Preparation and microstructure of in-situ (ZrB₂+Al₂O₃+Al₃Zr)p/A356 composite synthesized by melt direct reaction

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Abstract: (ZrB₂+Al₂O₃+Al₃Zr)/A356 composites were synthesized by melt direct reaction from A356−(K₂ZrF₆+KBF₄+Na₂B₄O₇) system. The phase compositions and the microstructures of the as-prepared composites were investigated by XRD, SEM and TEM. The results show that the reinforcements are composed of ZrB₂ and Al₂O₃ ceramic phase particles and Al₃Zr intermetallic particles. The ZrB₂ particulates are easy to join together to form some particle clusters and distribute along the α(Al) grain boundary. The morphologies of the ZrB₂ particulates are in hexagon-shape with the size of about 50 nm. The TEM investigation results of Al₃Zr indicate that Al₃Zr grows in the form of facet with the length-diameter ratio of about 20. The morphologies of Al₂O₃ particles are in rectangular-shape and ellipsoidal-shape, with the size of about 0.1 μm. In addition, the interfaces of the matrix and particles are net and no interfacial outgrowth is observed.

Key words: aluminum matrix composites; melt direct reaction; in situ particle; microstructure

1 Introduction

In situ aluminum matrix composites have received widespread attention in aerospace, automobile and electronic areas because of their good performances, such as high specific intensity and stiffness, excellent high temperature mechanical properties, good abrasion resistance and excellent near-net-shape production capacity [1–5]. Compared with the traditional ex situ composites, the in situ particulate reinforced aluminum matrix composites possess more advantages in microstructure, such as clean interfaces, strong interfacial bonding, fine particles and uniform distribution in matrix. Most of the previous reports are focused on single-phase particulate reinforced aluminum matrix composites. For instance, LAKSHMI et al [6] developed TiB₂/Al matrix composite successfully in 1990’s via the melt in-situ reaction, where the exothermic reaction occurred when two kinds of reactants (K₂TiF₆ and KBF₄) were added into the aluminum melt; HUANG et al [7] fabricated α-Al₅O₃/Al–Cu–Si alloy matrix composite by creating a substitution reaction from pure Al melt and CuO, SiO₂ powders. The single-phase particulate reinforced aluminum matrix composites have less variability in properties and applications than the multi-phase particulates reinforced aluminum matrix composites (MPRACMs) because the size and the distribution of the reinforcements of MPRACMs can be mutual adjusted for the application requirements. So, the development and optimization of the MPRACMs became a new subject [8–10]. But the reports on MPRACMs are rare. Thus in this work, (ZrB₂+Al₂O₃+Al₃Zr)p/A356 MPRAC composite were synthesized by melt in-situ reaction from A356−(K₂ZrF₆+KBF₄+Na₂B₄O₇) system, and the microstructures were investigated.

2 Experimental

Raw materials were A356 alloy ingots (alloying component shown in Table 1) and three kinds of technical powders with 99.5% purity: potassium fluoroborate (KBF₄), zirconium potassium fluoride (K₂ZrF₆) and natrium boricum (Na₂B₄O₇·10H₂O). Firstly, potassium fluoroborate, zirconium potassium fluoride, natrium boricum were pre-heated to dehydrate the
bonded water in an electric oven at 523 K for 3 h. Then the dried KBF₄, K₂ZrF₆ and Na₂B₄O₇ powders were cooled, ground and screened. At the same time, A356 alloy ingots were molten in the electric furnace and held at 1123 K. Certain amount of dehydrated reactants powders were added with mechanical stirring assistance, the melt temperature was tested with thermal couple continuously. During the melt reaction process, the in situ reinforcements were formed in the molten A356 alloy. After 30 min, the melt was degassed and refined with the ZnCl₂. When the melt temperature was 993 K, the melt was cast into a permanent mould.

The specimens (in the form of a block: 15 mm×15 mm×10 mm) were obtained from the as-prepared composite. The observed surface of the specimen was ground on emery paper from 180# to 1000# and polished. The XRD, SEM and TEM technologies were used to determine the phase component, microstructure and in situ particulate crystal morphology of the composite.

Table 1 Chemical composition of A356 alloy (mass fraction, %)

<table>
<thead>
<tr>
<th>Si</th>
<th>Mg</th>
<th>Ti</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
<th>Sn</th>
<th>Pb</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>0.37</td>
<td>0.15</td>
<td>≤0.16</td>
<td>≤0.05</td>
<td>≤0.10</td>
<td>≤0.05</td>
<td>≤0.01</td>
<td>≤0.03</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

3 Results and discussion

3.1 XRD analysis of prepared composite

In the experiment, natrium boricum was used as a part of the reaction system due to that: 1) natrium boricum can be taken as the source of boron during the composite process because the boron content of the Na₂B₄O₇ is 2.4 times as much as that of KBF₄; 2) natrium boricum is a good flux for it can decrease the melting point of the reactants and accelerate the reaction.

According to the above two XRD patterns and Refs. [11] and [12], the possible reaction occurring in the Al–Na₂B₄O₇–K₂ZrF₆–KBF₄ system can be illustrated as follows:

2KBF₄+3Al=AlB₂+2KAlF₄

3K₂ZrF₆+13Al=3Al₂Zr+K₃AlF₆+3KAlF₄

Na₂B₄O₇+6Al=Na₃O+2Al₂O₃+2AlB₃

4K₂ZrF₆+4Al+2Na₂O=4K₂NaAlF₆+2ZrO₂

3ZrO₂+13Al=2Al₂O₃+3Al₂Zr

AlB₂ obtained from reactions (1) and (3) reacts with part of Al₂Zr which are formed in reactions (2) and (5):

AlB₂+Al₂Zr=ZrB₂+3Al

Due to no AlB₂ found in Fig. 1, reaction (6) goes completely and ZrB₂, Al₂O₃ and Al₂Zr particles are achieved finally in the composite.

The prepared composite melt could not be polluted by the oily K₂NaAlF₆, KAlF₄ and K₃AlF₆ because they floated on the surface of composite melt and could be stripped off. In addition, those substances are good fluxes like the natrium barium, especially when the reactants were added in batches because they become the flux for the later reaction.

![Fig. 1](image1.png)

![Fig. 2](image2.png)
3.2 Microstructure of composite

Figure 3 shows the SEM images of the in-situ particle reinforcement composites with different theoretical volume fractions ($\phi_t$): 5%, 10% and 15%. Due to the kinetic condition the in-situ reaction could not proceed sufficiently. So, the actual volume fractions of particulates are often less than the calculated theoretical values. Average recovery rate is 60%−80%, which is decreased with the increase of adding amount of reactants. It can be seen from Fig. 3, the particles are easy to join together to form some “particle clusters” and distribute along the $\alpha$(Al) grain boundary.

![Fig. 3 SEM images of as-prepared composites with different theoretical volume fractions: (a) 5%; (b) 10%; (c) 15%](image)

The high magnified SEM and TEM images and EDS patterns of the ZrB$_2$ particulate of (ZrB$_2$+Al$_2$O$_3$+Al$_3$Zr)/A356 composite are shown in Fig. 4. Figure 4(a) shows the high magnification SEM image of ZrB$_2$ clusters and its EDS pattern. The morphologies of the ZrB$_2$ particulate are mainly hexagon-shaped and the size is about 50 nm, and the interfaces for the in-situ particulates and the aluminum matrix are net where no interfacial reactions are found. The calibration result of the diffraction ring indicates that the ZrB$_2$ is close-packed hexagonal structure and its lattice parameters are $a=b=3.169$ Å, $c=3.530$ Å.

Based on the stokes particle floating rate formula, when the particle is small, it will move slowly and be captured by the growing matrix crystal grains to form a homogeneous and stable composite during the solidification [13]. The size of in-situ ZrB$_2$ particles is about 50 nm, so they would be captured by $\alpha$(Al) grains at usual setting rate and there would be less particles in the grain boundary. However, there is a great difference between the theoretical situation and the structure shown in Fig. 3 that most particles did not distribute in the $\alpha$(Al) grains while conglobated along the Al−Si grain boundary. It is considered that though the size of the in-situ ZrB$_2$ particles is quite small, but the interfacial energy of the aluminum melt is so high that the small particles reduce self-energy by getting together to form some “particulate clusters”. Moreover, the sedimentation of the particles in the melt becomes severe because of the increase of traveling speed of the clusters and the action of gravity. At the same time, during the solidification, the traveling speed of the clusters is superior to the solidification of the $\alpha$(Al) crystal grains, and then the particulate clusters are pushed to the front of solidification by the residual melt and eventually concentrate in the $\alpha$(Al) grain boundary.

Figure 5 shows TEM image and diffraction pattern of Al$_3$Zr reinforcements in (ZrB$_2$+Al$_2$O$_3$+Al$_3$Zr)/A356 composites. It can be found that the morphology of the Al$_3$Zr is rod like with the length-diameter ratio of 20. According to the crystal growth theory, the intermetallic compound grows in the form of facet. The atomic arrangement at the interface of liquid−solid is smooth. Thus single molecule is difficult to accumulate up on the smooth surface of the crystal and the growth of this interface will only depend on the stages occurring at the interface where the atoms diffused from the melt sedimentate [14,15]. The TEM results indicate that the facet is found on the surface of the Al$_3$Zr crystal which becomes the basis of Al$_3$Zr crystal growth. The result of the diffraction pattern shows that Al$_3$Zr crystal is tetragonal crystal and its lattice parameters are $a=b=4.009$ Å, $c=17.281$ Å.
Figure 4 SEM (a) and TEM (b) images, and EDS pattern (c, d) of ZrB$_2$ reinforcements in (ZrB$_2$+Al$_2$O$_3$+Al$_3$Zr)/A356 composites.

Figure 5 TEM image (a) and EDS pattern (b) of Al$_3$Zr reinforcements in (ZrB$_2$+Al$_2$O$_3$+Al$_3$Zr)/A356 composites.

Figure 6 shows the TEM and high resolution electron microscopy images of in situ Al$_2$O$_3$ ceramic reinforcements in (ZrB$_2$+Al$_2$O$_3$+Al$_3$Zr)/A356 composite. The size of Al$_2$O$_3$ particles is about 0.1 μm and the particles show two morphologies: rectangular and ellipsoidal which are showed as areas B and C in Fig. 6. The size of the particles with different morphology is about 0.1 μm and the particle/Al interfaces are smooth. The high resolution electron microscopy results show that Al$_2$O$_3$ particles with different morphologies both belong to the orthorhombic system and the lattice parameters are $a=7.934$ Å, $b=7.956$ Å, $c=11.711$ Å.

4 Conclusions

1) ZrB$_2$, Al$_2$O$_3$, and Al$_3$Zr multi-phase particulates reinforced A356 matrix composites are fabricated from A356-(KBF$_4$+K$_2$ZrF$_6$+Na$_2$B$_4$O$_7$) system by in-situ melts reaction technology.

2) The XRD results show that ZrB$_2$, Al$_2$O$_3$, and Al$_3$Zr particles are contained in the as-prepared composite. The crystal structure of ZrB$_2$ is close-packed hexagonal with lattice parameters, $a=b=3.169$ Å, $c=3.530$ Å and the micro morphologies of the ZrB$_2$
particulate are mainly hexagon with the size of about 50 nm. The fine ZrB₂ particles are joined together to form some “particle clusters” and distribute along the α(Al) grain boundary. Al₃Zr crystal is tetragonal with the lattice parameters, \( a=b=4.009 \) Å, \( c=17.281 \) Å. The morphology of Al₃Zr is rod-like with the length-diameter ratio of about 20. The morphologies of Al₂O₃ particles with size of 0.1 μm are rectangular and ellipsoidal, and crystals are orthorhombic with the lattice parameters, \( a=7.934 \) Å, \( b=7.956 \) Å, \( c=11.711 \) Å. The interfaces of the matrix and particles are net and no interfacial outgrowth is observed.
(ZrB₂+Al₂O₃+Al₃Zr)/A356 复合材料的原位直接反应法制备及微观组织

杨华静，赵玉涛，张刚，张松利，陈登斌

摘 要: 采用 A356−(K₂ZrF₆+KBF₄+Na₂B₄O₇) 作为熔体直接反应体系制备 (ZrB₂+Al₂O₃+Al₃Zr)/A356 复合材料。利用 XRD、SEM 和 TEM 等测试技术研究复合材料的相组成和微观组织。结果表明，复合材料增强相由 ZrB₂ 和 Al₂O₃陶瓷相颗粒和 Al₃Zr 金属间化合物相颗粒组成。ZrB₂ 颗粒易团聚形成颗粒团簇并沿 α(Al)合金晶界分布；ZrB₂ 颗粒的微观形貌为六边形，尺寸在 50 nm 左右。TEM 研究发现，Al₃Zr 颗粒以小面形式生长，其长径比约为 20；Al₂O₃ 颗粒形貌为长方体状和椭圆状，尺寸约为 0.1 μm。此外，基体与颗粒的相界面干净，无界面反应物生成。

关键词: 铝基复合材料；熔体直接反应；原位颗粒；微观组织

(Edited by YANG Hua)