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Preparation of in-situ ZrB2/A356 composites and high-temperature tribological studies

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Abstract

The ZrB2/A356 composite material was prepared by using chemical in situ reaction technology. The high-temperature friction and wear test of ZrB2/A356 aluminum matrix composites was carried out. The friction and wear test temperatures were normal temperatures, 50 °C, 100 °C, 150 °C, 200 °C, 250 °C, and 300 °C. XRD, TEM, SEM, and XPS were used to analyze the microstructure, phase and the formation of surface compounds of the composites under different wear temperatures. The results show that the composite phase is composed of ZrB2 and α-Al, and there is a small amount of Al-Si eutectic phase; ZrB2 particles are small, hexagonal nearly elliptical, flocculent and well bonded to the matrix; Combined with the stress-strain curve and tensile fracture morphology analysis, the composite material is a ductile fracture, and the plasticity of the A356 alloy is higher than that of the composite material; The wear properties of composites are susceptible to temperature changes, and the wear rate is small below 200 °C. The wear mechanism is mainly oxidative wear and abrasive wear. When the temperature reaches above 250 °C, the wear rate begins to rise sharply, and a large number of plastic deformation traces and wear debris appear on the surface of the wear spot, and the surface of the wear debris adheres to the protrusions. The primary wear mechanism is adhesive wear. In the stages of oxidative wear, and abrasive wear, although the friction coefficient changes, it is stable. But in the adhesive wear stage, the friction coefficient becomes very unstable and a sharp peak appears. XPS analysis showed that the compounds formed in the wear scar were mainly Al2O3.

1. Introduction

A356 aluminum alloys are increasingly used in the automotive industry in recent years in the context of the era of automotive lightweight because of their excellent casting properties [1–3]. Especially in complex castings with high requirements such as automotive wheels, engine blocks, and cylinder heads, traditional aluminum alloys are increasingly difficult to meet the demand [4–6]. Compared with conventional aluminum alloys, nanoscale reinforced aluminum alloys have higher specific strength and specific stiffness, better fatigue and wear resistance, better damping properties, and stable performance at high temperatures. The commonly used reinforcing phase particles in aluminum matrix composites are TiC, TiB2, Al2O3, and ZrB2. ZrB2 as a hexagonal crystal system quasi-metallic structure compound with lattice constant a = 3.169Å, b = 3.533Å and atomic bonding between Zr and B chemically. Its chemical bonding and atomic structure determine its high hardness, low coefficient of thermal expansion, low density, and good seismic properties, as well as exhibiting good oxidation resistance and high strength under high-temperature conditions [7, 8]. There have been some reports on ZrB2 nanoparticles. Erdem et al prepared ZrB2 nanoparticles by self-propagating high-temperature synthesis and found that the addition of a certain amount of NaCl could significantly refine the ZrB2 particles; Zhang et al obtained submicron particle-reinforced (Al7Zr + ZrB2)/A356 composites by low-power ultrasound (less than
was pressed into the aluminum solution, and a magnetic field was applied for electromagnetic stirring with a frequency of 20 Hz, and the reaction was carried out for 30 min under this condition. The temperature of the reaction process, and the workpiece is easy to produce cracking. AMCs prepared by the in situ generation method have a good matrix and reinforcement binding, good wear resistance, and clean particle surface. In recent years, studies have focused on the applied nanoparticle method or in situ endogenous micron-scale reinforced composites, while the in situ reaction is regulated by an applied magnetic field to prepare light alloy composites has rarely been reported. In this paper, the composite (A356 + ZrB2) was prepared by studying a new Al-Zr-B alloy system with A356 alloy as the matrix, and the morphology of the ZrB2 reinforced phase was investigated by XRD, SEM and TEM for phase analysis. The friction and wear properties of (A356 + ZrB2) composites were investigated by high-temperature friction and wear experiments. The investigation of the effect of temperature on the friction and wear properties of (A356 + ZrB2) composites and the associated mechanisms were carried out by analyzing the morphology of the wear surface, the friction coefficient, and the wear rate.

2. Materials and methods

2.1. Preparation of particle reinforced AMCs

The materials tested were cast aluminum A356 (the micro-element chemical composition of which is shown above), K2ZrF6, and KBF4. All three materials were purchased from Jiangsu Juyuan Experimental Technology.

The reaction equations involved in the in situ formation of ZrB2 [14]:

\[
\begin{align*}
K_2Zr + 13/3AL &\rightarrow AL(Zr) + 4/3AlF_3 + 2KF \\
2KBF_4 + 3AL &\rightarrow ALB_2 + 2AlF_3 + 2KF \\
\text{Al}_2Zr + \text{AlB}_2 &\rightarrow \text{ZrB}_2 + 4\text{Al}
\end{align*}
\]

The two fluorine salts were kept in a desiccator under a vacuum at 200 °C for 3 h to dry. After cooling, K2ZrF6 (93.2 g) and KBF4 (97.7 g) were mixed and ground in a ball mill (YXQ-4L), the rotational speed is 250r min⁻¹, and the fluorine salts were mixed well and wrapped in aluminum foil to form a small package for backup. The A356 aluminum alloy (1200 g) was melted and heated in a graphite crucible, and the prepared fluorine salt was pressed into the aluminum solution, and a magnetic field was applied for electromagnetic stirring with a frequency of 20 Hz, and the reaction was carried out for 30 min under this condition. The temperature of the solution was measured with a thermocouple during the reaction to ensure that the temperature was maintained at 870 °C. The slag was removed at the end of the reaction time and then poured into the copper model to obtain the electromagnetic stirred in situ endogenous ZrB2 nanoparticle reinforced composite (200 mm × 100 mm × 20 mm, L × W × H).

2.1.1. Microstructure characterization of particle reinforced AMCs

Polish the sample with 400 #, 600 #, 800 #, 1200 #, 1500 #, 2000 # sandpaper, and then use the metallographic polishing paste to polish on the polishing machine. The phase structure of the samples was studied by physical phase analysis using a BRUKER D8 ADVANCE x-ray diffractometer, the microstructure of the prepared samples was viewed by Zeiss Merlin Compact SEM and JEM-2100F transmission electron microscopy, and the enhanced phases were analyzed by EDS spectroscopy.

| Elements | Si   | Mg | Ti | Fe | Mn | Zn | Sn | Al |
|----------|------|----|----|----|----|----|----|----|
| Weigh%   | 7.2  | 0.42 | 0.15 | <0.12 | <0.1 | <0.05 | <0.01 | Bal |

Table 1. Trace element chemical compositions of aluminum A356.
2.2. Tensile properties testing of particle-reinforced AMCs
The tension properties of A356 alloy and ZrB2/A356 composite were tested on a material testing machine. The total length of the tensile specimen is 60 mm, the parallel size is 20 mm, and the width is 13 mm. The elongation was calculated after stretching. Tensile fractures were analyzed by SEM.

2.3. Friction performance analysis of aluminum matrix composites
Wire cut the composite into 15 mm \( \times \) 15 mm \( \times \) 4 mm (L \( \times \) W \( \times \) H) sample. Variable temperature test using HT-1000 high-temperature friction and wear tester. The load is 6N, the speed is 150r min\(^{-1}\), and the test temperature is average, 50\(^\circ\)C, 100\(^\circ\)C, 150\(^\circ\)C, 200\(^\circ\)C, 250\(^\circ\)C, and 300\(^\circ\)C for dry sliding friction test. The wear scars of the samples were characterized by SEM, EDS, and 3D laser confocal microscopy. XPS is used to analyse the formation of chemicals on worn surfaces.

3. Materials and methods

3.1. Phases of in situ generated aluminum matrix composites
Figure 2(a) is the XRD pattern of the composite prepared. According to the figure, it can be observed that the prepared aluminum matrix composites are mainly composed of Al, Si, and ZrB\(_2\) reinforcements. The Al-Si eutectic phase is formed during solidification at the Al grain boundary, due to the high reaction temperature and active atoms. As shown in figure 2(b).

Figure 3 displays the SEM Image of the prepared composite. The reinforcements of the materials prepared at this temperature are uniformly distributed on the whole. The particle morphology is mainly square or hexagon, and there are also nearly elliptical particles with round shapes. The particle size of the reinforced phase is 15–90 nm. Figure 3 shows the EDS energy spectrum analysis of the points marked by the arrows in, which shows the presence of Al, Si, Zr, and B elements. Combining the previous XRD analysis results and the reaction equation for the analysis, the enhanced phase particles can be identified as ZrB\(_2\) particles. The improved phase ZrB\(_2\) particles are fine and exist in the form of agglomerated flocs.

To further characterize the morphological features of the reinforcing phase in AMCs, TEM observation and characterization were performed. The results are shown in figure 4, which is a TEM of reinforcing phase ZrB\(_2\).
particles, and it can be shown that the reinforcing phase of the ZrB$_2$/A356 composite shows hexagonal and sub elliptical reinforcing particles with a pure interface and no other generated phases.

Studies of the mechanical properties show that the tensile strength $\sigma_b$ of the ZrB$_2$/A356 composite is substantially higher than that of the matrix A356, but the elongation $\delta$ decreases. The yield strength $\sigma_y$ of ZrB$_2$/A356 composite material is 240.7 MPa, which is 21% higher than the 197.8 MPa of matrix A356. The elongation $\delta$ of the composite material decreased by 10.5%.

Figure 3. SEM image and EDS analysis results of the reinforced phase particles in the composite.

Figure 4. TEM image of ZrB$_2$/A356 composite reinforced phase particles.

Figure 5. Tensile stress—strain curves of ZrB$_2$/A356 composites and A356 alloy.
The tensile fracture morphology of the aluminum matrix composite shown in figure 6, shows the tensile fracture morphology of ZrB$_2$/A356 composites. Use the tensile tester model DDL100. As can be seen from the diagram, the composite specimen has many pits and torn edges at the tensile fracture. Small particles are distributed in the dimples, and the tearing edges are finely curved and entangled. The primary fracture mode is dimple fracture. And the size of the tough nests is not uniform, only a few of them are equiaxed challenging nests, and the challenging nests are shallow, indicating the plasticity of ZrB$_2$/A356 composites is not high. However, the number of dimples and tearing edges on the tensile fracture of the A356 matrix is relatively large, and the fracture is plastic. At the same time, the dimple size is small and deep, indicating that its corresponding elongation is better than that of ZrB$_2$/A356 composite material.

3.2. Study of friction properties of ZrB$_2$/A356 composite material composites
Friction factor profiles for AMCs at different test temperatures using the HT-1000 high-temperature friction and wear tester are shown in figure 8(a). The friction process parameters were 6N load. The friction speed is 150r min$^{-1}$. The friction time is 30 min, and the grinding ball is SiN, the friction radius is 4 mm. According to figure 8(a), the significant ups and downs of the composite friction coefficient curve are due to the considerable variation of the friction coefficient in the first few seconds at the beginning of the friction test. As the friction test proceeds, the friction coefficient rises rapidly. This is since during the initial run-in phase of friction, the more enormous load is carried on the ZrB$_2$ reinforced particles, the actual contact area between the composite material and the friction sub is small, the resistance during friction is more minor, and the friction coefficient is more minor. As the friction test proceeds, the contact area increases, the friction resistance gradually increases, and the value of the friction coefficient climbs rapidly [2, 15, 16]. At lower temperatures (room temperature, 50°C, 100°C, 150°C), the overall friction coefficient of ZrB$_2$/A356 composites was relatively flat, with less fluctuation as the test proceeded, no sharp peaks, and relatively stable friction properties. However, as the test temperature increased, the friction coefficient of the composite began to fluctuate significantly, and the
fluctuation was more evident as the test proceeded \cite{17, 18}. Figure 8(b) shows the variation of the average friction coefficient for different experimental temperatures.

3.3. Study of wear mechanism of AMCs

Several wear mechanisms are recognized for abrasive wear, fatigue wear, corrosion wear, peeling wear, and adhesive wear. Yet the wear behavior of ZrB$_2$ particle-reinforced AMCs becomes quite complex, mainly in terms of oxidation wear, abrasive wear, and adhesive wear. However, as the test conditions change, the wear mechanism of ZrB$_2$ particle-reinforced AMCs changes accordingly. Either a particular form of wear or several forms of wear exist at the same time; either a specific form of wear is dominant, accompanied by other wear, or the combined effect of several wears.

Figures 9(a)–(g) show the wear surface morphology of ZrB$_2$/A356 composites at different test temperature conditions. From figures 9(a), (b), it can be illustrated that the scratches are parallel to the sliding direction, the abrasion marks are shallow, there are fine abrasive chips, shallow grooves, and tiny cracks on the surface of the composite material. There are also a few tear pits left by the material being torn by adhesion, and the wear mechanism is mainly adhesion wear and a small amount of abrasive wear. With the increase of the test temperature, the friction surface produced an oxide layer covering \cite{19, 20}. As shown in figures 9(c), (d) can be observed that the composite surface oxide layer received damage, producing a large number of abrasive chips, plastic deformation increased, there is material off the appearance of the crater. As the friction test proceeds, the friction is repeated, the material is continuously cut, sheared, and tiny cracks are generated on the friction pressure surface and gradually grow to the friction surface. When the crack elongates to a given length, the material between the crack and the surface exfoliates in the form of flakes of abrasive debris, so the wear mechanism is flake wear \cite{19}. As shown in figures 9(e), (f), a stair-like pattern appears, with increased wear and cracks on the abraded surface. The softening of the material has resulted in an improvement in the contact area between the friction sub and the composite material and an increase in the coefficient of friction. Severe plastic deformation occurred on the surface of the abrasion marks, a large number of obvious cracks existed, material shedding was serious, and the main wear mechanisms were adhesive wear and oxidative wear. As shown in figure 9(g), due to the dual influence of friction heat and applied high temperature, the material adhesion phenomenon is serious, the material after friction and then stick to the surface of the abrasion marks to form a

![Figure 8](image_url)

**Figure 8.** (a) Coefficient of friction as a function of time for aluminum matrix composite tested at different temperatures (b) Average friction coefficient at different test temperatures.
Figure 9. SEM images showing the surface morphology of the composite abrasion (a) 30 °C (b) 50 °C (c) 100 °C (d) 150 °C (e) 200 °C (f) 250 °C (g) 300 °C.

bump, the friction coefficient fluctuations are very violent at this time. Figure 10 shows the XPS spectra of the abrasion marks, as shown in the figure Al2p is present in the form of Al3+ at the peak of the binding energy of 74.3 eV, which corresponds to the Al element in Al2O3; O1s is present in the form of O2− at the peak of 531.8 eV, which corresponds to the O element in Al2O3, thus proving the existence of the Al2O3 oxide film. The oxide film can reduce the friction coefficient, similar to the principle of lubricating film, which makes the surface roughness
Figure 9. (Continued.)

Figure 10. XPS analysis of the worn surfaces of AMCs.
decrease significantly and the friction coefficient decreases. In the \textit{in situ} reaction process, trace amounts of Al$_2$O$_3$ and other by-products are generated, and there are no obvious diffraction peaks in the XRD pattern, as well as no obvious by-product organization, which proves that the amount of Al$_2$O$_3$ and other by-products generated is small, and the impact on the microstructure and properties of the composite material is negligible [21–23].

The 3D images of the wear marks of ZrB$_2$/A356 composites at different friction test temperatures are shown in figure 11, from which the wear of the composites can be seen. At low temperatures, the depth of the wear marks is shallow, and the surface is rough. As the experimental temperature increases, the width of the wear marks becomes more expansive, and the depth becomes more profound. Under the high-temperature friction test condition, the surface oxidation of the composite material was severe, and a large amount of oxide layer peeled off with the friction, which made the wear marks more undulating [24–26]. As shown in figure 11(g), a large amount of peeled composite material adhered to the surface to form a bump, and because of the severe oxidation, the friction performance decreased.

Using a laser confocal microscope (LEXTOLS4000) to observe and measure the abrasion marks of the composite material at various temperatures, different abrasion cross-sections at different locations were selected, and three abrasion marks were selected at each location to measure the average cross-sectional area of the abrasion marks. The wear rate was obtained using the equation $K = \frac{CS}{FL}$, C is the circumference, S is the cross-sectional area, F is the load, and L is the length of the abrasion marks [27, 28]. The calculated wear rate is shown in figure 12 (the wear rate could not be calculated because the abrasion marks were in the form of a bump at 300 °C). It can be seen that the wear rate of the composite material is lowest at the test temperature of 200 °C. Due to the oxide film covering the surface at high temperatures, a mechanically mixed layer is formed on the
surface of the composite material, which improves the wear resistance of the composite material, and reduces the wear rate \[29]\.

4. Conclusion

1. ZrB₂/A356 composites were prepared by a chemical in situ reaction process. XRD results showed that the prepared composites consisted of three phases: Al matrix, Si phase, and ZrB₂ reinforced phase; SEM analysis showed that the prepared materials were dense, with defects such as pores, and the reinforced phase was very small and agglomerated; TEM analysis showed the presence of the reinforced phase ZrB₂ and the interface was pure.

2. The plasticity and tensile rate of ZrB₂/A356 composites are lower than those of A356 alloy, and tensile fracture is mainly in the form of tough nest fracture. The tensile fracture of A356 alloy is mainly in the form of plastic fracture.

3. When it is below 200 °C, the wear rate of composite material is low and shows slight wear; but when the temperature increases above 250 °C, the wear rate rises sharply and enters the severe wear stage.

4. At room temperature, the friction factor of the composite material is stable, and the friction coefficient shows an increasing trend as the temperature increases; when the temperature exceeds 200 °C, the friction factor is unstable, and the curve shows a sharp peak, and this difference is closely related to the change in the shape of the wear spot.

5. When the temperature is below 200 °C, the primary wear mechanism is oxidation wear and abrasive wear. When the temperature reaches above 250 °C, the wear rate starts to rise sharply, and a large number of plastic deformation traces and wear debris appear on the surface of the wear spot, in contrast, the raised surface of the abrasive chip adhesion appears, and the primary wear mechanism is mainly adhesion wear.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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