the microstructures and tensile performances of the final products were studied in detail. The optimized Al/TiB_2 composite is suggested to serve as excellent "master composite" for subsequent dilution in the processing of aluminum foundry alloy based composites. This envision will be validated in Part II.

2. Experimental

Al–5 wt% TiB_2 composites were prepared in the laboratory via the improved halide salt route. The starting materials were pure Al ingots (commercial purity, 99.85% Al), K_2TiF_6 and KBF_4 powders of analytical purity (99% purity). The Al ingots were melted in a graphite-clay crucible using an electrical resistance furnace on a 500 g batch scale. The K_2TiF_6 and KBF_4 salts, weighed and mixed in a stoichiometric Ti:B ratio of 1:2, were preheated at 350 °C for 2 h to remove the moisture thoroughly. The mixed halide salts were added gently to the melt at different temperatures, ranging from 750 to 950 °C. The melts thus obtained were held for different holding durations (15, 30, 60 and 90 min) to investigate the effects of holding on the microstructures and tensile performances of the final composites. The residual K–Al–F salt was allowed to remain on the melt surface and no stirring was introduced until before casting. Yet, additional mechanical stirring was employed shortly after adding the mixed salts in a separate experiment. Finally, the by-product K–Al–F salt was decanted and the melt was stirred with a graphite impeller at 240 r/min for 120 s before it was cast into a permanent mold. Another experiment was carried out in accordance with the optimized procedure we just identified except for the stirring step before casting. In the experiment, the stirring speed was set at 480 r/min for 120 s to investigate if a more intensive mechanical stirring could improve the dispersion of the in situ TiB_2 particles in the final product. A total of 8 experiments were conducted in the present study.

The Ti and B recoveries in the as-received composites were measured using an inductive coupled plasma (ICP) emission spectrometer calibrated for Ti and B. KBF_4 salt was tested in a differential thermal–thermo gravimetry analysis (DT–TGA) unit to investigate its stability to thermal exposure at temperatures ranging from ambient to 750 °C. Standard metallographic specimens were sectioned 20 mm from the bottom of the experimental ingots. The distribution and morphology of in situ TiB_2 particles were examined by field emission scanning electron microscope (FESEM). The average grain size of each sample was measured using linear intercept method. Tensile tests (0.2% offset yield strength ($\sigma_{0.2}$), ultimate tensile strength (UTS) and elongation (δ)) were conducted on a computerized universal testing machine. The tensile specimens were machined from the experimental ingots according to ASTM B557 standard. Fig. 1 shows the geometry of the tensile specimen employed in this study. For each sample, the test was repeated three times and average values were reported. The FESEM was also used for examining the fractographs of the as-tested specimens.

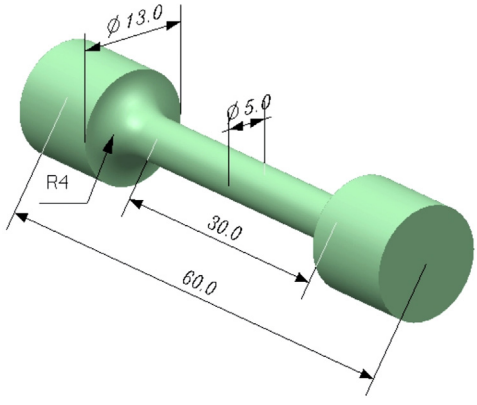

Fig. 1. Geometry of the specimens for tensile testing.

3. Results and discussion

3.1. Holding duration

Four experiments were performed to assess the effect of holding duration on the quality of the in situ Al/TiB_2 composites. The reaction temperature in these experiments was fixed at a moderate 850 °C. The Ti recovery in the final composite was only 87.7% with 15 min holding after salt addition. Holding the melt in the furnace for 30 min offered a marked increase in the Ti recovery (sample 2, 95.1%). After 60 min holding of the melt, a 98.6% Ti recovery was obtained in the final composite. This value, however, has dropped back to 93.6% when the melt was further held up to 90 min. The lower Ti recovery with holding durations longer than 60 min is believed to be associated with the excessive oxidation of the melt [33]. Also seen in Table 1 are the B recoveries in these experimental composites. Unlike Ti, the B recoveries were all higher than 90.4% once the holding duration exceeds 15 min. But no further improvement was obtained in the samples with increasing holding durations. This is because that the addition of KBF_4 results in such a rapid transfer rate that holding the melt for 5 min is sufficient for its reaction with Al melt to reach completion [35].

Fig. 2 shows the microstructures of the in situ composites after 15, 30, 60, 90 min (samples 1–4) respectively, of holding duration. It can be seen that the TiB_2 particles in samples 1 and 2 were formed in agglomerates, most of which segregated at the α-Al grain boundaries. Since the melt was cast without finishing the reaction, some large AlB_2 blocks still remained in the final product. The in situ TiB_2 particles did not disperse in the matrix either. In contrast with the former two, sample 3 revealed an adequate uniform distribution of TiB_2 particles in the final composites. Holding the melt for 60 min has eliminated unwanted AlB_2 and/or $TiAl_3$ blocks. The TiB_2 particles were still but more slightly clustered with sizes of 1–2 μm. After 90 min holding, the TiB_2 particles were distributed more homogeneously throughout the matrix. The grain-form TiB_2-free regions observed in samples 1–3 were no longer present in sample 4 in spite of the presence of a few individual clusters smaller than 10 μm. It is interesting to note

Table 1
Effect of holding duration on the Ti and B recoveries in the final in situ composites.

Sample no.	Reaction temperature (°C)	Holding duration (min)	Stirring speed (r/min)	Stirring duration (s)	Stirring during reaction	Ti recovery (%)	B recovery (%)
1	850	15	240	120	No	87.7	90.4
2	850	30	240	120	No	95.1	91.9
3	850	60	240	120	No	98.6	90.8
4	850	90	240	120	No	93.6	91.0