Influence of TiB₂ nanoparticles on elevated-temperature properties of Al–Mn–Mg 3004 alloy

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Abstract: Two contents (1.5% and 3%) of TiB₂ nanoparticles were introduced in Al–Mn–Mg 3004 alloy to study their effects on the elevated-temperature properties. Results show that TiB₂ nanoparticles were mainly distributed at the interdendritic grain boundaries with a size range of 20–80 nm, which is confirmed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Therefore, the volume fraction of the dispersoid free zones is greatly reduced and the motion of grain boundaries and dislocations is inhibited more effectively at elevated temperature. After peak precipitation heat treatment, the yield strengths in the alloy with 3% TiB₂ addition at room temperature and 300 °C were increased by 20% and 13% respectively, while the minimum creep rate at 300 °C was reduced to only 1/5 of the base alloy free of TiB₂, exhibiting a considerable improvement of elevated-temperature properties in Al–Mn–Mg alloys.

Key words: Al–Mn–Mg 3004 alloy; TiB₂ nanoparticle; dispersoid free zone; elevated temperature property; creep

1 Introduction

Recently, Al–Mn–Mg 3xxx alloys have been developed as one of the most promising candidates in light alloys for the elevated-temperature applications (250–350 °C) due to the formation of thermally-stable dispersoids after proper heat treatments [1–3]. During heat treatment, the dispersoids can precipitate to increase the alloy properties. Meanwhile, the dispersoid free zone (DFZ) is always present in the interdendrites due to the depletion of Mn by forming the Mn-containing intermetallics during the solidification, resulting in a decrease of the properties [2]. Therefore, optimizing the dispersoid distribution and controlling the DFZ are two key factors to improve the elevated-temperature properties. Many works have been performed aiming to increase the volume fraction of dispersoids and control their size through modifying the alloying elements or/and heat treatments [2,4–6]. MUGGERUD et al [5] reported that increasing Mn and Si can enhance the precipitation of dispersoids while various heat treatments have been performed to study their influence on dispersoids by HUANG and OU [4]. However, the balance between dispersoids and DFZ is hard to control. Due to the high precipitation temperature of dispersoids [2], a large volume fraction of DFZ often forms in the peak precipitation condition. On the other hand, DFZ can be decreased by modifying the heat treatment but the size of dispersoids may become bigger with lower volume fraction of dispersoids than their peak condition [5,7]. Therefore, how to control the DFZ in the microstructure is a significant concern on further improving the elevated-temperature properties of 3xxx alloys.

Introducing the ceramic particles that can be presented in the interdendritic area is one potential approach to decrease the volume fraction of DFZ. The transition metal ceramics are one of them, such as TiC and TiB₂, which are reported to be preferentially located in interdendritic regions during solidification [8,9]. Meanwhile, it is reported that the addition of high volume of metal ceramic particles to aluminum alloys can improve their alloy properties [10–12]. For instance, the stiffness and ductility have been increased in 1xxx alloys due to the addition of 10% TiB₂ particles [8]. Besides, the creep resistance of the composite has been also increased by two orders of magnitude higher than that of pure aluminum due to the addition of 20% ceramic particles, including SiC, Al₂O₃ and TiB₂ [12].

However, the fabrication difficulties and cost significantly rise with increasing volume fraction of metal ceramic particles due to the poor wettability...
between them and liquid aluminum. Besides, the size of ceramic particles in the conventional particle-reinforced metal matrix composites is quite big, which often ranges from several to few tens micrometres, limiting the strengthening effect on aluminum matrix [8,12]. Furthermore, limited open literatures in 3xxx alloys about the influence of nanoparticles on properties, especially at elevated temperature, were reported. Therefore, relatively low volume fractions of TiB₂ nanoparticles (1.5%–3%) were introduced to Al–Mn–Mg 3004 alloy in the present work aiming to discover their impact on the elevated-temperature strength and creep resistance.

2 Experimental

Three alloys have been designed in the present work and their nominal compositions are shown in Table 1. Two contents of TiB₂ nanoparticles (1.5% and 3%) were added to the liquid aluminum by flux-assisted melt stirring process [9]. The TiB₂ powder and the K₂ZrF₆ flux were mechanically mixed with a mass ratio of 1:3 in a ball milling unit and then the powder mixture was pressed to a cylindrical perform. The Al–Mn–Mg base alloy was prepared with pure Al, pure Mg, Al–50%Si, Al–25%Mn and Al–25%Fe master alloys and melted at 850 °C in an electrical resistance furnace. When the melt is ready, the prepared cylindrical perform of powder mixture was added to the melt under mechanical stirring of 900 r/min for 10 min. Then, the melt was skinned, poured and solidified in a steel mold preheated at 450 °C. The details about alloy preparation and casting process parameters can be found in our previous work [2,9].

Table 1 Nominal chemical compositions of alloys used in present work (mass fraction, %)

<table>
<thead>
<tr>
<th>Alloy code</th>
<th>Mn</th>
<th>Mg</th>
<th>Fe</th>
<th>Si</th>
<th>TiB₂</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1.1</td>
<td>1.0</td>
<td>0.6</td>
<td>0.25</td>
<td>0</td>
<td>Bal.</td>
</tr>
<tr>
<td>T15</td>
<td>1.1</td>
<td>1.0</td>
<td>0.6</td>
<td>0.25</td>
<td>1.5</td>
<td>Bal.</td>
</tr>
<tr>
<td>T30</td>
<td>1.1</td>
<td>1.0</td>
<td>0.6</td>
<td>0.25</td>
<td>3</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

In order to reach the peak precipitation condition, a low temperature heat treatment (375 °C for 48 h) followed by water quenching was adopted on all experimental alloys [2]. The yield strengths (YS) at both room temperature (RT) and 300 °C were measured in the compression tests performed on a Gleeble 3800 thermomechanical testing unit using the cylindrical specimens with sizes of 15 mm in length and 10 mm in diameter. The total deformation of the specimen was set to 0.2, and the strain rate was fixed at 1×10⁻³ s⁻¹. For the compression test at 300 °C, the specimen was heated to 300 °C with a heating rate of 2 °C/s and held for 3 min to stabilize. An average value of YS was obtained from 3 tests. In addition, the compressive creep tests were performed at 300 °C and the specimens were the same size as the Gleeble samples. Creep behaviors were first tested at a constant load of 38 MPa and then multiple loads have been applied to calculating the creep threshold stress and stress exponent. For each condition, three tests were repeated to confirm the reliability of the results.

The microstructural features, including characters of TiB₂ nanoparticles, intermetallics, dispersoids and grain structures in both as-cast and heat-treated conditions were observed by X-ray diffraction (XRD), optical microscope (OM) and electron microscopes. To reveal the dispersoids clearly, the polished samples were etched in 0.5% HF for 30 s. A scanning electron microscopy (SEM) equipped with electron backscatter diffraction (EBSD) was used to examine the grain structure of alloys. A transmission electron microscopy (TEM) operated at 200 kV was used to observe the distribution of TiB₂ nanoparticles and dispersoids. In this study, the volume fraction of DFZ was converted from the area fraction of DFZ measured in image analysis from optical images according to the Delesse’s principle [13]. The volume fraction of dispersoids (V_d) was calculated according to the model introduced in Ref. [6] and shown in Eq. (1):

\[
V_d = A_d \frac{D}{KD + t}(1 - A_{DFZ})
\]

where D is the average equivalent diameter of dispersoids, which is calculated according to Ref. [6]; t is the TEM foil thickness measured with electron energy loss spectroscopy (EELS); A_d is the area percentage of dispersoids from TEM observation; A_{DFZ} is the area percentage of DFZ from OM measurements; and K is the average shape factor of dispersoids [6].

3 Results and discussion

3.1 As-cast and heat-treated microstructures with various contents of TiB₂ nanoparticles

In order to show the general distribution of TiB₂ particles in alloys, Fig. 1 illustrates the as-cast microstructures of Alloys B, T15 and T30. In the base alloy (Alloy B, Fig. 1(a)), it can be seen that the microstructure is composed of α(Al) cells/grains surrounded with Al₉(MnFe) intermetallic particles [2,3]. With the addition of TiB₂ nanoparticles in Alloys T15 and T30, those nanoparticles preferentially occurred in the interdendrite regions. As shown in Figs. 1(b) and (c), TiB₂ nanoparticles are always present with interdendritic intermetallics. Besides, the volume fraction of nanoparticles in Alloy T30 remarkably increases compared with Alloy T15.
Figure 2 displays the XRD analysis of experimental alloys in as-cast condition. Compared with the base alloy of Alloy B, there are more peaks appeared in Alloys T15 and T30 besides the peaks of Al6(MnFe) [14]. According to Refs. [15,16], these additional peaks are identified from the TiB2 particles, confirming the presence of TiB2 nanoparticles in solidified microstructure of Alloys T15 and T30. Besides, it seems that the peak intensity of TiB2 increases from Alloy T15 to Alloy T30, as shown in dashed box, indicating the higher volume fraction of TiB2 nanoparticles in Alloy T30 than in Alloy T15.

Furthermore, TEM was used in the present work to study the incorporation and distribution of TiB2 nanoparticles. As an example, the TEM observation of Alloy T30 with 3% TiB2 in as-cast condition is displayed in Fig. 3. It can be found in Fig. 3(a) that the TiB2 particles are successfully incorporated into aluminum in the form of either cluster or single particle, which is much clear in the enlarged area shown in Fig. 3(b). In Fig. 3(b), major particles present as single particle with overlaps between them and the size of these particles is in the range of 20–80 nm. Besides, Fig. 3(c) shows the TEM–EDS result of the particle A in Fig. 3(b). It can be seen that the particles are composed of Al, Ti and B, confirming the particles as TiB2 nanoparticles. In addition, the well-indexed selected area diffraction pattern (SADP) from TEM further identifies the particle as the hexagonal close-packed (HCP) TiB2 [17].

During solidification, TiB2 nanoparticles have a great tendency to segregate at the interdendrite grain boundaries [9]. Using this feature, it is expected to have less DFZ in Alloys T15 and T30 after the peak precipitation heat treatment at 375 °C for 48 h. As an example, the microstructure of Alloys B and T30 after heat-treatment is shown in Fig. 4 with the distribution of intermetallics, nanoparticles, dispersoids and DFZ. As general, the dispersoids precipitated in α(Al) cell/grains while the DFZ formed in the interdendritic regions surrounding with the intermetallics. Figures 4(a) and (b) show the similar characters of dispersoids in both Alloys B and T30, which are uniformly precipitated in α(Al) matrix. This is also confirmed by the TEM observation of dispersoid zone in Figs. 4(c) and (d).

Table 2 summarizes the characters of dispersoids as well as DFZ of experimental alloys after heat treatment. As shown in Table 2, the average size of dispersoids in three experimental alloys is all in the range of 70–75 nm. However, major difference of the DFZ volume fraction can be found among three alloys. As shown in Fig. 4(b), though the DFZ still can be observed in Alloy T30, its volume fraction has been reduced due to the presence of TiB2 nanoparticles in the interdendrite regions. It is also displayed in Table 2 that the volume fraction of DFZ has been decreased from 31% in Alloy B to 26% in Alloy T15 and further to 19% in Alloy T30 (volume fraction). According to Eq. (1), the calculated volume fraction of
Fig. 3 TEM images (a, b), EDS result (c) and SADP (d) of TiB$_2$ nanoparticles in as-cast Alloy T30

Fig. 4 Distribution of dispersoids and DFZ in Alloy B (a, c) and Alloy T30 (b, d) after heat treatment at 375 °C for 48 h
Table 2 Characteristics of dispersoids and DFZ in experimental alloys after heat treatment at 375 °C for 48 h

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Dispersoid</th>
<th>DFZ</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>D/μm</td>
<td>V_d/%</td>
</tr>
<tr>
<td>B</td>
<td>73±12</td>
<td>2.54±0.58</td>
</tr>
<tr>
<td>T15</td>
<td>75±15</td>
<td>2.71±0.75</td>
</tr>
<tr>
<td>T30</td>
<td>71±13</td>
<td>2.96±0.62</td>
</tr>
</tbody>
</table>

dispersoids increases due to the decreasing volume fraction of DFZ with the addition of TiB₂ nanoparticles. The volume fraction of dispersoids rises from 2.54% in Alloy B to 2.71% in Alloy T15 and further to 2.96% in Alloy T30 (Table 2).

3.2 Evolution of elevated-temperature properties with addition of TiB₂ nanoparticles

As shown in Fig. 4 and Table 2, the volume fractions of DFZ and dispersoids varied with the addition of TiB₂ nanoparticles after heat treatment. Therefore, different alloy properties are expected. In the present work, the compressive YS at both RT and 300 °C as well as the creep resistance at 300 °C after heat treatment (375 °C, 48 h) was measured (Fig. 5). As shown in Fig. 5(a), it can be seen that the YS increases with the increasing content of TiB₂ particles at both RT and 300 °C. For instance, YS increased from 101 MPa, 74 MPa in Alloy B to 107 MPa, 78 MPa in Alloy T15 and further to 120 MPa and 84 MPa at RT and 300 °C, respectively, which is 20% at RT and 13% at 300 °C of strength improvement with the addition of 3% TiB₂ nanoparticles relative to the base alloy. Therefore, the improvement on strength confirms the positive influence of TiB₂ nanoparticles on alloy properties at both RT and elevated temperature.

As shown as Table 2, the volume fraction of dispersoids increases while the DFZ area decreases with the addition of TiB₂ nanoparticles. Therefore, the strength can be improved due to effectively pinning dislocations by dispersoids according to the Orowan strengthening mechanism [1,2,5]. Besides, TiB₂ is reported to an effective grain refiner in aluminum alloys [18]. In the present work, the grain size was measured using EBSD and the results are shown in Fig. 6. It can be found that the grain size is greatly reduced due to the addition of TiB₂ nanoparticles. The average grain size is decreased from 356 μm in Alloy B to 122 μm in Alloy T15 and further to 95 μm in Alloy T30. Therefore, the alloy strength can be further improved due to the finer grains in Alloys T15 and T30 according to the Hall–Petch strengthening [19,20].

Besides, the creep tests at 300 °C under a constant load of 38 MPa were also carried out (Fig. 5(b)) to show the evolution of creep resistance with the addition of TiB₂. It can be found that the total creep strain in 100 h decreased with an increasing level of TiB₂ nanoparticles. As shown in Fig. 5(b), the total creep strain decreases from 0.006 in Alloy B to 0.004 in Alloy T15 and further to 0.003 in Alloy T30, indicating the improvement of creep resistance from the addition of TiB₂ nanoparticles. Moreover, the minimum creep rate \( \dot{\varepsilon} \) also descends with increasing addition of TiB₂ nanoparticles. The minimum creep rate is calculated to be \( 1.1 \times 10^{-8} \text{ s}^{-1} \) for the base alloy (Alloy B), and it drops to \( 7.2 \times 10^{-9} \text{ s}^{-1} \) in Alloy T15 with 1.5% TiB₂ and further decreases to \( 2.1 \times 10^{-9} \text{ s}^{-1} \) in Alloy T30 with addition of 3% TiB₂ nanoparticles. The minimum creep rate of Alloy T30 is reduced to 1/5 of the base alloy (Alloy B). Similar to the improvement of yield strength from pinning effect of dislocations, the reduced DFZ and higher volume fraction of dispersoids due to the addition of TiB₂ nanoparticles also leads to the better creep properties [2,3]. However, the finer grain structure caused by TiB₂ addition can reduce the high-temperature creep resistance [21]. It is most likely that TiB₂ nanoparticles at the interdendritic grain boundaries effectively inhibited the motion of grain boundaries. Therefore, the negative influence of finer grains on creep properties has been
overcome. The synergistic effect of higher volume fraction of dispersoids and the inhabitation effect on grain boundaries from TiB₂ nanoparticles still results in the improvement of the creep resistance.

In order to better understand the creep behavior of TiB₂-containing materials, the creep tests at different loads were performed to determine two important creep parameters, namely the threshold stress $\sigma_{th}$ and true stress exponent $n$ [22]. The threshold stress $\sigma_{th}$ is calculated as a stress value when the minimum creep rates ($\dot{\varepsilon}$) at different loads are extrapolated to $1 \times 10^{-10}$ s$^{-1}$, below which the creep is experimentally not measurable. The true stress exponent $n$ is the slope of $\ln \dot{\varepsilon} - \ln (\sigma - \sigma_{th})$ curve [23]. The calculated results are shown in Fig. 7. As shown in Fig. 7(a), the minimum creep rate $\dot{\varepsilon}$ decreases with the increasing addition of TiB₂ nanoparticles at all applied loads and the threshold stress $\sigma_{th}$ increases from 22.4 MPa in Alloy B to 24.2 MPa in Alloy T30. It is reported that an increase of 3 MPa in threshold stress can make an order of magnitude decrease in the minimum creep rate [24]. In the present work, the minimum creep rate of Alloy T30 has been decreased to only 1/5 of base alloy with an increase of threshold stress of 1.8 MPa, confirming an overall positive influence of TiB₂ nanoparticles on creep resistance. Besides, the true stress exponent $n$ is calculated to be close 3 for the three experimental alloys (Fig. 7(b)), which suggests that the creep is still controlled by dislocation glide mechanism rather than the grain boundaries [25], further confirming that the motion of grain boundaries has been effectively restricted by the TiB₂ nanoparticles distributed in interdendrite regions.

As shown in Figs. 5 and 7, the elevated-temperature properties, such as the yield strength and creep resistance, have been increased due to TiB₂ nanoparticles, which results in a strong pinning effect on dislocations and effective inhibition on the grain boundary motion. A
superior YS (84 MPa) and excellent creep resistance (2.1×10⁻⁹ s⁻¹ of minimum creep rate) at 300 °C have been achieved with 3% TiB₂ of alloy treated, providing a novel possibility to further improve the properties of Al–Mn–Mg 3xxx alloys for elevated-temperature applications.

4 Conclusions

1) TiB₂ nanoparticles have been successfully incorporated into aluminum, and during solidification, those particles are mainly distributed in the interdendritic regions with a size range of 20–80 nm.

2) Lower volume fraction of dispersoid free zone and finer grain size due to the addition of TiB₂ nanoparticles result in the higher strength at both RT and 300 °C. In heat-treated alloy containing 3% TiB₂, the yield strengths have been improved by 20% and 13% at room temperature and 300 °C, respectively, relative to the base alloy free of TiB₂.

3) The creep resistance at 300 °C also increases with the addition of TiB₂ nanoparticles. Compared with the base alloy free of TiB₂, the minimum creep rate has been reduced to 1/5 of base alloy with an increase of 1.8 MPa in the threshold stress in the alloy with 3% TiB₂.

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References


TiB₂纳米颗粒对Al–Mn–Mg 3004合金中高温性能的影响

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摘 要: 不同含量的TiB₂纳米颗粒(1.5%和3%)分别加入3004合金研究TiB₂纳米颗粒对Al–Mn–Mg 3004合金中高温性能的影响。透射电镜和X射线衍射结果表明,TiB₂纳米颗粒主要分布在枝晶界,尺寸在20–80 nm。因此,合金中弥散相无析出带的体积分数大幅减少,同时,TiB₂纳米颗粒的添加有效钉扎了晶界和位错的移动,从而提高了合金的强度和抗蠕变性能。在经过峰值析出热处理后,与未添加TiB₂纳米颗粒的合金相比,加入3% TiB₂纳米颗粒的3004合金在常温和300 °C下的屈服强度分别提高了20%和13%。同时,该合金在300 °C下的最小蠕变速率也降低至未添加TiB₂纳米颗粒合金的1/5,体现了TiB₂纳米颗粒对Al–Mn–Mg合金中高温性能的强化作用。

关键词: Al–Mn–Mg 3004合金; TiB₂纳米颗粒; 弥散相无析出带; 中高温性能; 蠕变

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