Effect of TiB₂ Particles on Microstructure of 7075 Al Alloy in Semi-Solid State Near Liquidus

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TiB₂/7075 Al matrix composites were formed by *in situ* reaction, and effect of the TiB₂ particles content on microstructure of 7075 Al alloy in semi-solid state near liquidus were investigated. The results have shown that the average grain size decreased with increased the amount of TiB₂, and the microstructure became uniform rosette grains. The morphology of grains became big dendrite grains when the particles content were over 4.5 mass%. Globular grains of 7075 Al alloy whose size reached 94 μm can be got for 7.5 min at 630°C. The minimum grain size of 3 mass%TiB₂/7075, 4.5 mass%TiB₂/7075 and 9 mass%TiB₂/7075 Al matrix composites at 630°C were 88 μm, 51 μm and 69 μm for 30 min, 20 min and 50 min, respectively. The TiB₂ particles located in the grain boundary can hinder the Al atoms from diffusing within the semi-solid state of the 7075 Al alloy and restrain α-Al phase growth, but it can be conducive to improve the stability of semi-solid slurry in near-liquidus thixoforming. [doi:10.2320/matertrans.M2014447]

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1. Introduction

Semisolid forming (SSM) was a near-net-shape forming technology for metals and alloys developing at MIT during the 1970s.^{1,2)} SSM was considered as one of the most prospective materials processing technologies in 21 century. The key issue of semi-solid forming is how to fabricate the proper slurry containing the non-dendritic microstructure.³⁾ Semisolid slurry of thixocasting is prepared by reheating at the solid state, which need no stirring.

7075 Al alloy have been widely used as structural materials in aeronautical industries due to their attractive comprehensive properties, such as low density, high strength, ductility, toughness. Previous work has shown that SSM processing were appropriate for 7075 Al alloy, including rheocasting⁴⁻⁹⁾ and thixocasting.¹⁰⁻¹²⁾ The author also studied the effect of TiB₂ on the semi-solid microstructure of 7075 Al alloy in the rheocasting process.¹³⁻¹⁷⁾ But the effect of the TiB₂ particles on microstructure of 7075 Al alloy slurry by thixocasting in semi-solid state near liquidus has no in-depth study. The present work is, combining with *in-situ* reaction, to prepare 7075 Al alloy semi-solid slurry by reheating at semisolid temperature after adding TiB₂ particles.

2. Experimental

The material we studied was a commercial wrought 7075 Al alloy. The liquidus and solidus temperature of the alloy were 639.1°C and 477.4°C, respectively.¹³⁾ The chemical composition of 7075 alloy used in present study was Al-5.52 mass%Zn-2.36 mass%Mg-1.51 mass%Cu-0.18 mass%Si-0.26 mass%Fe-0.15 mass%Mn-0.25 mass%Cr. K₂TiF₆ (mass > 97%) and KBF₄ (mass > 97%) mixture were put into the molten of 7075 alloy at 850°C. After stirring at the same temperature for about 30 min and degassing by using C₂Cl₆,

the molten of TiB₂/7075 Al composites and 7075 Al alloy at 720°C was casted in 15-mm diameter's graphite mould. Casts were cut out respectively n height of 8 mm, and then these were put into the holding furnace at 630°C. Finally, the samples can be obtained by immediately quenching with the different holding time.

The grain size and area of the primary solid phase were analyzed statistically by a quantitative image analysis system. A close observation of microstructure can be given by average gain diameter $D = 2(A/\pi)^{1/2}$ and shape factor $F = 4\pi A/P^2$, where A and P are average area and average perimeter of primary phase, respectively.

3. Results and Discussion

3.1 Influence of the TiB₂ particles content on microstructure of 7075 Al alloy

Figure 1 shows the microstructure of 3% (in mass, similarly hereinafter) TiB₂/7075 and 4.5%TiB₂/7075, 6%TiB₂/7075 and 9%TiB₂/7075 Al matrix composites after pouring into graphite mould at 720°C. After adding 3%TiB₂, the microstructure becomes uniform rosette grains, and the grain size shows a decreasing tendency with increasing of TiB₂ particles. The morphology of grains become big dendrite grains after adding 6%TiB₂. 9%TiB₂/7075 Al matrix composites is also mainly composed of the dendrite grains, but the grain size is smaller than 6%TiB₂/7075 Al matrix composites.

Quested¹⁸⁻²¹⁾ found that the grain size shown a minimum as average particle diameter was decreased. Although it shown a different experiment result of minimum grain size and its average particle diameter, the tendencies are generally the same. As the average particle diameter is decreased, the number of particles must increase, and this leads to a decrease in grain size. But smaller particles give intrinsically less good refinement as their activation at greater undercooling leads to faster growth. It is found that smaller particle

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Fig. 1 The microstructure of the solid TiB_2 /7075 Al matrix composites; (a) 3% TiB_2 /7075, (b) 4.5% TiB_2 /7075, (c) 6% TiB_2 /7075, (d) 9% TiB_2 /7075.

Fig. 2 SEM images of TiB_2 particles in as-cast aluminum based composite materials; (a) 3% TiB_2 /7075, (b) 9% TiB_2 /7075.

gives larger grain size if the number of particles is held constant. Particles larger than $\sim 1 \mu\text{m}$ are mostly active, while those smaller than $\sim 0.5 \mu\text{m}$ are mostly inactive.¹⁹⁾

The micrograph of TiB_2 particles in the TiB_2 /7075 Al matrix composites is as shown in Fig. 2. Most TiB_2 particles reach about 900~1400 nm in 3% TiB_2 /7075 composites, even individual up to 2000 nm. Large size of TiB_2 particles are distributed in grain boundary area, and a large number of scattered small TiB_2 particles with size of 100~400 nm are irregular polygon near the boundary inside the nucleus in 9% TiB_2 /7075 composites. Tiny TiB_2 particles are engulfed easily in the interface, bringing about the pushing of TiB_2 particles. More active TiB_2 particles and much less small TiB_2 particles can be found in 4.5% TiB_2 /7075 composites, so the grain size is the smallest, comparing with 9% TiB_2 /7075 composites.

The XRD of TiB_2 /7075 and the area scanning of 3% TiB_2 /7075 composites are listed as shown in Fig. 3(a) and (b)~(h), respectively. It can be seen that the microstructure consists of Al and TiB_2 phases, and no other phase can be found. At the same time, the peak intensity of TiB_2 became more intense with the increasing of TiB_2 . The results show that the elements of Mg, Cu and Zn to be determined are homogeneously distributed in samples. Ti elements and B elements mainly concentrate on the grain boundary, but some Ti elements and B elements distribute in the grain from Fig. 3(f) and (g) which is to say that some TiB_2 particles can play as the stable nucleus during solidification.

3.2 Influence of the holding time on microstructure of 7075 Al alloy in semi-solid state near liquidus

Figure 4 shows the microstructure of the solid 7075 Al

Fig. 3 The XRD of TiB_2 /7075 (a) and the area scanning of 3% TiB_2 /7075 composites. The scanning area (b); the distribution of Mg (c), Cu (d), Zn (e), Ti (f), B (g), Al (h).

alloy with the different holding time at 630°C which is near liquidus in semi-solid state, the maximum grain size is about $250\text{ }\mu\text{m}$ of the solid 7075 Al alloy. The branch of rosette grains begins to melt increasing gradually with time, and α -Al grains contract to sphere because spherical surface has the smallest surface energy. It can be got good globular grains for 7.5~10 min. The mean grain size can reach $94\text{ }\mu\text{m}$, and the shape factor can reach 0.65 and 0.78 for 7.5 and 10 min, respectively.

The magnified microstructure of the solid 7075 Al alloy with the different holding time at 630°C are shown in Fig. 5. The dendrite structures of α -Al grains melt to form globular grain with holding 7.5 min, and the very small grain exists on the grain boundary. After holding 10 min, globular grain melt to form the melt because the liquid fraction at 630°C is about 73.05%. We can see very small grain around globular grain in Fig. 5(d), which is entirely different from small grain with holding 7.5 min.

The microstructure evolution of 7075 Al alloy semi-solid slurry contains three parts: the phenomenon of necking and remelting of dendrite grains can be found at first, then rosette grains melt and shrink into the globular grain, finally the globular grains begin to melt with increasing of the holding time because of no stable crystal nucleus. This is to say that

the holding time control is the key factor in near-liquidus thixoforming.

3.3 Influence of the TiB_2 particles content and the holding time on microstructure of 7075 Al alloy in semi-solid state near liquidus

α -Al phase of big rosette grain begin to fuse, small dendrite grains begin to grow up at 630°C for 20 min in Fig. 6. The microstructure becomes uniform rosette grains in 3% TiB_2 /7075 Al matrix composites, but it can be get semi-solid microstructure in 4.5% TiB_2 /7075 Al matrix composites whose mean grain size and shape factor can reach $51\text{ }\mu\text{m}$ and 0.68, respectively. It can be seen that the grains are elongated in 6% TiB_2 /7075 aluminum matrix composites, and the grain boundary of 9% TiB_2 /7075 aluminum matrix composites gets wider. After holding 25 min, the microstructure becomes uniform globular grain in 3% TiB_2 /7075 and 4.5% TiB_2 /7075 aluminum matrix composites, the mean grain size and shape factor can reach $94\text{ }\mu\text{m}$ and $84\text{ }\mu\text{m}$, 0.71 and 0.78, respectively.

The microstructures of TiB_2 /7075 Al composite samples have similar effect rules after held for 30 min in Fig. 7. The mean grain size and shape factor of 3% TiB_2 /7075 and 4.5% TiB_2 /7075 aluminum matrix composites can reach $88\text{ }\mu\text{m}$ and $81\text{ }\mu\text{m}$, 0.67 and 0.72, respectively.

Dendrite grains can be found only in 6% TiB_2 /7075 Al matrix composites after being held for 35 min, and it can be get semi-solid microstructure in 9% TiB_2 /7075 Al matrix composites whose mean grain size and shape factor can reach $82\text{ }\mu\text{m}$ and 0.60, respectively. The mean grain size and shape factor of 3% TiB_2 /7075 and 4.5% TiB_2 /7075 Al matrix composites can reach $114\text{ }\mu\text{m}$ and $98\text{ }\mu\text{m}$, 0.70 and 0.67, respectively.

The mean grain size of 3% TiB_2 /7075, 4.5% TiB_2 /7075 and 9% TiB_2 /7075 aluminum matrix composites can reach $111\text{ }\mu\text{m}$, $99\text{ }\mu\text{m}$ and $69\text{ }\mu\text{m}$, respectively, the shape factor can reach 0.76, 0.78 and 0.66 for 50 min, respectively. The mean grain size and the shape factor of 9% TiB_2 /7075 Al matrix composites can reach $111\text{ }\mu\text{m}$ and 0.72, respectively for 60 min.

Table 1 is the formation time and the grain size of globular grain at 630°C . 4.5% TiB_2 /7075 Al matrix composites are easier to form globular grain because the original microstructure is uniform rosette grains and the mean grain size is the smallest. It needs only about 20 min to form globular grain and the minimum grain size are about $51\text{ }\mu\text{m}$. Whereafter, globular grains begin to grow, but the mean grain size is no significant change from 35 min to 50 min.

The change of the shape factor with the holding time are not obvious from 0.67 to 0.78. But the globular grains become rounder in the process of growth from minimum grain to maximum grain.

As we know, TiB_2 has high melting point and is thermodynamically stable. The TiB_2 particles located in the grain boundary can hinder the Al atoms from diffusing within the semi-solid state of the 7075 Al alloy, and restrain α -Al phase growth. Therefore, it need more time to form globular grain after adding TiB_2 particles, comparing with 7075 Al alloy. The minimum grain size of 3% TiB_2 /7075, 4.5% TiB_2 /7075 and 9% TiB_2 /7075 Al matrix composites are $88\text{ }\mu\text{m}$,

Fig. 4 The microstructure of the solid 7075 Al alloy with the different holding time at 630°C; (a) 0 min, (b) 7.5 min, (c) 10 min, (d) 15 min.

Fig. 5 The magnified microstructure of the solid 7075 Al alloy with the different holding time at 630°C; (a) 0 min, (b) 7.5 min, (c) 10 min, (d) 15 min.

51 μm and 69 μm , respectively. Maybe it need more time to get the globular grain in the experiment because dendrite grains of 6%TiB₂/7075 Al matrix composites is the biggest size in all TiB₂/7075 Al matrix composites. The micro-

structure evolution mechanism of the solid TiB₂/7075 Al matrix composites with the different holding time at 630°C is proposed and schematically shown in Fig. 8. With increasing holding time, on one hand, some contiguous grains merge

Fig. 6 The microstructure of the solid TiB_2 /7075 Al matrix composites at 630°C for 20 min; (a) 3% TiB_2 /7075, (b) 4.5% TiB_2 /7075, (c) 6% TiB_2 /7075, (d) 9% TiB_2 /7075.

Fig. 7 The microstructure of the solid TiB_2 /7075 Al matrix composites at 630°C for 30 min; (a) 3% TiB_2 /7075, (b) 4.5% TiB_2 /7075, (c) 6% TiB_2 /7075, (d) 9% TiB_2 /7075.

into some bigger grains by coalescence. On the other hand, Ostwald ripening occurs: small grains disappear in favor of bigger grains by diffusion through the solid phase because of 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 increasing holding time.²¹⁾ Grains no longer melt at 630°C because of TiB_2 particles as the stable nucleus. This is to say that TiB_2

Table 1 Formation time, grain size and shape factor of globular grain at 630°C.

Composites	Globular grain	Minimum grain			Maximum grain		
	Formation time/min	Size/ μm	Shape factor	Time/min	Size/ μm	Shape factor	Time/min
3%TiB ₂ /7075	25	88	0.67	30	111	0.76	50
4.5%TiB ₂ /7075	20	51	0.68	20	99	0.78	50
9%TiB ₂ /7075	35	69	0.66	50	111	0.72	60

Fig. 8 The microstructure evolution mechanism of the solid TiB₂/7075 Al matrix composites with the different holding time at 630°C.

particles can be conducive to improve the stability of semi-solid slurry in near-liquidus thixoforming.

4. Conclusions

The results described in this work can be summarized as follows:

- (1) TiB₂/7075 Al matrix composites are formed by *in situ* reaction in matrix melt. The microstructure becomes uniform rosette grains after adding 3%TiB₂, and the grain size shows a decreasing tendency with increasing of TiB₂ particles. The morphology of grains become big dendrite grains when the TiB₂ particles content are over 4.5%.
- (2) It can be got good globular grains with the different holding 7.5~10 min at 630°C. The mean grain size can reach 94 μm , which is smaller than the as-cast microstructure. The phenomenon of necking and remelting of dendrite grains can be found at first, then rosette grains melt and shrink into the globular grain, finally the globular grains begin to melt with increasing of the holding time.
- (3) The minimum grain size of 3%TiB₂/7075, 4.5%TiB₂/7075 and 9%TiB₂/7075 Al matrix composites are 88 μm , 51 μm and 69 μm for 30 min, 20 min and 50 min, respectively. The TiB₂ particles located in the grain boundary can hinder the Al atoms from diffusing within the semi-solid state of the 7075 Al alloy and

restrain α -Al phase growth, but it can be conducive to improve the stability of semi-solid slurry in near-liquidus thixoforming.

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