In situ (Al₃Zr + Al₂O₃np)/2024Al metal matrix composite with novel reinforcement distributions fabricated by reaction hot pressing

B. Kaveendran a, G.S. Wang a,⇑, L.J. Huang a, L. Geng a, H.X. Peng b

a School of Materials Science and Engineering, Harbin Institute of Technology, P.O. Box 433, Harbin 150001, PR China
b Advanced Composites Centre for Innovation and Science (ACCIS), Bristol University, Bristol BS8 1TR, United Kingdom

A R T I C L E   I N F O

Article history:
Received 30 May 2013
Received in revised form 21 June 2013
Accepted 24 June 2013
Available online 4 July 2013

Keywords:
Composite materials
Hybrid reinforcements
Differential thermal analysis
Sintering
Microstructure
Mechanical properties

A B S T R A C T

In situ hybrid (Al₃Zr + Al₂O₃np)/2024Al metal matrix composites with unique controlled reinforcement distributions were fabricated using low energy ball milling and reactive hot pressing. The reaction system between 2024Al and ZrO₂ was studied using differential thermal analysis (DTA). In situ formed aluminium oxide (Al₂O₃) and zirconium tri-aluminide (Al₃Zr) with varying morphology and sizes were produced under different fabricating conditions. Al₃Zr with varying morphologies such as particle, plate and flakes were observed. With a total 10 vol% of reinforcements, the composite containing a three-dimensional network of closely spaced in situ synthesized Al₃Zr and Al₂O₃ particles had a YS of 175 MPa and a UTS of 261 MPa, effectively strengthening the 2024Al matrix. The effect of different sintering conditions on the microstructure and tensile properties of the composite was systematically investigated.

1. Introduction

The past few decades have seen the extensive development of discontinuously reinforced metal matrix composites (DRMMCs) because of their good mechanical properties, formability, low costs and adaptable processing methods [1]. In particular, aluminium based DRMMCs have been widely used in the automobile, aerospace and marine sectors due to their increased stiffness, wear resistance when compared to unreinforced alloys [2,3]. Attempts to further improve the performance of DRMMCs have been reported by the tailoring of unique composites with microstructural control such as interpenetrating, quasi-continuous and bi-continuous composites [4–8]. These breeds of composites have demonstrated an improvement in performance over conventional DRMMCs, with a homogeneous microstructure.

Alongside utilising ceramic reinforcements, the use of trialuminide intermetallics (Al₃Zr, Al₃Ti, Al₃Ni, and Al₃Fe) to reinforce Al alloys have been widely investigated due to their high specific strength at ambient and high temperatures [9–12]. Trialuminide intermetallics (Al₃Zr, Al₃Ti) have been sought after for high temperature structural applications owing to their advantages, such as low density, good thermal conductivity, superior thermal stability, good machinability and easier consolidation [9,13–15]. Most notably, Al₃Zr is in thermodynamic equilibrium with the Al matrix, which means that there is a direct chemical bonding between the Al and trialuminide reinforcement rather than an intermediate reaction zone [9]. Due to its low density (4.11 g/cm³), high melting point (1580 °C) and competitive elastic modulus (205 GPa) coupled with its resistance to oxidation and corrosion, Al₃Zr is considered a potential candidate for aerospace applications [16–18]. In situ methods have been adopted to form Al₃Zr in aluminium matrices because clean interfaces between the reinforcement and matrix can be attained. Reactive hot pressing (RHP), which is similar to sintering in powder metallurgy except that chemically reactive components are made to react to form the reinforcements followed by hot compaction, has proved to be an efficient technique to in situ synthesize reinforcements in metal matrices [19,20].

Even though concerted efforts have been made to study Al₃Zr reinforced aluminium composites, little has been reported regarding the effect of sintering parameters on the reinforcement morphology, microstructural evolution and properties of these composites. Therefore, reactive sintering was employed to produce the reinforcing phases, Al₃Zr particles and Al₂O₃ nanoparticles, via the reaction between aluminium and ZrO₂ as shown in the reaction:

\[ 13\text{Al} + 3\text{ZrO}_2 \rightarrow 3\text{Al}_3\text{Zr} + 2\text{Al}_2\text{O}_3 \] (1)

Using differential thermal analysis (DTA), an attempt to study the reaction mechanism of the 2024Al/ZrO₂ system has also been made. In the present study the effects of sintering parameters – temperature, pressure and holding time – on the microstructural evolution and reinforcement morphology along with the properties of the composite has been investigated for the first time.
2. Materials and methods

2024Al alloy powders with good sphericity (50-150 μm) and commercially pure ZrO₂ powders (0.5-0.8 μm) were used for the fabrication of the composites. The elemental composition of 2024Al, in wt.%, contained Cu-4.5, Mg-1.14, Si-0.5, Fe-0.3, Mn-0.8, Zn-0.1 and the balance Al. Initially, to produce a composite with reinforcement volume fraction of 10 vol.%, 2024Al (92.1 wt.%) and ZrO₂ (7.9 wt.%) powders, were weighed and mixed using low energy ball milling, according to the expected reaction Eq. (1). The milling process was carried out in stainless steel vials with ball to powder ratio of 5:1 and 150 rpm for 2 h. Stainless steel balls with varying sizes (d = 5, 10, 15, 20 mm) were used. The use of low energy to mill the powders inhibited any reaction between the stainless steel balls and the raw materials. The milled powders did not reveal any increase in the content of Fe, thereby indicating the absence of contamination during milling. Furthermore, in order to avoid surface oxidation of the powders, the entire ball milling process was carried out in a high purity argon environment. As a result of low energy ball milling, the ZrO₂ powders were evenly dispersed on the surface of the 2024Al particles as shown in Fig. 1.

The milled powders were then transferred to a graphite mould and sintered under a pressure of 25 MPa at 600 °C for 60 min. The as-sintered composite was cut into several smaller samples and experiments with different sintering parameters were carried out as summarised in Table 1. The sintering procedures were carried out under a vacuum of 10⁻³ Pa and a heating and cooling rate of approximately 10 °C/min.

Differential thermal analysis (DTA) was carried out on the as-sintered ZrO₂/2024Al composite by heating it in the furnace of a thermal analyser (METTLER TGA/SDTA851e), with an argon environment, where the temperature was increased from 25 °C to 1000 °C at a heating and cooling rate of 10 °C/min. Tensile tests were carried out on samples with a gauge length of 15 ± 5 × 2 mm² using an Instron 5569 universal tensile testing machine with a constant crosshead speed of 0.5 mm/min. A total of three samples were tested for each material. X-ray diffraction (XRD) analysis was conducted using Philips X’pert. Scanning electron microscopy (SEM, Quanta 200FEG) and transmission electron microscopy (TEM, TECNAIF30) along with energy-dispersive X-ray spectroscopy (EDX) were used to perform microstructural examinations.

3. Results and discussion

3.1. Differential thermal analysis

The reaction between Al–ZrO₂ can be expressed as in Eq. (1). According to Zhu et al. [11] the reaction proceeds as follows,

\[ 4\text{Al} + 3\text{ZrO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Zr} \] (2)

\[ \text{Al}_y + \text{Zr}_y \rightarrow \text{Al}_2\text{Zr}_y \] (3)

The standard Gibbs free energy variation \( \Delta G \) can be expressed as,

\[ \Delta G = \Delta H - T \Delta S \] (4)

where \( \Delta H \) and \( T \Delta S \) are standard state enthalpy and standard state entropy at room temperature, respectively. Using available thermodynamic data [21] the variation of the standard Gibbs free energy for Eq. (2) can be expressed as,

\[ \Delta G = -49,600 + 45.7T \] (5)

At equilibrium when \( \Delta G = 0 \), i.e., \(-49,600 + 45.7T = 0\), \( T \) is found to be 1085.4 K (~812 °C). This is to say that Eq. (5) can take place spontaneously below 812 °C. As shown in Fig. 2 the reaction temperature in this study is well less than 812 °C. At 600 °C the value of \( \Delta G \) for Eq. (5) is ~9.7 kJ indicating Eq. (2) is spontaneous.

The DTA curve indicates the presence of two peaks, as shown in Fig. 2. One is an endothermic peak occurring at around 650 °C which corresponds to the melting of 2024Al. Another peak occurs at around 740 °C, which corresponds to the reaction as in Eq. (2). At 650 °C, the 2024Al melts to form a liquid–solid interface with ZrO₂. From 650 °C to 730 °C there is no major change in the microstructure of the composite. As the temperature is incremented to 740 °C, Al reacts with ZrO₂ firstly to form \( \text{Al}_2\text{O}_3 \). This is because the value of \( \Delta G \) for Eq. (2) at 740 °C is ~3.30 kJ which indicates that the reaction can take place spontaneously. Furthermore, the formation priority of \( \text{Al}_2\text{O}_3 \) is much more than that of \( \text{Al}_2\text{Zr} \) as reported by Zhu et al. [11]. Also, according to Eq. (1) \( \text{Al}_2\text{O}_3 \) phase must be present in the composite but XRD and SEM images did not verify clearly the presence of the \( \text{Al}_2\text{O}_3 \) particles. This could be because the \( \text{Al}_2\text{O}_3 \) particles are too fine and little. Nevertheless,

---

**Table 1** Composite nomenclature with corresponding sintering parameters.

<table>
<thead>
<tr>
<th>Composite designation</th>
<th>Temperature (°C)</th>
<th>Holding time (min)</th>
<th>Pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-sintered</td>
<td>600</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>M1</td>
<td>740</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>M2</td>
<td>840</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>M3</td>
<td>840</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>M4</td>
<td>900</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>M5</td>
<td>900</td>
<td>30</td>
<td>0</td>
</tr>
</tbody>
</table>

---

Fig. 1. Fabrication process of ZrO₂/2024Al composite.

Fig. 2. DTA curve of the as sintered ZrO₂/2024Al composite.
TEM and EDX analysis performed on the composites confirms the presence of nanoparticles comprising of Al and O, as shown in Fig. 3, which corresponds to Al$_2$O$_3$.

In spite of the fact that experimentally it was only possible to observe the presence of Al$_2$O$_3$ and Al$_3$Zr together, the much lower level of $\Delta G$ of Al$_2$O$_3$ ($\approx$1675285.5 + 329.24T) compared to that of the Al$_3$Zr ($\approx$251,383 + 319.4T) [11], suggests that Al$_2$O$_3$ may have formed prior to the formation of the Al$_3$Zr phase. From the Al–Zr binary phase diagram [22], it can be observed that when the weight percent of Zr is less than 52%, the Al$_x$Zr$_y$ phase will exist as Al$_3$Zr.

3.2. XRD analysis and microstructure

The XRD analysis and microstructure of the as sintered ZrO$_2$/2024Al composite is shown in Fig. 4 and Fig. 5(a) respectively. Two distinct regions can be observed, a continuous unreacted ZrO$_2$ phase and large 2024Al particles. A significant change in microstructure is observed at 740°C, which is directly attributed to the exothermic reaction at 740°C as indicated in Fig. 2. Since the ZrO$_2$ particles are concentrated only on the outer surface of the Al particles the reaction is limited to this region making the intended microstructural control possible. The Al$_2$O$_3$ nanoparticles, and the Al$_3$Zr blocks with polyhedron and rectangular morphologies are only distributed along the outer surface of the 2024Al particles forming a discontinuous network as shown in Fig. 5(b).

The holding time of the composite at 740°C was varied from 1 h up to 4 h. XRD analysis reveal the presence of a single ZrO$_2$ peak at 4 h when compared to 1 h as shown in Fig. 4, suggesting that the reaction has progressed. Also the number of Al$_3$Zr peaks at 4 h is more when compared to 1 h. Therefore, it can be said that the reaction progresses towards completion as the holding time is increased. From 740°C to 820°C, a holding time of 1 hr was not sufficient for Eq. (1) to complete. This is confirmed by the XRD spectra according to Fig. 4 and SEM observations of composite M1 as seen in Fig. 5(b). The presence of unreacted ZrO$_2$ particles as shown in Fig. 5(b), confirms that a time of 1 h was not sufficient for the completion of the reaction Eq. (1). The size of the Al$_3$Zr particles from 740°C to 820°C vary from 5 to 20 μm.

When the sintering temperature is raised to 840°C with a holding time of 1 hr and an applied pressure of 25 MPa, composite M2, displayed a significant change in microstructure consisting of a particle lean matrix region (Phase 1-2024 Al matrix) and a particle rich reinforcement network (Phase 2-Al$_3$Zr + Al$_2$O$_3$/2024Al) as shown in Fig. 5(c). It is important to understand that region Phase 2 is a composite phase in its own right, having a relatively high volume fraction of reinforcements when compared to the composite on a whole. In other words Phase 2 is a composite within a composite. Also, at 840°C a time of 1 h was sufficient for the completion of Eq. (1) as confirmed by the XRD analysis in Fig. 4. At 840°C with a holding time of 1 hr and no applied pressure (composite M3), the particle Al$_3$Zr transformed into plates of length up to 200 μm and a width of up to 40 μm as shown in Fig. 5(d). The time required is sufficient for the reaction to complete as established by the XRD analysis in Fig. 4. This phenomenon can be observed only in the absence of sintering pressure. The Al$_3$Zr crystal grows in a faceted manner; initially having an octagonal morphology when their size is small. Also, the final morphology of the Al$_3$Zr is determined by the migration capacity of its facets during its growth [16,23]. Therefore, it is suggested that as the energy of the system – temperature and holding time – is raised, the migration capacity of Al$_3$Zr increases leading to the growth and merging of the blocks (particles) to form plates. Furthermore, as...
proposed by Wang et al. [24] the presence of alloying elements in the Al-alloy, in the Al–Al3Ti system, can substantially modify the surface tension of the liquid alloy, thereby also altering interfacial energy of the solid–liquid interface resulting in a major change in the growth rates of the solid phase. Therefore, similarly it is suggested that the increase in interfacial energy leads to the mass transfer and merging of the Al3Zr blocks to become plates.

At 900 °C, a number of significant microstructural changes took place. When the holding time is 10 min with no applied pressure, the microstructure of the composite M4 exemplified the presence of Al3Zr with a flaky morphology as shown in Fig. 6(a). Moreover, the time required for the completion of reaction Eq. (1), is not sufficient because the XRD analysis shows traces of ZrO2 present, as shown in Fig. 4. At 900 °C, when the holding time is raised to 30 min with no applied pressure the microstructure of composite M5 indicates the presence of Al3Zr plates of length up to 200 μm and a width of up to 40 μm as shown in Fig. 6(b) similar to that of composite M3. The XRD analysis in Fig. 4 confirmed the absence of the ZrO2 phase indicating 30 min is sufficient for Eq. (1) to complete at 900 °C. Al3Zr plates with branched morphology can be observed under these fabricating conditions as shown in Fig. 6(b). Interestingly the plates appear only in the absence of sintering pressure. However, when pressure is applied at temperatures above 660 °C to the composites during the cooling stage then the microstructure transforms into that of M2 – a particle lean matrix region (Phase 1-2024 Al matrix) and a particle rich reinforcement network (Phase 2-Al3Zr + Al2O3/2024Al). These observed changes in microstructure are largely attributed to the temperature, holding time and sintering pressure of the system.

Fig. 7 shows a probable explanation of the effect of pressure on the microstructure of the composite. As the temperature is raised above 740 °C, Al2O3np and Al3Zr particles begin to form. When
the temperature and holding time is further increased, the $\text{Al}_3\text{Zr}$ particles have a tendency to merge and grow to become plates of length 200 $\mu$m and a width of up to 40 $\mu$m. If there is no pressure applied to the system during cooling, then the microstructure consists of homogeneously distributed $\text{Al}_3\text{Zr}$ plates as well as a network of $\text{Al}_2\text{O}_3\text{np}$ in the 2024Al matrix. However, when pressure is applied during the process the microstructure consists of a particle lean matrix region (Phase 1) and a particle rich reinforcement network (Phase 2).

3.3. Tensile properties

A comparison of the tensile properties of the composites is given in Table 2.

Fig. 8(a and b) reveals the fracture surfaces of the as sintered $\text{ZrO}_2$/2024Al composite; it can be seen that the $\text{ZrO}_2$ phase is continuous thereby not allowing the Al phase to be interpenetrating. This explains the limited strength of the as sintered $\text{ZrO}_2$/2024Al. It can be observed that the composite M2 with a network microstructure consisting of $\text{Al}_3\text{Zr}$ particles and $\text{Al}_2\text{O}_3$ nanoparticles display superior strength when compared to the as-sintered $\text{ZrO}_2$/2024Al composite.

As indicated by Hansen [8,25–27] for aluminium matrix composites containing a three-dimensional network of closely spaced reinforcement particles the network strengthens the matrix effectively. The small spacing between particles in such a structure shows good resistance to slip as the stresses required to push the dislocations through the particle barriers is high. Composite M2 shows a 108% increase in the yield strength and 141% increase in ultimate tensile strength when compared to the as sintered $\text{ZrO}_2$/2024Al composite. The ductility of composite M2 is significantly more than the as sintered $\text{ZrO}_2$/2024Al composite. This superior strength can be attributed to the unique microstructure of the composite which contains two phases as shown in Fig. 7. The strengthening effect of this composite can be explained by the Hashin–Shtrikman (H–S) theorem [28] where a stronger phase (Phase 2-($\text{Al}_3\text{Zr} + \text{Al}_2\text{O}_3\text{np}$)/2024Al composite) surrounds a weaker (Phase 1-2024Al matrix). This is also confirmed by the fractographs which depict tortuous crack propagation along Phase 2 of the composite, as shown in Fig. 8(c). Phase 2 has a relatively high local volume fraction when compared to the composite on a whole. The crack propagates along Phase 2 and does not divert into the large matrix regions thereby allowing Phase 2 to dominate the performance of the composite. $\text{Al}_3\text{Zr}$ particles showed brittle cleavage fracture characteristics, as shown in Fig. 8(d), implying that there is a strong interfacial bonding between the Al matrix and $\text{Al}_3\text{Zr}$ reinforcements. Additionally, cracks in the $\text{Al}_3\text{Zr}$ reinforcements indicate that the reinforcement contributes to the strengthening effect and load bearing capacity of the composite. The dimples confirm that the 2024Al phase is continuous and interpenetrating, contributing to the ductility of the composite.

Composites fabricated under the absence of sintering pressure – M3, M4, M5 – displayed mediocre tensile properties due the large number of pores present.

4. Conclusions

- $\text{Al}_3\text{Zr}$ and $\text{Al}_2\text{O}_3$ have been in situ synthesized in the 2024Al matrix at 740 °C using the 2024Al–$\text{ZrO}_2$ system.
Al3Zr displayed different morphologies – particle, plate, and flake – under different sintering conditions. The different MMCs that were fabricated consisted of a 2024Al matrix with (a) a continuous ZrO2 network, (b) a quasi-continuous network consisting of Al3Zr particles and Al2O3np, (c) a network consisting of Al3Zr flakes and Al2O3np and (d) homogeneously distributed Al3Zr plates and a network of Al2O3np.

Sintering temperature, pressure and time play a key role in determining the microstructure and mechanical properties of the (Al3Zr + Al2O3np)/2024Al MMCs. The composite with a quasi-continuous reinforcement network consisting of Al3Zr particles and Al2O3 nanoparticles effectively strengthened the 2024Al matrix.

Acknowledgements

This work was financially supported by (a) the National Basic Research Program of China (Project No.: 2012CB619600), (b) the National Natural Science Foundation of China (Project No.: 51201047 and 51228102), (c) the Fundamental Research Funds for the Central Universities (Contract No.:HIT.NSRIF.2013001) and (d) China’s postdoctoral Fund (Project No.: 20110491038). I, B. Kaveendran (first author), would like to express my gratitude to Elisha Achieng Ogada who helped me proof read this paper.

References