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Microstructural evolution and mechanical properties of in situ TiB_2/Al composites under high-intensity ultrasound

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Abstract Microstructural evolution and mechanical properties of in situ TiB_2/Al composites fabricated with exothermic reaction process under high-intensity ultrasound produced by the magnetostrictive transducer were investigated. In this method, the microstructure and grain refining performance of the TiB_2/Al composites were characterized by optical morphology (OM), scanning electron microscopy (SEM), energy-dispersive spectrometer (EDS), and X-ray diffraction (XRD) analysis. Microstructural observations show a decreasing trend in the grain size of the composites due to the ultrasound and the content of TiB_2 particles in the composites. Compared with the process without ultrasound, the morphology and agglomeration of TiB_2 particles are improved by high-intensity ultrasound. Meanwhile, it is proposed that the formation of TiB_2 particles occurs via the transformation from $TiAl_3$, and at the optimal amount of the reactants, the conversion efficiency of $TiAl_3$ into TiB_2 almost reaches up to 100 %. Finally, the effects of high-intensity ultrasound and TiB_2 particles on the mechanical properties of the TiB_2/Al composites were also discussed.

Keywords Microstructural evolution; Mechanical properties; In situ; High-intensity ultrasound; Magnetostrictive transducer

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1 Introduction

It is well known that aluminum matrix composites (AMCs) are considerably prominent due to their potential to offer desirable properties, including low density, high specific strength, high specific stiffness, excellent wear resistance, and controllable expansion coefficient. These advantages make AMCs receive great attention for numerous applications in aerospace, automobile, and military industries [1, 2]. In recent decades, particles reinforced aluminum matrix composites (PRAMCs) have become more and more significant in the research field of AMCs [3, 4]. Currently, there are several methods for fabricating PRAMCs, which can be classified into three categories: solid-phase process, liquid-phase process, and semi-solid fabrication process. Among them, liquid processes, such as stir casting and compocasting, have several advantages including high production rate, low cost, and the feasibility of producing complex parts [5]. But it is extremely challenging for stir casting to disperse submicron- and nano-sized particles uniformly in the melt due to their large surface-to-volume ratio and poor wettability.

Ultrasonic vibration is applied extensively in the treatment of metallic melt, such as degassing, refinement, and purifying [6–11]. In addition, ultrasonic vibration is used in the fabrication of particles reinforced metal matrix composites, for it can improve the wettability between reinforcements and matrix. However, the ordinary ultrasonic equipment mainly consists of the piezoelectric ceramic transducer, whose energy output is limited. Thus, the ultrasonic treatment does not perform as well as expected. There is a patented process termed flux-assisted synthesis (FAS) (also known as mixed-salt reaction or reaction cast) which was developed by the London Scandinavian Metallurgical Company (LSM) to produce in situ aluminum matrix composites [12]. Although some works [13–17] investigated the reactions between molten aluminum and Ti- and B-bearing potassium fluoride salts, K_2TiF_6 and KBF_4, few studies were reported on the production of in situ TiB_2/Al composites using K_2TiF_6 and KBF_4 under high-intensity ultrasound produced by magnetostrictive transducer.

In this work, the conventional K_2TiF_6 and KBF_4 were used as the reaction system. The objective of this paper is to study the morphologies and distribution of in situ TiB_2 particles and $TiAl_3$ phase in aluminum matrix via ultrasonic treatment produced by magnetostrictive transducer. Their impacts on mechanical properties of this versatile composite were also discussed.

2 Experimental

2.1 Materials and apparatus

In this research, raw materials used were refined aluminum ingot for re-melting (99.99 % purity) as the composite matrix, and two types of commercial inorganic salt, namely potassium hexafluorotitanate (K_2TiF_6, 99 % purity) and potassium tetrafluoroborate (KBF_4, 98 % purity), were used to produce TiB_2 reinforcement. In casting process, the atmospheric control electrical resistance furnace with the ultimate temperature of 1,200 °C was used. The ultrasonic processing system mainly consisted of ultrasonic probe made of TC4 titanium alloy and magnetostrictive transducer (4 kW power, 20 kHz frequency) made of Fe–Ga alloy.

2.2 Material preparation

The mixed salts of K_2TiF_6 and KBF_4 with the stoichiometric atomic ratio in accordance with Ti/2B were dried at 200 °C to remove moisture and reduce the temperature difference subsequently. When the pure aluminum ingot was superheated to the given temperature (850 °C) and held for 10 min, the desired amount of the mixture of fluoride salts was added into the melt in batches and the liquid matrix was stirred for 10 min by the graphite agitator to facilitate the melting of the salts mixture. In order to protect materials against oxidation and other undesirable reactions during casting process, pure argon gas had to be charged in an appropriate amount into the furnace. After adequately stirring the melt, the melt was reheated to 800–820 °C and held for 5 min. Then, the ultrasonic probe was dipped into the melt from the upper surface and sonicated for 15 min to make the generated TiB_2 particles agglomeration scatter, the particles distribute uniformly in the melt and the composite melt degas as well.

Specimens with different TiB_2 contents of 0 wt%, 2.5 wt%, 5.0 wt%, and 7.5 wt% were melted in graphite crucible; after cooling down to 720–740 °C and holding for 10 min, the melt was poured into a preheated Reynolds standard golf tee mold [6] made of copper. In order to compare the properties and structures of the samples, the composite melts with the same components were prepared without ultrasonic treatment but in other identical conditions (including casting temperature, furnace, crucible types).

2.3 Microstructural and properties characterization

Optical microstructures of the resulting composites were examined under optical microscope (OM, Olympus BX60M) after being etched by Keller's reagent (1.5 ml HCl, 2.5 ml HNO_3, 1 ml HF, and 95 ml H_2O). The morphology, size, and dispersion of in situ TiB_2 particles in the matrix were observed by scanning electron microscope (SEM, LEO-1450) and field emission scanning electron microscope (FESEM, SUPRA^{TM} 55) equipped with energy-dispersive spectroscopy (EDS) detector. X-ray diffraction (XRD) patterns were obtained on Rigaku DMAX-RB X-ray diffractometer, using monochromatic Cu Kα radiation with the wavelength of 0.154 nm, at 40 kV and 150 mA.

According to China's National Standard (GB/T 228-2002), tensile tests were carried out at room temperature with the tensile rate of 0.5 mm·min^{-1} on a CMT-4105 testing machine. The tensile properties reported in this paper were the average values of three tensile samples.

3 Results and discussion

3.1 Grain microstructure

Figure 1 shows the grain size variation of as-cast 5.0 wt% TiB_2/Al composites without and with ultrasonic treatment, respectively. The metallographic microstructure of as-cast TiB_2/Al composites containing different TiB_2 contents with

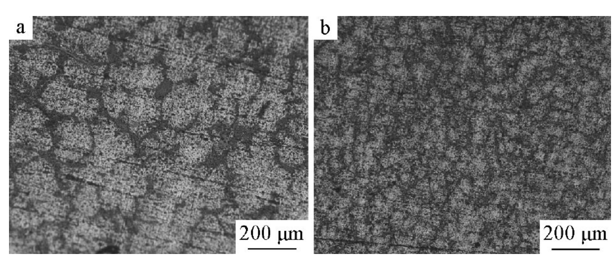

Fig. 1 OM images of as-cast 5.0 wt% TiB_2/Al composites prepared **a** without and **b** with ultrasonic treatment

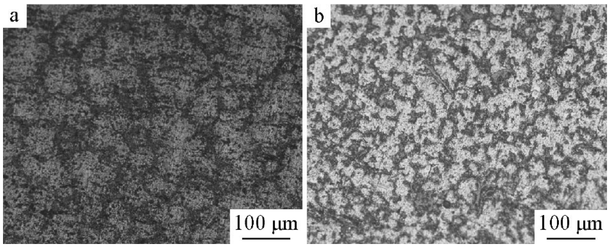

Fig. 2 OM images of as-cast composites with different TiB_2 contents prepared by ultrasonic method: **a** 5.0 wt% TiB_2 and **b** 7.5 wt% TiB_2

ultrasonic treatment is shown in Fig. 2. The in situ TiB_2 content level is 5.0 wt% and 7.5 wt%, respectively. It can be observed clearly that the primary α-Al phase is effectively refined due to high-intensity ultrasound. With the ultrasonic vibration, the composite presents a fine uniform microstructure, which is composed of fine grains with average size of 50 μm. Most of the TiB_2 particles are found to be distributed along the grain boundary regions, and very minimal agglomerations of the particles are observed in grains. The results indicate that the average grain size of as-cast 7.5 wt% TiB_2/Al composite is reduced to 25 μm or so, half of the size of 5.0 wt% TiB_2/Al composite. It can be attributed to coupled effects of the TiB_2 contents in the aluminum matrix and the ultrasonic vibration.

3.2 Distribution and morphology of $TiAl_3$ and TiB_2

Microstructures of as-cast TiB_2/Al composites with different TiB_2 contents with and without ultrasonic treatment applied in the melting process are shown in Fig. 3. Unlike the coarse acicular or plate-like $TiAl_3$ particles which were reported by many researchers [6, 13], the $TiAl_3$ phase produced in the aluminum matrix in this experiment is in the shape of irregular gullies as shown in Fig. 3a, b, d. Meanwhile, $TiAl_3$ is found in two different morphologies as shown in Fig. 4. Blocky and rounded particles are generated with the same time as TiB_2. In addition, the second morphology is elongated. TiB_2 particles form inside the banded structure of $TiAl_3$ when the amount of the reactants (K_2TiF_6 and KBF_4) increases.

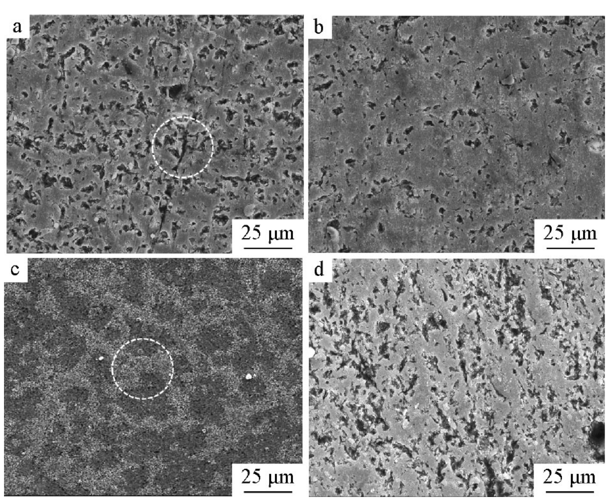

Fig. 3 SEM images of as-cast composites with different TiB_2 contents: **a** 2.5 wt% TiB_2, **b** 5.0 wt% TiB_2, **c** 7.5 wt% TiB_2 with ultrasonic treatment, and **d** 5.0 % TiB_2 without ultrasonic treatment

The results show that with the increase in TiB_2 content, the $TiAl_3$ particles gradually disappear under the ultrasound field. Emamy et al. [14] stated that the formation of TiB_2 particles was expected during the following reaction:

$$TiAl_3 + 2B \rightarrow TiB_2 + 3Al \quad (1)$$

$$\Delta G^0 = -43.4 \times 10^3 + 15.8\,T \quad (2)$$

where ΔG^0 is the Gibbs' free energy and T is the reaction temperature. When TiB_2 particles account for 7.5 wt%, the conversion efficiency of $TiAl_3$ into TiB_2 almost reaches up to 100 % from the comparison among Fig. 3a–c. This means that at the lower amount level of the reactants, K_2TiF_6 and KBF_4, the reaction to form TiB_2 is less complete and the intermediate $TiAl_3$ exists in a larger quantity than required to form TiB_2.

In order to identify the TiB_2 crystals, FESEM, EDS, and XRD were employed in the study. Figure 5 shows the morphologies of the crystallites in the matrix. It can be seen that the size is 100–500 nm and the shape is regular polygon with clear profile, such as hexagonal platelet. It can be seen from the EDS analysis result that these particles contain both titanium and boron, which are pushed into the inter-dendritic region by the α-Al dendrites.

XRD analysis of the particles, which were extracted by a special extraction method using solution of 10 % HCl, indicates that the particles have the same crystal structure as TiB_2 as shown in Fig. 6. So it is reasonable to confirm that these particles are TiB_2 crystals. The isolated TiB_2 particles do not cling to each other although they are still in

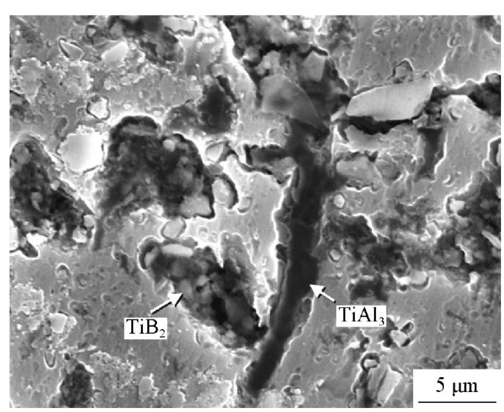

Fig. 4 High-magnification SEM image of dotted circle region in Fig. 3a

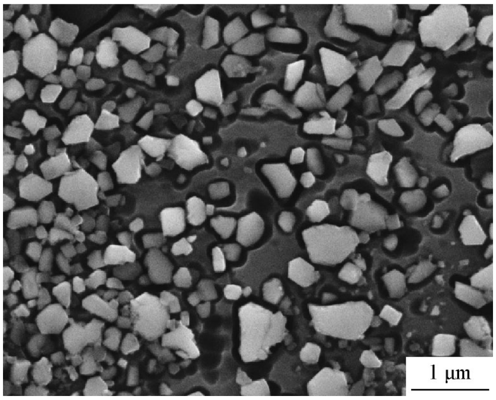

Fig. 5 FESEM image of TiB_2 particles from dotted circle region in Fig. 3c

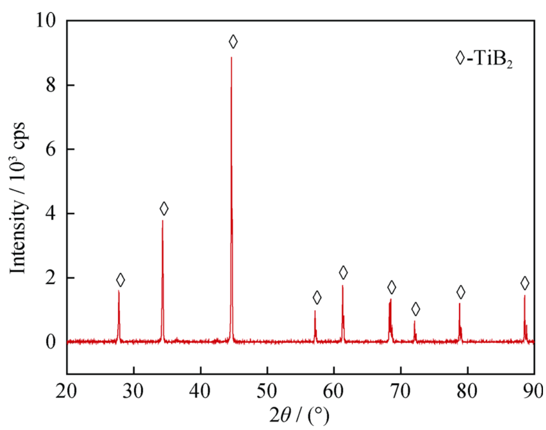

Fig. 6 XRD pattern of extracted TiB_2 particles

the form of loose agglomeration. Therefore, both the mean size and size distribution of TiB_2 particles in the aluminum matrix are significantly modified by applying ultrasonic vibration produced by the magnetostrictive transducer in the manufacture process.

3.3 Tensile properties

Figure 7 shows the ultimate tensile strength (UTS), yield strength (YS), and elongation of as-cast pure aluminum and TiB_2/Al composites under the ultrasound field. It can be clearly seen that the UTS and YS of the composites are simultaneously enhanced compared with those of as-cast pure aluminum with the same treatment. Furthermore, with 7.5 wt% TiB_2, the UTS and YS of the composite are enhanced by 63 % and 75 %, respectively, compared with the aluminum matrix. To our knowledge, these results would be attributed to the coupled effects of the increase in grain boundary region due to the grain refinement and the obstruction of dislocation movement by TiB_2 particles. The gliding dislocations have to overcome the barriers of TiB_2

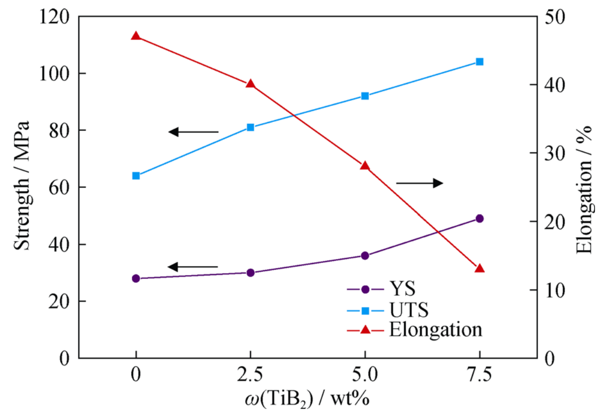

Fig. 7 Tensile properties of as-cast pure aluminum and TiB_2/Al composites with ultrasonic treatment

particles either by Orowan mechanism or by the processes of cross-slip or climb [18].

However, compared with the ultrasonically cast pure aluminum, there is a gradually decreasing tendency of the elongation (a measure of ductility) of the composites with TiB_2 content increasing. The elongation of the ultrasonically cast pure aluminum is about 47 % and, as anticipated, reduces to 13 % in the case of 7.5 wt% TiB_2/Al composite. The results demonstrate that the dispersion of submicron-sized TiB_2 in pure aluminum results in a significant increase in the tensile strength with the huge sacrifice of ductility. This may be the result of greater agglomeration of TiB_2 particles and higher degree of micro-porosity present in the composite with higher TiB_2 content. Besides, the increased TiB_2 content would decrease the effective slip distance of dislocations during the deformation, which would lead to the decrease in the elongation [19].

For the subsequent studies, it is expected that if the optimal content of TiB_2 particles is better understood and the process parameters are optimized, the dispersion and mechanical properties of the composites will be further improved.

4 Conclusion

In this study, the effects of high-intensity ultrasonic treatment on microstructural features and tensile properties of in situ TiB_2/Al composites were investigated. The results show that the improvement in grain refining performance benefits from coupled effects of the increasing stoichiometric mass fraction of TiB_2 particles and the ultrasonic vibration produced by the magnetostrictive transducer in the melt. Ultrasound applied in the process of manufacturing the TiB_2/Al composites changes the morphology of

$TiAl_3$ phase into irregular gullies shape, accelerates the dissolution of coarse $TiAl_3$ phase, and makes the distribution of TiB_2 particles more uniform in the melt. It is demonstrated that the formation of TiB_2 particles occurs via the transformation from $TiAl_3$, and at the optimal amount of the reactants, K_2TiF_6 and KBF_4, the conversion efficiency of $TiAl_3$ into TiB_2 almost reaches up to 100 %. Compared with the aluminum matrix, the UTS and YS of the TiB_2/Al composites can be enhanced by 63 % and 75 %, respectively. The improvement is due to the uniform distribution of reinforcement and grain refinement of aluminum matrix.

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