Effect of TiB$_2$ on Microstructure of 7075 Al Alloy Semi-Solid Slurry at Different Solid Fraction

Guisheng Gan$^{1,2,*}$, Chunhong Zhang$^1$, Donghua Yang$^1$, Mingbo Yang$^1$, Xin Jiang$^1$ and Yun-long Shi$^1$

$^1$Chongqing Municipal Engineering Research Center of Institutions of Higher Education for Special Welding Materials and Technology (Chongqing University of Technology), Chongqing 400054, China
$^2$College of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

TiB$_2$/7075 Al matrix composites were fabricated by in situ reaction, and the effect of TiB$_2$ particle content on the microstructure of 7075 Al alloy slurry in semi-solid state at different solid fraction was investigated. The results showed that the grain sizes of TiB$_2$/7075 Al matrix composites firstly decreased then increased and finally decreased again with the increase of TiB$_2$ content because the role of particles shifted from dominating by locating to dominating by nucleation as the quantity of TiB$_2$ particles increased due to the decrease of the mean diameter of TiB$_2$ particles. As the holding time increasing in the semi-solid state, dendritic grains were necked and remelted at first, then rosette grains melted and shrank into the globular grain, finally the globular grains began to grow, but the number of grains decreased and their mean grain size increased. The minimum grain size of 3.0, 4.5 and 9.0%TiB$_2$/7075 Al matrix composites slurry were 81 μm, 51 μm and 69 μm after holding for 35, 20 and 50 mins at 630°C, respectively. However, the minimum grain size of 3.0 and 4.5%TiB$_2$/7075 Al matrix composites slurry were 100 μm and 75 μm after holding for 120 and 90 mins at 620°C, respectively. However, the maximum size of globular grains was not associated with the TiB$_2$ particle content, the maximum grain sizes of 3.0%TiB$_2$/7075 and 4.5%TiB$_2$/7075 Al matrix composites slurry at 620°C were approximately 126 μm.

(Received December 26, 2016; Accepted February 15, 2017; Published March 27, 2017)

**Keywords:** 7075 aluminium alloy, semi-solid, TiB$_2$ particles, solid fraction, thixoforming

1. Introduction

7075 Al alloy has been widely used as structural materials in aeronautical industry due to its attractive comprehensive properties, but wrought aluminum alloy is difficult to cast due to hot tearing formed during the solidification process of the alloys.$^{1,2}$ Semisolid metal (SSM) processing which is considered as one of the most prospective materials processing technology in the 21st century provides the possibility of producing near-net-shape casting of wrought aluminum alloy. The key of semisolid forming is how to fabricate the proper slurry containing the non-dendritic microstructure.$^{3}$ Semisolid slurry for thixoforming is prepared by reheating in the solidification state without stirring, and has high capability for near net shaping due to less solidification shrinkage and less deformation resistance, lower forming temperature, lower energy consumption and cost, and higher performance as compared to conventional casting and forging. Previous work has shown that SSM processing was appropriate for 7075 Al alloy, including thixoforming and rheocasting.$^{4-8}$

TiB$_2$ particles can not only improve the strength and modulus of aluminum alloy due to high hardness and modulus, but also effectively refine the microstructure of the aluminum alloy.$^9$ The authors have studied the effect of TiB$_2$ on the semi-solid microstructure of 7075 Al alloy in the rheocasting process.$^{9-12}$ But the effect of TiB$_2$ particle content on the microstructure of 7075 Al alloy slurry by thixoforming in different solid fraction has no in-depth study. In the present work, the 7075 Al alloy semi-solid slurry was prepared by in-situ reaction and reheating at a semisolid temperature and the effect of TiB$_2$ on the microstructure of the 7075 Al alloy slurry was studied.

2. Experimental

The liquidus and solidus temperatures of 7075 Al alloy are 635°C and 477°C, respectively. The chemical composition of 7075 alloy used in the present study is Al-5.52%Zn-2.36%Mg-1.51%Cu-0.18%Si-0.26%Fe-0.15%Mn-0.25%Cr (in mass, similarly hereinafter). Different content of TiB$_2$ (3.0, 4.5, 6.0 and 9.0%) were produced by adding a mixture of K$_2$TiF$_6$ and KBF$_4$ (the particle size of mixture is 74±300 micrometers) in a 1:2 molar ratio into the alloy at 850°C. After stirring about 30 minutes and then degassing by using C$_2$Cl$_6$, the melt of TiB$_2$/7075 Al composites at 720°C was poured into a graphite mould of 15 mm in diameter. Castings of TiB$_2$/7075 Al composites were cut into pieces of 8 mm thickness respectively, and then placed into the holding furnace with 620 ± 1°C and 630 ± 1°C respectively. Finally, the samples were obtained by immediately water quenching at different holding time.

After sanding and polishing, the specimens were etched in solution of mixed acids (1 mL HF+1.5 mL HCl+2.5 mL HNO$_3$+95 mL H$_2$O). The microstructures of composites were examined by using a ZEISS SUPRA55 scanning electron microscope (SEM) and an optical microscope (OM). The grain size and area of the primary solid phase were analyzed statistically by a quantitative image analysis system. The microstructures were characterized by average grain diameter $D = 2A/\pi P^{1/2}$ and shape factor $F = 4\pi A/P^2$, where A and P were average area and average perimeter of primary α-Al phase, respectively.

3. Results and Discussion

3.1 Influence of TiB$_2$ particle content on microstructure of 7075 Al alloy

The reaction to form TiB$_2$ in the molten 7075 aluminium alloy fabricated by this technique can be expressed as $^{9,13}$:

\[ \text{Ti} + \text{B} \rightarrow \text{TiB}_2 \]
In addition to the expected TiB$_2$, it is found that KF and AlF$_3$ were also present in the reactants. The KF and AlF$_3$ can be eliminated easily from the dregs. After adding 3.0 and 4.5% TiB$_2$, the microstructure was changed from dendrite to uniform rosette grain, and the grain size was decreased with the increase of TiB$_2$ particles; then the morphology was changed into large dendrites again as 6.0 and 9.0% TiB$_2$ was added. With increasing of TiB$_2$ particle, the number of large TiB$_2$ particle in the melt raises, but the size of large TiB$_2$ particle will decrease and the number of small TiB$_2$ particle will also increase because the heat of reaction of in-situ synthesis will also increase to refine the particles in Fig. 1. The diameter of most TiB$_2$ particles are about 600–1000 nm in 3.0%TiB$_2$/7075 composites. However, large TiB$_2$ particles are distributed in the boundary area of grain, and parts of small TiB$_2$ particles whose size are smaller than 600 nm are dispersing in the grain near the grain boundary of 9.0%TiB$_2$/7075 composites. Figure 2 shows the SEM images of as-cast TiB$_2$/7075 composites. The majority of the TiB$_2$ particles in the settled layer appear to be located on $\alpha$-Al grain boundaries, however, small agglomerates of TiB$_2$ particles could be found in the grains of 6.0% and 9.0%TiB$_2$/7075 composites respectively, even in 4.5%TiB$_2$/7075 composites. With increasing of TiB$_2$ particle, the aggregation of particles increased due to the decreases of the TiB$_2$ particle size, so the microstructure of 9.0%TiB$_2$/7075 composites become smaller than 6.0%TiB$_2$/7075 composites due to the aggregation of particles in the boundary area of grain.

Lakshmi et al. found that the grain size varied from 73.58 $\mu$m to 12.75 $\mu$m, and then increased to 23.11 $\mu$m with the increase of a reaction holding time. At the same time, the mean size of TiB$_2$ particles also varied from 570 nm to 430 nm, and then increased to 530 nm. Quested et al. also found the same tendencies that the grain size of Al matrix composites decreased at first and then grew up again with decreasing of the mean diameter of TiB$_2$ particles, but the minimum grain size and its corresponding size of TiB$_2$ particles were different with our research. TiB$_2$ particles have the strongest nucleation abilities when the mean size of TiB$_2$ particles are 400–600 nm, as shown in Fig. 1 in Ref. 15).

TiB$_2$ particle smaller than 600 nm can be found in the grain near the grain boundary in Fig. 3(a)(b), most of large TiB$_2$ particles and parts of small TiB$_2$ particle are distributed in the boundary area of grain. There are more small TiB$_2$ particle (white dot in the picture) in the grain of 9.0%TiB$_2$/7075 Al matrix composites, comparing with 4.5%TiB$_2$/7075 Al matrix composites in Fig. 3(c)(d), which means that parts of
TiB₂ particle value a major role locating in the grain boundary and others become the nucleus of α-Al phase. Most of particles smaller can easily act as heterogeneous nucleus which will induce the grain growth and be captured by solid-liquid interface. However, most of large particles are pushed into the grain boundary by solid-liquid interface, locating in the grain boundary can hinder the Al atoms from diffusing during the solidification of the 7075 Al alloy and restrain α-Al phase growth. The role of particles is a process from dominating by locating to dominating by nucleation due to changing of the size of particles with increasing the addition level of TiB₂ particle, which make to change from dendrites to uniform rosette grain and again to large dendrites.

3.2 Influence of TiB₂ on microstructure of 7075 Al alloy semi-solid slurry at different solid fraction

Microstructure of the solid 3.0 and 4.5, 6.0 and 9.0% TiB₂/7075 composites under different holding time at 630°C (abcd) and 620°C (efgh) are shown in Figs. 4–7 respectively. Table 1 is grain size (D) and shape factor (F) of TiB₂/7075 composites under different holding time at 630°C. The grain becomes globular in 3.0% TiB₂/7075 aluminum matrix composites after holding for 25 mins, and the minimum grain size can be found at 630°C after holding for 35 mins. The globular grain can be obtained in 4.5% TiB₂/7075 aluminum matrix composites after holding for only 20 mins, and the grain size is exactly the minimum. Thereafter, globular grains begin to grow, but the mean grain size has no significant change from 35 mins to 50 mins. However, 9.0% TiB₂/7075 aluminum matrix composites need much more time to obtain uniform globular grain and its minimum grain size can reach 69 μm after holding for 50 mins.

The microstructure of 3.0% TiB₂/7075 composites becomes globular grain after holding for 60 mins, since then the mean grain size begins to decrease. The minimum grain size is 100 μm after holding for 120 mins, after that the mean grain size begins to increase again, and then keeps stable. The microstructure evolution of 4.5% TiB₂/7075 aluminum matrix composites under different holding time at 620°C has a similar variation trend, but it is easier to form uniform globular grain and the minimum grain size is only about 75 μm. Microstructure of the solid 9.0% TiB₂/7075 composites have no significant change at 620°C from 20 mins to 120 mins in Fig. 7(e) and (f), globular grain can be found in some area of the sample after holding for 150 mins, while dendritic grain still exist in other area according to these two pictures of the same sample at different location in Fig. 7(g), and the

Table 1 Grain size (D) and shape factor (F) of TiB₂/7075 composites under different holding time at 630°C.

<table>
<thead>
<tr>
<th>Composites</th>
<th>20 mins</th>
<th>25 mins</th>
<th>30 mins</th>
<th>35 mins</th>
<th>50 mins</th>
<th>60 mins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D (μm)</td>
<td>F</td>
<td>D (μm)</td>
<td>F</td>
<td>D (μm)</td>
<td>F</td>
</tr>
<tr>
<td>3% TiB₂/7075</td>
<td>94</td>
<td>0.68</td>
<td>84</td>
<td>0.78</td>
<td>81</td>
<td>0.72</td>
</tr>
<tr>
<td>4.5% TiB₂/7075</td>
<td>51</td>
<td>0.71</td>
<td>88</td>
<td>0.67</td>
<td>81</td>
<td>0.70</td>
</tr>
<tr>
<td>9.0% TiB₂/7075</td>
<td>82</td>
<td>0.60</td>
<td>69</td>
<td>0.66</td>
<td>111</td>
<td>0.72</td>
</tr>
</tbody>
</table>
mixed microstructure of globular grain and dendritic grain in the same sample still exists after holding for 180 mins in Fig. 7(h). It means that much more time is needed to obtain globular microstructure in all area of the sample.

It can not to get globular grain after holding for 90 mins in 6.0%TiB$_2$/7075 aluminum matrix composites at 630°C in Fig. 6, and maybe need more time than 150 mins to get globular grain at 620°C, because it was composed of large dendrites and we know that it cannot be spheroidized in semi-solid forming without stirring.

### 3.3 Mechanism of microstructure evolution of Al matrix composites slurry

The microstructure evolution of TiB$_2$/7075 Al matrix composites at different solid fraction is proposed and schematically shown in Fig. 8. The phenomenon of necking and remelting of dendritic grains can be found at first, then rosette grains melt and shrink into globular grains, finally the globular grains begin to grow with the increase of holding time. It takes only about 25, 20 and 35 mins at 630°C to form globular grain for 3.0, 4.5 and 9.0%TiB$_2$/7075 Al matrix composites respectively. 9.0%TiB$_2$/7075 Al matrix composites forming globular grain are the most difficult since the as-reflowed microstructure is dendritic grains and the mean grain size is the biggest. Globular grain can not be got after holding for 90 mins at 630°C because there has the most largest dendritic grains in 6.0%TiB$_2$/7075 Al matrix composites. In other words, the formation time of globular grains primarily depends on the as-reflowed microstructure, that is, dendritic grains take much more time to form globular grains than big rosette grains, and small rosette grains need the least time.

As the holding time increasing, on one hand, some contiguous grains merge into bigger ones by coalescence. On the other hand, Ostwald ripening occurs: small grains disappear by diffusion through the solid phase due to the reduction of surface energy and overlapped solution fields of neighboring grains, so the number of grains decreases and their mean grain size increases with the increase of holding time. As a consequence, the mean grain sizes of TiB$_2$/7075 composites firstly decrease then increase and finally keep stable dimensions as the holding time increasing, and the shape factor become rounder in Tables 1 and 2. The maximum grain size of 3.0%TiB$_2$/7075 and 9.0%TiB$_2$/7075 Al matrix composites are the same, approximately 111 μm at 630°C, and their size have no significant change compared with 4.5%TiB$_2$/7075 Al matrix composites, which means that the maximum size of globular grains is not associated with the TiB$_2$ particle content.

4. Conclusions

1. With increasing of TiB$_2$ particle, the number of large TiB$_2$ particle in the melt increased, but the size of large TiB$_2$ particle decreased and the number of small TiB$_2$ particle also increased because the heat of reaction of in-situ synthesis will also increase to refine the particles. The grain sizes of TiB$_2$/7075 Al matrix composites firstly decreased then increased and finally decreased again with the increase of TiB$_2$ content because the role of particles shifted from dominating by locating to dominating by nucleation as the quantity of TiB$_2$ particles increased due to the decrease of the mean diameter of TiB$_2$ particles.

2. The minimum grain size of 3.0, 4.5 and 9.0%TiB$_2$/7075 Al matrix composites slurry were 81 μm, 51 μm and 69 μm for 35, 20 and 50 mins at 630°C respectively. The minimum grain size of 3.0%TiB$_2$/7075 and 4.5%TiB$_2$/7075 Al matrix composites slurry were 100 μm and 75 μm for 120 and 90 mins at 620°C respectively. However, the maximum size of globular grains was not necessarily associated with the TiB$_2$ particle content, the maximum grain size of 3.0%TiB$_2$/7075 and 4.5%TiB$_2$/7075 Al matrix composites slurry at 620°C were both approximately 128 μm.

3. As the holding time increasing in the semisolid state, dendritic grains were necked and remelted at first, then rosette grains melted and shrank into globular grains, finally the globular grains began to grow, but the number of grains decreased and their mean grain size increased since some contiguous grains merged into bigger grains by coalescence and small grains disappeared by diffusion through the solid phase. The mean grain sizes of TiB$_2$/7075 composites firstly decreased then increased and finally kept stable dimensions as

<table>
<thead>
<tr>
<th>Composites</th>
<th>40 mins D (μm)</th>
<th>F</th>
<th>60 mins D (μm)</th>
<th>F</th>
<th>90 mins D (μm)</th>
<th>F</th>
<th>120 mins D (μm)</th>
<th>F</th>
<th>150 mins D (μm)</th>
<th>F</th>
<th>180 mins D (μm)</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%TiB$_2$/7075</td>
<td>112</td>
<td>0.67</td>
<td>128</td>
<td>0.68</td>
<td>100</td>
<td>0.79</td>
<td>115</td>
<td>0.75</td>
<td>127</td>
<td>0.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5%TiB$_2$/7075</td>
<td>83</td>
<td>0.71</td>
<td>81</td>
<td>0.65</td>
<td>75</td>
<td>0.72</td>
<td>77</td>
<td>0.84</td>
<td>128</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the holding time increasing, and the shape factor became rounder.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No.51505051).

REFERENCES

12) G.S. Gan and B. Yang: Rare Met. 35 (2016) 858–862.