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Microstructures and properties of in-situ (ZrB₂ + Al₂O₃)ₙp/AA6111 composites synthesized under magnetic and ultrasonic fields

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Abstract

ZrB₂ and Al₂O₃ nanoparticle-reinforced aluminum matrix composites were successfully prepared by in situ chemical reaction of the Al-Na₂B₄O₇-K₂ZrF₆ system with magnetic field applied in the in situ reaction and ultrasonic field introduced in solidification. The results indicated that the optimized magnetic frequency was 10 Hz, and the ultrasonic power was 1.0 kW. XRD analysis showed that ZrB₂ and Al₂O₃ nanoparticles have been obtained. The smaller clusters were evenly distributed in the matrix. ZrB₂ and Al₂O₃ nanoparticles were dispersed and uniformly distributed. The average size of particles and grain size of (ZrB₂ + Al₂O₃)ₙp/AA6111 composites were refined to 45 ± 10 nm and 50.4 ± 12 μm, respectively. The maximum Vickers hardness, tensile strength, yield strength and elongation of the composites synthesized under the optimized magnetic and ultrasonic fields were 142.2 HV, 355.4 MPa, 259.4 MPa and 22.4%, which were 1.34, 1.36, 1.35 and 1.33 times higher than that of AA6111 alloy, respectively.

1. Introduction

The Al-Mg-Si alloy AA6111 is extensively used in automotive body industries for their high yield ratio, good corrosion resistance, good formability and process performance [1]. However, with the development of lightweight technology, there are higher requirements for its performance. Particle reinforced aluminum matrix composites (PRAMCs) have been utilized in aerospace, automotive industry, precision instruments and other civil industries due to their high elastic modulus, high strength and excellent corrosion resistance [2–4].

Nowadays, the binary particles reinforced aluminum matrix composite have attracted widespread attention in the field of materials science because of the desire for enhanced mechanical properties compared with single particle aluminum matrix [5, 6]. Nanoscale contributed to the strong surface activity of reinforcing nanoparticles in the composite [7], leading to the formation of strong interaction between the matrix interface and particles Kaveendran et al.[8], prepared in situ hybrid (Al₃Zr + Al₂O₃)ₙp/2024 Al metal matrix composites by low energy ball milling and reactive hot pressing. Al₃Zr was micron scale needle and sheet. The (Al₃Zr + Al₂O₃)ₙp/2024 Al composites effectively strengthen the 2024Al matrix, and had a Yield Stress (YS) of 175 MPa and an Ultimate Tensile Strength (UTS) of 261 MPa. Binary nanoparticles can combine the advantages of two kinds of particles to improve the mechanical properties. The previous research of our research group prepared and investigated the microstructures and mechanical properties of in situ (TiB₂ + ZrB₂)/AlSi9Cu3 composites [9] and (ZrB₂ + Al₂O₃ + Al₃Zr)ₚ/Al-4Cu composites [10]. For (TiB₂ + ZrB₂)/AlSi9Cu3 composites, the size of particles was 20–100 nm, and the tensile strength and elongation reached 265 MPa and 14.8% respectively. For (ZrB₂ + Al₂O₃ + Al₃Zr)ₚ/Al-4Cu composites, the mechanical properties and wear resistance of the composite material have been greatly improved compared with the Al-4Cu alloy.

There are various ceramic particles commonly used as the reinforcing phase of the composite material such as Al₂O₃, SiC, ZrB₂, TiB₂ [11]. Among these particles, the thermal expansion coefficients of Al₂O₃ and ZrB₂ are both low (Al₂O₃: \( 7.92 \times 10^{-6}/\text{°C} \), ZrB₂: \( 8.28 \times 10^{-6}/\text{°C} \)), and both have high hardness and elastic modulus,
The starting materials were commercial AA6111 alloy ingots, zirconium potassium fluoride (K₂ZrF₆) powder (purity 99.95%, average particle size 20 μm), and natrium boricum (Na₂B₄O₇) powder, (purity 99.97%, average particle size 25 μm). The two salts were pre-heated to eliminate the bonded water in an electric oven at 300 °C for 3 h and then cooled, ground, screened and thoroughly mixed in a mortar for 30 min with a mass ratio of Na₂B₄O₇ : K₂ZrF₆ = 37 : 64. Meanwhile, the AA6111 alloy ingots (930 g) were melted in an induction electric furnace and maintained at 850 °C. Then the powder mixture of K₂ZrF₆ and Na₂B₄O₇ with a weight ratio of 30% relative to the total AA6111 melt were added into metal. Then the composite melt was poured into a copper mold. When the temperature was 680 °C, applying the ultrasonic field in solidification for 2 min, and the power of ultrasonic field was 1 kW and 1.5 kW. Then the as-cast endogenous nanoparticles reinforced aluminum matrix composites were studied in detail.

## 2. Experimental

### 2.1. Materials and experimental procedure

The starting materials were commercial AA6111 alloy ingots, zirconium potassium fluoride (K₂ZrF₆) powder (purity 99.95%, average particle size 20 μm), and natrium boricum (Na₂B₄O₇) powder, (purity 99.97%, average particle size 25 μm). The two salts were pre-heated to eliminate the bonded water in an electric oven at 300 °C for 3 h and then cooled, ground, screened and thoroughly mixed in a mortar for 30 min with a mass ratio of Na₂B₄O₇ : K₂ZrF₆ = 37 : 64. Meanwhile, the AA6111 alloy ingots (930 g) were melted in an induction electric furnace and maintained at 850 °C. And then the powder mixture of K₂ZrF₆ and Na₂B₄O₇ with a weight ratio of 30% relative to the total AA6111 melt were added into metal. Then the in situ melt reactions began, and the magnetic field system was turned on. The frequency of the magnetic field was 5 Hz and 10 Hz. When the magnetic field is greater than 10 Hz, the centrifugal force provided by Lorenz is too large, which will cause liquid splashing in the reaction process. The designed volume fraction of nano particulates (ZrB₂ and Al₂O₃) were 3%. After the reaction, the melt was kept at 850 °C for 15 min, and then de-slaged, degassed with C₂Cl₆, and then held for another 5 min. Then the composite melt was poured into a copper mold. When the temperature was continue reduced to 680 °C, applying the ultrasonic field in solidification for 2 min, and the power of ultrasonic field was 1 kW and 1.5 kW. Then the as-cast endogenous nanoparticles reinforced aluminum matrix composites were obtained, and the size of the casting was 145 × 100 × 18 mm³. According to the previous research basis and relevant literature [13–15] of our research group, the parameters of the magnetic field and ultrasonic field were shown in table 1.

### 2.2. Material characterization and mechanical properties measurement

Direct reading spectrometer (SPECTRO MAXx mm06) has been used to analyze the chemical compositions of the commercial AA6111 alloy and the (ZrB₂ + Al₂O₃)ₜₜp/AA6111 composites and the results were shown in table 2.

Metallographic specimens obtained from the fabricated composites were machined to a size of 10 × 10 × 10 mm³, as shown in figure 1, then grounded using emery paper from 200 # to 1500 #, polished.
using diamond spray polishing compounds (up to 0.5–1 μm). Then the samples were etched by Keller’s etchant (95 ml H2O, 2.5 ml HNO3, 1.5 ml HCl, 1 ml HF) for 6 s to clearly observe the microstructure. Optical microscopy (OM, Zeiss-Observer. Z1 m) was employed to observe the grain structure and particle distribution of the composites. X-ray diffractometer (XRD, D/max 2500 PCXR) was used to identify the reinforcement phases of the composites. The phase composition of the composites was determined by Energy dispersive spectrometry (EDS, JEOL-JSM-7800 F). The grain structure, particle distribution and tensile fracture surfaces were analyzed by Scanning electron microscopy (SEM, JEO-JSM-7800F). The microstructural refinement was examined and the micrographs were obtained by a Leica Polyvar microscope (LWICA DM750P) with polarized light after anodizing using a 38% H2SO4 + 43% H3PO4 + 19% H2O solution for about 2 min at 20 V. The linear intercept method was employed for the measurement of the grain size. And transmission electron microscopy (TEM, JEM-2100 (HR)) was used to analyze the nanoparticles and dislocations in the composite materials.

Prior to the mechanical properties (hardness and tensile properties) test, T6 heat treatment was carried out on the composites through the following steps: solution treatment at 550 °C for 2 h, quenching in cold water quickly, then heating to 180 °C and cooling with the furnace after holding for 3 h. Hardness of the AA6111 alloy and composites was estimated by Vickers hardness testing at 5 Kgf load for a dwell time of 15 s. The hardness value was the average of five test values. The tensile specimens with a gauge length of 15 mm, a width of 4 mm and a thickness of 2 mm were prepared according to the ASTM E8M-04 standard, as shown in figure 2. Tensile test was carried out in a computer-controlled electronic tensile testing machine (DWD-200) at ambient temperature, and the tensile velocity was 1 mm min⁻¹. Three tests were performed on each composite to obtain a precise value for tensile properties.

3. Results and discussion

3.1. Microstructural characterization

The XRD patterns of the in situ synthesized composites from Al-K2ZrF6- Na2B4O7 reaction system are shown in figure 3, and the diffraction peaks of Al, ZrB2 and Al2O3 phases were observed, respectively. All dissolved Zr elements were transformed into ZrB2 particles due to the excess of B element, and there was no intermediate product Al3Zr left. The results showed that the reinforcing phases in the system Al-K2ZrF6- Na2B4O7 were Al2O3 and ZrB2. The possible reaction occurring in the Al-K2ZrF6- Na2B4O7 system can be illustrated as follows [16–18]:

\[
3K_2ZrF_6 + 13Al = 3Al_2Zr + 4AlF_3 + 6KF
\] (1)

\[
Na_2B_4O_7 + 2Al_2Zr = 2ZrB_2 + 2Al_2O_3 + Na_2O + 2Al
\] (2)
The overall reaction can be expressed as follows:

\[ 4\text{K}_2\text{ZrF}_6 + 4\text{Al} + 2\text{Na}_2\text{O} = 4\text{K}_2\text{NaAlF}_6 + 2\text{ZrO}_2 \]  

The overall reaction can be expressed as follows:

\[ 9\text{Na}_2\text{B}_4\text{O}_7 + 30\text{K}_2\text{ZrF}_6 + 60\text{Al} = 12\text{ZrO}_2 + 18\text{ZrB}_2 + 13\text{Al}_2\text{O}_3 + 18\text{K}_2\text{NaAlF}_6 + 16\text{AlF}_3 + 24\text{KF} \]  

Figure 4 shows the typical micrograph of AA6111 alloy and the in situ 3 vol% (ZrB\(_2\) + Al\(_2\)O\(_3\)) particles synthesized without magnetic and ultrasonic fields. As shown in the figure 4(a), AA6111 exhibited a typical irregular coarse and dendrite grain microstructure, the average grain size was about 180 ± 12 \(\mu\)m. While in figure 4(b), the dendrite size decreased significantly due to the introduction of (ZrB\(_2\) + Al\(_2\)O\(_3\)) nanoparticles, and the equiaxed crystal with an average size of 120 ± 10 \(\mu\)m appeared. The above results showed that the (ZrB\(_2\) + Al\(_2\)O\(_3\)) nanoparticles and clusters contribute to the refinement of matrix grains. Firstly, the formation of ZrB\(_2\) and Al\(_2\)O\(_3\) nanoparticles can be regarded as possible heterogeneous nucleation points for the matrix grains [19–21], which thus nucleate owing to the continuous undercooling at the front of particle interface. In this way, the composition can be refined effectively. Secondly, in situ nanoparticles tend to aggregate at grain boundaries and form clusters [22]. As an obstacle, these clusters can effectively prevent the grain growth and refine the composite grain. Figure 4(c) shows a high-magnified SEM image of the composite with the (ZrB\(_2\) + Al\(_2\)O\(_3\)) volume fraction of 3%, as can be seen the size of most agglomerated particles were 50–400 nm, exhibited rectangular and nearly hexagon-shape. And the particle cluster size was larger than 1 \(\mu\)m which distributed unevenly. In addition, the composition of the particles in the area marked as A was verified by EDS analysis (figure 4(c)). Figure 4(d) shows the peaks of B, O and Zr elements, and combined with the XRD analysis of figure 3, it was indicated that these particles may be ZrB\(_2\) and Al\(_2\)O\(_3\).
3.2. Effects of magnetic and ultrasonic fields in different stages on nanoparticles distribution of composites

The influences of different parameters of magnetic field applied during the reaction and ultrasonic field applied in the solidification on nanoparticles distribution of the in situ 3 vol% (ZrB2 + Al2O3)np/AA6111 composites are shown in figure 5. The SEM images show that the large ZrB2 and Al2O3 particle clusters were distributed along the grain boundaries. Figure 5(a) shows that with the assistance of single low frequency (10 Hz) magnetic field applied during in situ reaction process, the large size of ZrB2 and Al2O3 particles was between 80 to 120 nm, and the particles shape were quadrangular or polygon. As shown in figure 5(b), the size of particles in the matrix was significantly reduced to 50–100 nm by the applied single ultrasonic field (1.0 kW) in the semi-solid stage during solidification. However, the particles volume fraction was very small. Figures 5(c)–(e) displays the SEM images of microstructure and particles in AA6111 composites synthesized with magnetic field applied in the in situ reaction and ultrasonic field introduced in solidification. As shown in figure 5(c), the magnetic frequency is 5 Hz, and the ultrasonic power is 1 kW. The amount of nanoparticles was barely increased and the nanoparticles distribution was slightly improved compared with single field. Besides, the size of nanoparticles was also slightly decreased compared with figure 5(a). Therefore, it can be concluded that the nanoparticles volume fraction was mainly affected by the magnetic frequency applied during in situ reaction, and the ultrasonic power applied during the solidification process mainly affected the distribution and size of the nanoparticles [14]. When the ultrasonic power increased from 1 kW to 1.5 kW, however, the size of nanoparticles became larger again (figure 5(d)). Figure 5(e) shows that the smaller particle clusters were evenly distributed across the grain boundaries and the nanoparticle size had apparently reduced to the ranging from 10–80 nm when the magnetic frequency was 10 Hz, and the ultrasonic power was 1 kW. In addition, the amount of in situ nanoparticles was considerably increased, indicating that the production of binary nanoparticles was improved. Meanwhile, the mainly ZrB2 and Al2O3 nanoparticles exhibited hexagon morphology; sharp corners were obviously blunted and form a spherical shape which can be seen from the high magnification image of local area in figure 5(e). Figure 5(f) shows that upon further increasing the ultrasonic power to 1.5 kW, however, the size of particle clusters increased again and the distribution become uneven in the composites. At the same time, the nanoparticles coarsened again with the size ranging from 60–100 nm. Figure 5(g) was the high magnified SEM image of (ZrB2 + Al2O3)np morphology under the assistance of magnetic (10 Hz) and ultrasonic (1.0 kW) fields, it indicated that Al2O3 nanoparticle was spherical-shape, while ZrB2 nanoparticle was square. The
Figure 5. SEM microstructure of (ZrB$_2$ + Al$_2$O$_3$)$_{np}$/AA6111 composites synthesized with different magnetic frequencies and ultrasonic powers: (a) 10 Hz, 0 kW; (b) 0 Hz, 1.0 kW; (c) 5 Hz, 1.0 kW; (d) 5 Hz, 1.5 kW; (e) 10 Hz, 1.0 kW; (f) 10 Hz, 1.5 kW. (g) High magnified SEM image of (ZrB$_2$ + Al$_2$O$_3$)$_{np}$ morphology (10 Hz, 1.0 kW).
optimized magnetic frequency and ultrasonic power for \((\text{ZrB}_2 + \text{Al}_2\text{O}_3)_{\text{np}}/\text{AA6111}\) fabrication were 10 Hz and 1.0 kW, respectively. There were obvious beneficial effects under the optimized external fields, in terms of the increase of the distribution uniformity and nanoparticles quantity in the matrix and the decrease of particle size.

When the magnetic field is applied \textit{in situ} reaction process, the working mechanism [23] is mainly based on two aspects: (1) the interaction between magnetic field and metal liquid leads to the appearance of induced current; (2) magnetic field interacts with current-carrying metal liquid to form electromagnetic force. When a current of density \(J\) passes in the metal liquid, a magnetic field with a magnetic induction strength of \(B\) is perpendicular to the current density [24], and a Lorentz force \(F_{\text{EM}}\), which can be described by the following equation [25] will be apply on the metal liquid:

\[
F_{\text{EM}} = J \times B (\text{N} \text{m}^{-3})
\]  

As a result, the metallic liquids are constantly driven by electromagnetic forces to flow in the crucible. In the \textit{in situ} reaction, during the process of nucleation and growth, the Lorentz force \(F_{\text{EM}}\) provided by magnetic field induces the aluminum liquid in violent mixed convection state, and intensifies heat and mass transfer, improves the contact probability of aluminum melt and reactants, thus promotes the chemical reaction and increases the number of reinforced particles in the matrix structure. In the final stage of diffusion, the mixing of the aluminum matrix and the reinforcing particles can be accelerated by stirring, thereby promoting the distribution of the reinforcing nanoparticles in the aluminum matrix [26]. Proper magnetic induction \(B\) is particularly important during \textit{in situ} reaction preparation. If the magnetic induction is too low, the stirring effect is insufficient. Conversely, if it is too high, the strong centrifugal force will make the particles move to the edge and gather into large clusters, which will greatly deteriorate the dispersion of particles. When the ultrasonic field is introduced into solidification process, different from the application of ultrasonic field in the \textit{in situ} reaction stage, the temperature of the melt is greatly reduced from above 850 °C to 650 °C–700 °C, which is beneficial to reduce the corrosion of ultrasound probe in aluminum solution. The ultrasonic wave will generate the chaotic cavitation regions and enhanced acoustic flow, and the solidifying phases and the Liquid–Solid interface are easily broken up attributed to the bursting of bubbles and the highspeed acoustic flow [27, 28]. More importantly, the bubble fragments produced by implosion bubbles can be used as the bubble nuclei of the next bubble evolution cycle. The cyclic fatigue effect caused by the momentum of the oscillating bubble and the sound wave flow is the main mechanism for breaking up the solidified phase at the liquid-solid interface [29]. Besides, the acoustic enhanced flow contributes to break up the solid flow or redistribute it back to the bulk liquid or semi-solid melt, restraining the sedimentation of particles and promoting grain rounding. In the subsequent solidification process, these solid fragments played the role of new crystal nuclei or small particles, which effectively promoted the tissue refinement and chemical homogeneity of the solidified composite material. In addition, the large cavitation bubbles float upward and escape from the melt surface, helping to degas the matrix [30]. As a result, the porosity in the ultrasonic degassing matrix is significantly reduced, which leads to an improvement in mechanical properties [31].

3.3. The refinement grain size of composites under the magnetic and ultrasonic fields

The grain refinement results of \((\text{ZrB}_2 + \text{Al}_2\text{O}_3)_{\text{np}}/\text{AA6111}\) composites synthesized under different magnetic frequencies and ultrasonic powers are shown in figure 6. It can be seen that the average grain size was 125 ± 10 μm in the \((\text{ZrB}_2 + \text{Al}_2\text{O}_3)_{\text{np}}/\text{AA6111}\) composites when no external field was applied (figure 6(a)). However, the average grain size was reduced to 116.2 ± 12 μm and 100.9 ± 11 μm for the composites refined by applied single magnetic field in reaction process (figure 6(b)) and ultrasonic field in solidification process (figure 6(c)), respectively. These revealed that both magnetic field and ultrasonic field applied into the preparation process could refine the \((\text{ZrB}_2 + \text{Al}_2\text{O}_3)_{\text{np}}/\text{AA6111}\) composites, although the grain refinement was not very effective. It was clear that the grain size can be further refined when the composites synthesized with magnetic and ultrasonic fields in different stages of composites preparation. As shown in figure 6(d), the average grain size in the centre of the ingot was about 94.6 ± 11 μm when the magnetic frequency was 5 Hz, and the ultrasonic power was 1 kW. An increase in the ultrasonic power to 1.5 kW, reduced the grain size to 80.0 ± 11 μm, as shown in figure 6(e). Moreover, when the magnetic frequency increased to 10 Hz, and the ultrasonic power was 1 kW, the effect of grain refinement was the best, which reduced to 50.4 ± 12 μm (figure 6(f)). Nevertheless, when the ultrasonic power increased to 1.5 kW, the grain size has a slight increased again, approximately to 68.8 ± 12 μm (figure 6(g)).

The mechanism of α-Al grain refinement by the application of ultrasonic field during solidification can be described in the following two stages: above the liquidus temperature at the stage 1, the effect of the grain refinement is well improved possibly by wetting of \text{ZrB}_2 and \text{Al}_2\text{O}_3 nanoparticles and de-agglomeration [32, 33]. The acoustic streaming helps to distribute nanoparticles evenly in the melt. During the stage 2, below the liquidus temperature, the nucleation of grains will be enhanced by cavitation, which may also promote the breakage and detachment of grains formed on the ultrasonic generator. In addition to transmitting the grains,
Figure 6. Optical micrographs showing the grain size of (ZrB$_2$ + Al$_2$O$_3$/AA6111 composites synthesized at different magnetic frequencies and ultrasonic powers: (a) without external fields; (b) 10 Hz, 0 kW; (c) 0 Hz, 1.0 kW; (d) 5 Hz, 1.0 kW; (e) 5 Hz, 1.5 kW; (f) 10 Hz, 1.0 kW; (g) 10 Hz, 1.5 kW.
the acoustic streaming also produces a uniform undercooling temperature in the melt \[34\], thereby ensuring the survival of these new grains and producing a uniform fine grain size throughout the composites ingot.

3.4. Hardness of AA6111 alloy and (ZrB\(_2\) + Al\(_2\)O\(_3\))\(_{np}\)/AA6111 composites

Variation of Vickers hardness of the AA6111 alloy and 3 vol\% (ZrB\(_2\) + Al\(_2\)O\(_3\))\(_{np}\)/AA6111 composites with different magnetic frequencies and ultrasonic powers are shown in figure 7. The results show that the hardness of the composites is significantly improved compared to the AA6111 alloy. This is because the hard (ZrB\(_2\) + Al\(_2\)O\(_3\)) nanoparticles increase the dislocation density in the aluminum matrix \[35\]. Furthermore, the hardness of the composites was further improved with the introduction of magnetic field/ultrasonic field, and increased with the increase of magnetic field frequency and ultrasonic power. Especially when the magnetic field frequency is 10 Hz and the ultrasonic power is 1 kW, the hardness of the composite material (142.2 HV) is the highest. Due to the effect of the magnetic field and the ultrasonic field, the grains are refined, and the better bonding between the matrix and the particles also contributes to the improvement of the hardness of the composites \[36\]. However, when the ultrasonic power is increased to 1.5 kW, the hardness value decreases.

3.5. Tensile properties of (ZrB\(_2\) + Al\(_2\)O\(_3\))\(_{np}\)/AA6111 composites

The tensile properties of the AA6111 alloy and 3 vol\% (ZrB\(_2\) + Al\(_2\)O\(_3\))\(_{np}\)/AA6111 composites in T6-treated condition (solution treatment and artificial aging) are shown in figure 8. Table 3 shows the values of hardness, ultimate tensile strength (UTS), yield strength (YS) and elongation for AA6111 alloy and the composites with different magnetic frequencies and ultrasonic powers. The results indicated that the introduction of ZrB\(_2\) and Al\(_2\)O\(_3\) nanoparticles significantly improved tensile strength, yield strength and elongation. Moreover, no matter
a single low frequency magnetic field applied into in situ reaction process or a single ultrasonic field applied in the semi-solid composites melt in solidification, the properties of the composites were further increased compared with those of the composites produced without any external fields. It was importance to note that the tensile strength has been remarkably enhanced by the introduction of both magnetic field and ultrasonic field, but the values of the yield strength and elongation showed no obvious increased. Especially, when the magnetic frequency and the ultrasonic power increased to 10 Hz, and 1 kW, respectively, the fabricate composite possess the highest mechanical properties, and the tensile strength, yield strength and elongation of 355.4 MPa, 259.4 MPa and 22.4%, respectively, which were 21.5%, 12.7% and 29.5% higher than that of AA6111 alloy and 1.21, 1.13 and 1.29 times better than that of the composite synthesized without any external fields. However, when the magnetic frequency is 10 Hz, continue to increase the ultrasonic power to 1.5 kW, the tensile strength, yield strength and elongation were decreased, which was attributed to the nanoparticles coarsened and the clusters distributed unevenly again in the composites. All in all, the findings from the tensile curve of composites were consistent with the results acquired from the microstructures shown in figure 5.

3.6. Strengthening mechanisms of the nanocomposite

According to the experimental results showed in table 3, it can be found that (ZrB2 + Al2O3) nanoparticle can significantly improve the mechanical properties of materials. In particularly, when the cooperation of magnetic field and ultrasonic field applied in different preparation stages of composite materials, the uniformity of the ZrB2 and Al2O3 nanoparticles distribution in the matrix was improved, and the matrix grains got more refined, which contributed to improving the tensile strength and yield strength. In this work, Orowan strengthening, Grain-refined strengthening and Dislocation strengthening may be the principal strengthening mechanisms

Table 3. Values of mechanical properties for AA6111 alloy and the composites with different magnetic frequencies and ultrasonic powers.

| Specimen | Hardness (HV) | UTS (MPa) | YS (MPa) | Elongation (%) |
|----------|--------------|-----------|----------|----------------|
| AA6111 alloy | 105.9 | 260.1 | 192.4 | 16.8 |
| AA6111 composite without external fields | 120.5 | 292.6 | 230.1 | 17.3 |
| AA6111 composite under 10 Hz and 0 kW | 125.8 | 308.1 | 221.0 | 17.1 |
| AA6111 composite under 0 Hz and 1 kW | 130.4 | 304.3 | 243.6 | 18.2 |
| AA6111 composite under 5 Hz and 1 kW | 136.6 | 324.6 | 244.1 | 18.6 |
| AA6111 composite under 5 Hz and 1.5 kW | 138.8 | 329.7 | 244.8 | 18.7 |
| AA6111 composite under 10 Hz and 1 kW | 142.2 | 355.4 | 259.4 | 22.4 |
| AA6111 composite under 10 Hz and 1.5 kW | 135.7 | 320.6 | 240.2 | 20.1 |

Figure 9. Fracture surfaces of the (a) AA6111 alloy and the composites prepared without (b) and with magnetic/ultrasonic fields (c) 10 Hz, 1 kW.
for (ZrB₂ + Al₂O₃) nanocomposites. According to Orowan strengthening, the introduction of ZrB₂ and Al₂O₃ nanoparticles can improve the yield strength of the composite by the interaction between dislocations and the dispersed particles in the Al matrix. When the composite is in a plastically deformed state, the ZrB₂ and Al₂O₃ nanoparticles with high elastic modulus can hinder the movement of dislocations, thus a large number of dislocation lines surround the particles, as shown in figure 10, which significantly improving the yield strength of the material. As the volume fraction of nanoparticles increases, this strengthening effect gradually increases, thus, it is also proved that the increase of particle volume fraction due to the introduction of magnetic field in the in situ reaction stage is beneficial to the improvement of mechanical properties of materials.

Secondly, the grain boundary can be used as a barrier for dislocation slip and dislocation source movement. The smaller the grain size is, the more the grain boundary is, the more obvious the grain boundary deformation is, which is beneficial to prevent the growth and propagation of cracks. Therefore, fine grain strengthening can lead to the improvement of elongation and higher tensile strength. The effect of grain size on the yield strength of composite can be expressed by the well-known Hall-Petch relationship by the equation:

\[ \Delta \sigma_y = k(d^{-1/2} - d_0^{-1/2}) \]  

Where \( \Delta \sigma_y \) is the yield strength contribution from grain refinement, \( d \) and \( d_0 \) are the grain size of composite and unreinforced matrix, respectively, \( k \) is the Hall-Petch slope, which is 70 MPa\( \mu \)m\(^{1/2}\) for pure Al. As a result, the yield strengthening \((\Delta \sigma_y)\) caused by grain refinement is calculated to be 12 MPa.

Thirdly, there is a significant difference between the thermal expansion coefficient of ceramic particles (ZrB₂: 6.88 \( \times \) 10\(^{-6}\) K\(^{-1}\), Al₂O₃: 7.92 \( \times \) 10\(^{-6}\) K\(^{-1}\)) and aluminum matrix (23.8 \( \times \) 10\(^{-6}\) K\(^{-1}\)). Therefore, a few dislocations are produced around the nanoparticles, improving the yield strength of the material. Furthermore, figure 11 shows a high-resolution TEM (HRTEM) image of the in situ (ZrB₂ + Al₂O₃)\(_{np}\)/AA6111 composites. It can be seen from the picture that the interface between the matrix and particle is well combined, no harmful intermediates were found, suggesting a high bonding strength, which ensures these nanoparticles can share the load applied on the matrix, thus improving the bearing capacity of the composite.

4. Conclusions

In this study, the (ZrB₂ + Al₂O₃)\(_{np}\)/AA6111 matrix composites were fabricated from Al- Na₂B₄O₇- K₂ZrF₆ system by in situ chemical reaction at 850 °C. The effects of magnetic field applied in situ reaction stage and ultrasonic field employed in solidification on the microstructures and mechanical properties of the composites were investigated. The following was drawn as:

(i) With the assistance of the magnetic field in reaction process and ultrasonic field in solidification process, the smaller ZrB₂ and Al₂O₃ nanoparticle clusters were distributed evenly in the matrix. The optimized magnetic frequency and ultrasonic power for (ZrB₂ + Al₂O₃)\(_{np}\)/AA6111 fabrication were 10 Hz and 1.0 kW, respectively.
The average size of reinforcing nanoparticulate of optimized composites was 10–80 nm and the grain size of composites was refined to 50.4 ± 12 μm. The mainly ZrB$_2$ and Al$_2$O$_3$ nanoparticles exhibited hexagon and spherical-shape morphology.

The mechanical properties testing shows a significantly enhancement of mechanical properties in the (ZrB$_2$ + Al$_2$O$_3$)$_{np}$/AA6111 composites by the combination of the magnetic field in reaction process and ultrasonic field in solidification. The highest Vickers hardness, tensile strength, yield strength and elongation were 142.2 HV, 355.4 MPa, 259.4 MPa and 22.4%, respectively, which were 34.3%, 21.5%, 12.7% and 29.5% higher than that AA6111 alloy.

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Data availability

The raw data/processed required to reproduce these findings are available from the corresponding author upon reasonable request.

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