Microstructural characteristics and evolution of in situ xTiB$_2$/Al-20%Si alloy

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Abstract
xTiB$_2$/Al-20%Si composite is a hypereutectic Al-20Si alloy containing x wt% TiB$_2$ sub-micron or nanometre level in situ particles. The xTiB$_2$/Al-20%Si composites were prepared using an 11% TiB$_2$/Al-6Si composite as the master alloy. The phases and microstructures in the composites were evaluated by use of XRD, OM, SEM, EDS, EPMA, and TEM. The microstructural evolution of the Al-20Si alloy with the addition of TiB$_2$ particles from 1 wt% to 6 wt% was investigated. The results showed that the primary Si, $\alpha$-Al phase, and eutectic Si could be refined and modified by TiB$_2$. Meanwhile, the crystal structures of Ti-B compound enwrapped by primary Si and $\alpha$-Al phase were identified and analysed and found to form a close-packed hexagonal structure. Compared with the microstructures of composites containing different amounts of TiB$_2$, the TiB$_2$ particles played an important role in the nucleation of primary Si and the growth of primary Si, eutectic Si, and $\alpha$-Al phases, also explaining the mechanism underpinning the effect of TiB$_2$ on the nucleation and growth of Si and $\alpha$-Al phases.

1. Introduction

Hypereutectic Al-Si alloys are widely used in the production of automobile parts, due to their excellent casting performance, light weight, wear resistance, and low coefficient of thermal expansion$^{[1,2]}$. However, the coarse primary Si phase and the eutectic Si phase in traditional hypereutectic Al-Si alloys are easily broken during service, which will cause the mechanical properties to decrease. The key to improving the mechanical properties of hypereutectic Al-Si alloys is to regulate their microstructure$^{[3,4]}$.

In order to obtain higher output power and longer service life of hypereutectic Al-Si alloy parts, extensive studies have been conducted on hypereutectic Al-Si alloys (especially with regard to their thermal stability and strength). For example, adding alloying elements such as Cu$^{[5]}$ and Zn$^{[6]}$, modifying with P$^{[7]}$ and Sr$^{[8]}$, and adding second phase particles have been undertaken. Compared with Al-Si alloys by traditional modification, the in situ composites have the following advantages: (1) the contact interface between the particles and the substrate is clean and more stable; (2) the in situ particles are more uniformly distributed in the matrix. The addition of second phase particles proved to be an effective way of improving the mechanical properties of Al-Si alloys$^{[9,10]}$. TiB$_2$ has been widely studied in Al matrix composites due to its high melting point, low coefficient of thermal expansion, and high elastic modulus. At the same time, TiB$_2$ and Al matrix are direct bonding interfaces$^{[11]}$, thus, TiB$_2$ particles have become an important reinforcement phase in Al matrix composites.

At present, there are many preparation methods for TiB$_2$ reinforced Al matrix composites: Westwood$^{[12]}$ prepared a TiB$_2$/Al composite by exothermic dispersion and its elastic modulus is 40% higher than that of the alloy matrix, and its high-temperature performance, wear resistance, and fatigue resistance are also improved; Zhu$^{[13]}$ prepared a 60 vol% TiB$_2$/2024Al composite by squeeze-casting. Test results show that the larger TiB$_2$
particles are surrounded by small particles and are distributed in the matrix. There are no casting defects such as pores and shrinkage holes in the composite. Wood [14] prepared 5.5% TiB2/A356 composites by mixed salt method and its tensile strength is 40% higher than that of the alloy matrix.

Although many scholars have investigated TiB2-reinforced Al-Si alloy matrix composites, their work is mainly concentrated on hypoeutectic or near-eutectic Al-Si alloys, but there is less research on the effect of in situ TiB2 particles on hypereutectic Al-Si alloys [15–19]. Therefore, in the present study the effect of in situ TiB2 particles on the microstructure of Al-20%Si alloy, especially the effect of TiB2 on the morphology and distribution of primary Si and eutectic Si, was investigated. The phases and microstructure of the composites were tested by XRD, OM, SEM, EDS, EPMA, XRF and TEM, and the evolution of microstructure of Al-20Si alloys with different amounts of TiB2 particles was analysed and the underlying behaviour mechanism was discussed.

2. Experimental procedures

2.1. Preparation of materials

In this experiment, xTiB2/Al-20%Si composites were prepared using an 11% TiB2/Al-6Si composite as the master alloy. The 11% TiB2/Al-6Si composite was melted with commercially pure Al (99.5%), metallic Si (98%), K2TiF6 (99.9%), and KBF4 (99.9%). Figure 1 shows the preparation process of this in situ 11% TiB2/Al-6Si composite. The K2TiF6 powder and KBF4 powder were mixed in the mass ratio of 1:1. Dehydration treatment was conducted for two hours at a temperature of 200 °C. Commercially pure Al and Si were melted in a resistance furnace. Then the mixed salt was added to the bottom of the bath with inert gas at 850 °C, then vigorous mechanical agitation was applied to the melt using a stirrer: the reaction process lasted for 30 min, then 30 min later, the melt was treated with C2Cl6 for slag-removal and poured into a graphite mould at 730 °C to obtain the 11% TiB2/Al-6Si composites.

The in situ reaction mechanism in this study is such that, when K2TiF6 and KBF4 in the mass ratio of 1:1, were added to the Al-6Si melt at 850 °C, the reaction is as follows

\[ 2KBF_4 + 3Al = 4AlB_2 + 2KAlF_4 \]  \hspace{1cm} (1)

\[ 3K_2TiF_6 + 13Al = 3TiAl_3 + K_3AlF_5 + 3KAlF_4 \]  \hspace{1cm} (2)

\[ AlB_2 + TiAl_3 = TiB_2 + 4Al \]  \hspace{1cm} (3)

According to the calculation [20], the Gibbs free energy of the above three reactions is less than zero, and the reaction can proceed smoothly. During the reaction, the mixed salt required for the in situ reaction was fed into the melt by inert gas, which can reduce the volatilisation of the salt and better control the amount of TiB2.

Figure 2 shows the microstructures of Al-6Si alloy and 11%TiB2/Al-6Si composites. It can be seen from figure 2(a) that the microstructure of Al-6Si alloy is mainly composed of an \( \alpha \)-Al phase and a eutectic Si phase (the \( \alpha \)-Al phase exists in plate-form and the eutectic silicon is acicular). With the addition of in situ TiB2 particles, the \( \alpha \)-Al phase was refined and the morphology was that of irregular clumps and small cylinders (figure 2(b)). The TiB2 particles were mainly distributed on the \( \alpha \)-Al grain boundaries with some present in the \( \alpha \)-Al phase.
Commercially pure Al, metallic Si, and the 11% TiB$_2$/Al-6Si composite were used to fabricate Al-20Si with 0 wt% TiB$_2$, 1 wt% TiB$_2$, 3 wt% TiB$_2$, and 6 wt% TiB$_2$, respectively. These materials were melted in a resistance furnace at 800 °C, and phosphorus was added to modify the material at 750 °C. Then the melt was treated with 0.5% C$_2$Cl$_6$ at 730 °C for slag-removal and degassing. After maintaining the temperature for 15 min, the melt was immediately squeeze-cast at about 730 °C to prepare TiB$_2$/Al-20%Si composite specimens. Table 1 shows the chemical compositions of the composites.

### Table 1. Chemical compositions of the composites (wt%).

| Composites         | Si/\% | Ti/\% | Al/\% |
|--------------------|-------|-------|-------|
| 11% TiB$_2$/Al-6Si | 6.4   | 10.3  | Balance |
| 1% TiB$_2$/Al-20Si | 19.7  | 1.2   | Balance |
| 3% TiB$_2$/Al-20Si | 20.3  | 2.7   | Balance |
| 6% TiB$_2$/Al-20Si | 21.4  | 6.5   | Balance |

Figure 2. Microstructures of alloy: (a) Al-6Si alloy; (b) in situ 11% TiB$_2$/Al-6Si composite.

2.2. Material characterisation

The specimens were formed from the composite castings after rough-grinding, fine-grinding, and polishing. The specimens were then etched using a 0.5% HF corrosion solution for 3 to 5 s, and then the corroded surface was cleaned using anhydrous ethanol. Microstructure observation of specimens required the use of an OM (FEI, Nova-450) and FESEM (Nova Nano, SEM-450) equipped with an energy-dispersive spectroscopy detector. Micro-area analysis of microstructures was undertaken by EPMA (Shimadzu, EPMA-1720H). A TEM (FEI, Tecnai G2 TF30) was introduced for identification of the phases present in the specimens. Phase identification was carried out by XRD (Bruker AXS D8 ADVANCE X, Cu target). The content of Al, Si and Ti elements in the composite was detected by XRF (ZSX-100e).

Image Pro-plus software was used to analyse the metallographic structure of specimens, the average diameter ($D$) and shape factor ($SF$) of the primary Si phase were calculated thus [21]:

$$D = \frac{\sum_{i=1}^{N} 4A_i / \pi}{N}$$

$$SF = \frac{\sum_{i=1}^{N} 4\pi A_i / P_i^2}{N}$$

Where $N$ represents the number of particles, $A_i$ is the area of particle $i$, and $P_i$ its circumference.

3. Results and discussion

3.1. Phase analysis

Figure 3 shows the XRD patterns of Al-20%Si alloy and 6% TiB$_2$/Al-20Si composite. It can be seen from figure 3(a) that only the $\alpha$-Al phase and Si phase were detected in Al-20Si alloy, however, significant TiB$_2$ peaks appeared in the TiB$_2$/Al-20%Si composites, and no obvious derivative was found (figure 3(b)). This indicated that the primary Si did not react with the in situ TiB$_2$ particles.
Figure 4 shows the TEM image of TiB$_2$/Al-20\%Si composites. Figures 4(a) and (d) show the morphology of TiB$_2$ particles in the $\alpha$-Al and primary Si. Figure 4(a) shows that the particles are widely dispersed in the $\alpha$-Al matrix, and measure about 0.2 to 1 $\mu$m. Figure 4(c) shows the selected area electron diffraction (SAED) results of TiB$_2$ with an axis of [0001], the lattice constants are $a = b = 0.250$ nm, which is about 3.5\% ($<5\%$) different from the standard lattice constant (0.262 nm), so the phase was identified as TiB$_2$. It also can be confirmed by SAED that TiB$_2$ particles formed a hexagonal close-packed structure. Similarly, according to figures 4(e) and (f), TiB$_x$ compounds in primary Si were present as TiB$_2$ particles. Based on the above testing and analysis, it was found that the particles containing Ti and B elements in the matrix of $\alpha$-Al and primary Si in the composite material are TiB$_2$ particles, and the addition of silicon during the melting process caused no reaction with TiB$_2$ particles.
Surface-scanning analysis was conducted on the primary Si phase and eutectic phase in TiB$_2$/Al-20Si composites. As shown in figures 5(a) and (f), a large amount of particulate matter was present in the primary Si and eutectic phase. According to the elemental distribution of Ti, Al, Si, and B in the microstructure, it can be seen that particles were mainly composed of Ti and B, as shown in figures 5(d), (e), (i), and (g). Figure 5(a) shows the microstructure of the primary Si phase. It can be seen that the TiB$_2$ particles are mainly distributed in the form of fine dispersion or coarse agglomerates in the interior of the primary Si phase and the grain boundaries. Due to the melt undergoing more cooling in the graphite mould, and as the speed of liquid/solid interface was greater than that of the particles, the TiB$_2$ particles were captured by the primary Si phase.

Figure 5(f) illustrates the microstructure of the eutectic phase. It can be seen that the eutectic Si phase was mainly distributed in short rod-shaped and acicular forms at the $\alpha$-Al grain boundary, and TiB$_2$ particles aggregated near the eutectic Si phase.

Figure 6 shows the SEM images and EDS results of the eutectic phase of TiB$_2$/Al-20Si composites. In the Al-Si eutectic phase, the $\alpha$-Al phase was a continuous growth phase, and the eutectic Si phase was distributed in acicular form in the Al matrix. When the eutectic transformation occurred in the TiB$_2$/Al-Si composites, the eutectic Si phase precipitated by the rigid nucleation was formed of small grains with a large specific surface area and a high surface energy, so that the TiB$_2$ particles were adsorbed on the surface of the eutectic Si or embedded in the growth layer of the Si. The TiB$_2$ particles present at the front edge of the solid-liquid interface hinder the continuous growth of the eutectic Si, thereby refining the eutectic silicon. Thus, it was distributed in short rods and fine needles at the $\alpha$-Al grain boundary. Due to the partially coherent relationship between TiB$_2$ particles and $\alpha$-Al, the $\alpha$-Al phase can take TiB$_2$ particles as a substrate for heterogeneous nucleation, and the atoms were stacked and grown on the coherent counterpart surface, thereby increasing the nucleation rate of $\alpha$-Al and refining the final grains. On the other hand, TiB$_2$ particles were pushed by the liquid/solid interface during solidification, which hindered the growth of $\alpha$-Al grains and refined grains.
3.2. Microstructural evolution induced by in situ TiB<sub>2</sub>/Al-20%Si particles

Figure 7 shows the microstructure of TiB<sub>2</sub>/Al-20Si composites with different TiB<sub>2</sub> contents. The average diameter and shape factor of the primary Si phase are shown in figure 8. The microstructure of Al-20Si alloy was composed of primary Si phase and eutectic structures, the average diameter of primary Si phase grains was about
31.2 μm, and the shape factor was about 0.66. There were a large number of continuous reticulated, and long acicular, eutectic Si phases distributed in the α-Al matrix with lengths of 20 to 50 μm. The fracturing of these brittle reticular ruptures and long acicular sharp corners will scratch the crystals during the service life of the material, resulting in the degradation of its properties [22]. With the addition of 1 wt% of TiB₂ particles, the average diameter of primary Si phase grains is about 27.8 μm, and the shape factor is about 0.68; eutectic Si mainly occurred as 10 to 20 μm acicular grains, and the α-Al formed a small-grained dendritic morphology (figure 7(b)). With addition of 3 wt% of TiB₂ particles, the average diameter of primary Si phase grains was about 25.7 μm, the shape factor was about 0.74, and the eutectic Si phase formed 5 to 15 μm fine acicular grains (figure 7(c)). While the amount of in situ TiB₂ particles reached 6%, it was notable that continuous web-like eutectic Si structures could hardly be seen in figure 7(d): the average diameter of grains in the primary Si phase was about 16.5 μm, and the shape factor was about 0.77. The eutectic Si phase contained mainly fine acicular grains with lengths of 5 to 15 μm and equiaxed shape grains of 2 to 4 μm in diameter. The morphology of the α-Al phase was a mainly fine isometric shape with diameters of 10 to 20 μm.

Figure 9 shows the process of microstructure evolution in an Al-20Si alloy and TiB₂/Al-20Si composites. The primary Si phase in Al-20Si alloy nucleation is shown to start at the liquidus temperature. As the temperature was increased, the primary Si phase grew rapidly and immediately consumed the supersaturated Si in the surrounding melt. The number of primary Si phases in Al-20Si alloys was limited by the nucleation
number at the initial stage of solidification. In TiB₂/Al-20Si composites, the TiB₂ particles can be used as the substrate for the heterogeneous nucleation of the primary Si phase [23–25], and the rate of nucleation of the primary Si phase was improved when in the presence of a large number of nucleation cores. The TiB₂ particles could be used not only as an effective nucleation core for primary Si, but also to prevent the growth of primary Si. Driven by reduced system interface energy, the TiB₂ particles dispersed in the melt tended to be adsorbed at the growth interface of the rigid nucleated primary Si phase. On the one hand, in situ TiB₂ particles can hinder the growth of the primary Si phase, and the shape of the primary Si phase is more rounded; On the other hand, in situ TiB₂ particles hinder the diffusion of Si elements from the melt around the nucleated primary Si phase to the primary Si grains, and the supersaturated Si elements in the surrounding melt can promote the nucleation of more primary Si phases. Therefore, as shown in figure 7 and figure 8, with the increase of the in situ TiB₂ content in the TiB₂/Al-20Si composite, the diameter of the primary Si phase is continuously reduced and the shape is more rounded.

4. Conclusion

(1) The TiB₂/Al-20Si composites were prepared using an in situ TiB₂/Al-6Si composite (prepared by the mixed salts method) as the master alloy. XRD and TEM tests proved that the fine dispersed particles present in the α-Al and primary Si in the composites were TiB₂, and the interface between the three was clear, suggesting good binding, and no reaction occurred that generated derivative products.

(2) The microstructure of Al-20Si alloy can be refined and modified by TiB₂ particles. Upon addition of 6% TiB₂, the average grain diameter of the primary Si phase decreased by 47% to 16.5 μm and the shape factor increased by 16% to 0.77.

(3) In situ TiB₂ particles could not only be used as an effective nucleation core for primary Si, but were also adsorbed at the grain boundary of the primary Si phase thus hindering element diffusion and inhibiting its growth. Moreover, the form of growth of eutectic Si was improved by the addition of TiB₂ particles. In addition, the α-Al phase was refined by the TiB₂ particles and the grains remained equiaxed.

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