Aging Behavior of In-Situ TiB₂ Particles Reinforced 2014Al Alloy Composites

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In-situ TiB₂ particles reinforced 2014Al alloy matrix composite was prepared using an exothermic reaction process with K₂TiF₆ and KBF₄ salts. The age-hardening behaviors of in-situ TiB₂/2014Al composites were studied using Vickers-hardness measurement, DSC and TEM. The results indicated that TiB₂ particles had a considerable effect on the aging response of 2014Al alloy matrix in the composite. Due to the introduction of TiB₂ particles, the time to achieve peak hardness in the composite is shorter at three aging temperatures compared with that of 2014Al alloy. While the age-hardness efficiency of the composites was lower than that of 2014Al alloy. Formation of G.P. zones was suppressed in composite, which was believed to be due to the introduction of vast particle-matrix interfaces that acted as a sink for vacancies during quenching. Moreover, TiB₂ particles caused increase in thermal-diffusion activation energy of θ' phase during aging, which made the precipitation of θ' phase more difficult. And the number and size of precipitates in the composite were relatively less and smaller than that of 2014Al alloy.

Keywords: aluminum matrix composites, TiB₂ particles, aging

1. Introduction

Most composites are based on age hardenable alloys, so that they may be heat-treated to develop the optimum balance of mechanical properties. Extensive studies have been carried on age-hardening behavior of particles reinforced Al alloy matrix composites, and many mature theory systems of the microstructure and strengthen mechanism were built.

Previous some studies showed the addition of particles may accelerate aging kinetics of the matrix alloy in composite.¹–⁴ Some others concluded a decrease or very little alteration in aging kinetics of the matrix alloy with reinforcement addition.⁵–⁹ The change in aging kinetics during aging of composites due to addition of reinforced particles depends on type of particles including their size, morphology and volume fraction.¹⁰–¹² However, the age-hardness efficiency of the composite depends mainly upon the nature of the interface between matrix and reinforcement.¹³

Particles reinforced Al alloy matrix composites usually are classified into two categories according to the addition methods of reinforcing particles: ex-situ particles reinforced composite and in-situ particles reinforced composite. The ex-situ particles reinforced composite is prepared by direct adding reinforced particles into matrix alloy, while during the preparation of in-situ particles reinforced composite reinforced particles are generated by the reaction between salts and matrix alloy. In case of ex-situ micro-particles reinforced Al alloy matrix composite, it has been conclusively shown that the addition of particles such as SiC leads to acceleration in the aging kinetics in comparison with the unreinforced matrix alloy. The acceleration is associated with the higher dislocation densities observed in the composite due to the introduction of particles into 2014Al alloy. Many dislocations may act as nucleation sites for precipitates and make solute atoms diffuse faster, which accelerates precipitate nucleating and growing up.¹²,²⁷ However, in contrast, different results have been reported when the size of reinforced particles is changed.⁸ L. T. Jiang et al.⁸ indicated that when the Al₂O₃ reinforced particles size changes from micro to sub-micro, with the same volume fraction, the number of the reinforcement will be more increased. Due to the volume effect and surface effect, the composite exhibited some unusual characteristics of lower dislocation density and the precipitation of age-hardening phases was suppressed. At present, in-situ particles reinforced Al alloy matrix composite has been the highlight of research interests due to clean interfaces, strong interfacial bonding, fine particles, which differs from that of conventional ex-situ particles reinforced composite. More importantly, the composite exhibits the advantages on mechanical properties and abrasive resistance over the ex-situ particles reinforced composites, which indicates that strengthening mechanism is different.¹⁴–¹⁷ Aging strengthening is one of the most important strengthening mechanisms for Al alloy matrix in composite. So, in order to fully utilizing the potentiality of the composite, it is more urgent to study the aging behavior of in-situ TiB₂ particles reinforced composite in details. Earlier, some studies¹⁸,¹⁹ have indicated the increase in mechanical properties of the composite in peak-aged conditions compared to that in as-cast conditions, and the enhancement in aging kinetics of matrix alloy due to the presence of TiB₂ particles. However, no systematic studies on age-hardness behavior of such composite and effect mechanism of TiB₂ particles on the aging response of Al alloy matrix were carried out.

The present work is aimed at studying age-hardness behavior of in-situ TiB₂/2014Al composite and the effect of TiB₂ particles on the aging response of 2014Al alloy matrix. Hence systematic studies on the age-hardening behavior and precipitate microstructures of the in-situ TiB₂/2014Al composite and 2014Al alloy was done by means of Vickers Hardness measurement, differential scanning calorimeter (DSC) and transmission electron microscopy (TEM).
2. Materials and Methods

2.1 Experimental materials

In-situ 5 vol% TiB₂/2014AI composite was prepared in advance by an exothermic reaction among K₂TiF₆, KBF₄ and 2014AI alloy (composition listed in Table 1) melts at 1123 K. Then the composite and 2014AI alloy were remelted and squeezed under 120 MPa, respectively. The specific process and squeeze casts have been reported in the previous paper.²⁻³) The specimens were taken from the top of the composite and 2014AI alloy casts, respectively. The microstructures of the composite were shown in Fig. 1. As shown in Fig. 1(a), TiB₂ particles were near discoid shape and their sizes were about 50 nm-1 μm². It can be seen from Fig. 1(b) that particles distributed homogeneously and no obvious defects were found.

2.2 Experiment methods

The specimens of composite were solution treated at 773 K for 4 h and water quenched at room temperature. After solution treatment, the specimens were aged at 423, 443 and 463 K for periods up to 100 h. For comparison, 2014AI alloy was also treated as the above-mentioned methods. After heat treatment, all samples were stored at 253 K to prevent possible natural aging.

The age-hardening responses of the composite and 2014AI alloy were characterized using Vickers hardness measurement at 5 kg load (hence the hardness is represented as Hv5). Each hardness value presented was an average of triplicate specimens and five measurements per condition to ensure the accuracy of results. DSC experiments were performed by using a C404/6/7 thermal analyzer made in Germany. Heating rates of DSC tests was from 5 K·min⁻¹ to 20 K·min⁻¹, and test temperature from room temperature to 773 K for all DSC tests is used to study the variation of activation energy for precipitates. The DSC thermograms were normalized to mass of the composite and 2014AI alloy.

The TEM specimens of the composite and 2014AI alloy were prepared by ion thinning at an accelerating voltage of 5 kV and 13 deg with a liquid nitrogen cold stage after using dimpler to ground to a 10 μm thickness. Transmission electron microscopy was performed on a JEM-2100F transmission electron microscope (TEM).

3. Results and Discussions

3.1 Hardness testing

Figure 2 shows the hardness of in-situ 5 vol% TiB₂/2014AI alloy at different aging temperatures.
composite and 2014Al alloy as a function of aging time at aging temperatures of 423, 443 and 463 K, respectively. All curves qualitatively show a similar development. Hardness of the two materials increases monotonically as a function of aging time and rises to a peak value, and then gradually decreases. In addition, it also can be seen that for both the composite and 2014Al alloy the peak-aging time decreases with increasing aging temperature, and the age-hardening kinetics becomes faster with increasing of aging temperature.

However, the attainments of the peak hardness value and peak-aging time in Fig. 2 reveal conspicuous differences in the two materials. It is seen that at the aging temperature of 443 K, the composite reaches a peak hardness value of 163Hv5 after 12 h of aging. While the peak hardness of 2014Al alloy is 138Hv5 observed after 17 h of aging. It is obvious that the time to attain the peak hardness is reduced 5 h for the composite. This indicates that the introduction of TiB2 particles accelerates aging kinetics of matrix alloy in the composite. And at three aging temperatures all curves have a similar variation trend, that is, the peak hardness of the composite is shifted towards shorter aging times compared to the 2014Al alloy.

Figure 3 gives the relative hardness increment of the composite as well as 2014Al alloy at three aging temperatures. It can be seen that for the composite and 2014Al alloy, the temperature with maximum hardness value are both 443 K, that is, when the aging temperature is 443 K, the hardness increment is the biggest for the two materials. In addition, it also can be seen that the peak hardness increment is lower at all temperatures for the composite compared with that of 2014Al alloy. When the aging temperature is 443 K, the peak hardness increment is ΔHv5 = 64 for 2014Al alloy, it is only ΔHv5 = 53 for the composite. It indicates that the composite shows a relatively weak aging response, that is, the age-hardening efficiency of the composite is lower than that of 2014Al alloy. In the case of in-situ TiB2 particles reinforced Al alloy matrix composite aging strengthening have a smaller contribution to hardness, and is not the major hardness mechanism. The thermal-diffusion activation energy during precipitation processes of θ'' and θ' phases can be calculated according to the following equation of Augis and Bennett,8,23,24)

\[
\ln \left( \frac{T_p - T_0}{Q} \right) = \frac{E}{RT_p} - \ln K_0
\]

Where \(T_p\) is the exothermic peak temperature of precipitates, \(T_0\) is the initial temperature, \(Q\) is the heating rate, \(K_0\) is the reactive constant, \(E\) is thermal-diffusion activation energy and \(R\) is gas constant. The results are put in formula (1), and a graph of relationship between \(\ln[(T_p - T_0)/Q]\) and \(1/T_p\) is given. Tan θ is the slope coefficient of the line:

![Figure 3](image1.png)

**Fig. 3** The relative hardness increments (the difference between the peak hardness and the solution treatment hardness) for the in-situ 5 vol% TiB2/2014Al composite and 2014Al alloy at three aging temperatures.

![Figure 4](image2.png)

**Fig. 4** DSC curves of the as-quenched specimens of 2014Al alloy (a) and in-situ 5 vol% TiB2/2014Al composite (b) at different heating rates.

3.2 DSC analysis

For comparison purposes, results from DSC thermograms of the in-situ 5 vol% TiB2/2014Al composite and 2014Al alloy quenched into water are shown in Fig. 4. The curve from 2014Al alloy obviously shows three exothermic peaks respectively associated with the formation of G.P. zones, θ'' and θ' phases, as shown in Fig. 4(a), which is similar to 2024Al reported by C. Badini.22 While the curve of composite have not obvious peak associated with G.P. zone in Fig. 4(b). There are only two exothermic peaks between the regions of 323 K and 600 K in Fig. 4(b). It can be concluded that the formation of G.P. zones in the composite is suppressed due to the introduction of TiB2 particles.
\[ \tan \theta = \frac{E}{R} \]  

(2)

According to formula (2), thermal-diffusion activation energies of precipitates of \(\theta''\) and \(\theta'\) phases during aging process of the composite and 2014Al alloy can be calculated. It can be seen from Fig. 5 that the thermal-diffusion activation energies of \(\theta''\) and \(\theta'\) phases in the composite are 74 kJ mol\(^{-1}\) and 100 kJ mol\(^{-1}\) respectively, while those in 2014Al alloy are 66 kJ mol\(^{-1}\) and 79 kJ mol\(^{-1}\) respectively. It is obvious that the thermal-diffusion activation energies in composite are higher than that in 2014Al alloy. The result shows that due to the introduction of TiB\(_2\) particles the precipitation of \(\theta''\) and \(\theta'\) phases become more difficult and need more energy, which is similar to the results on ex-situ sub-micron Al\(_2\)O\(_3\) particles reinforced Al matrix composite\(^8\), while is different from the results about ex-situ micro-particles reinforced Al matrix composite\(^7,23\).

3.3 TEM observation

In order to follow the microstructural changes associated with the aging process, TEM micrographs of 2014Al alloy and in-situ TiB\(_2\)/2014Al composite aged at 443 K for different periods are given in Fig. 6. As shown in Fig. 6(a), (b), the needle precipitates both in two materials aged at 443 K for 1 h are observed. However, for 2014Al alloy, a large number of precipitates are formed and the size is about 30–60 nm, while a few precipitates are observed in the composite and the size is relatively smaller. Figure 6(c), (d) shows the microstructures of 2014Al alloy and the composite aged at 443 K for 6 h. To some degree, the precipitates both in two materials grow up. But the number and size of precipitates in the composite are still less and smaller than that of 2014Al alloy. With continued aging (443 K/64 h), the size of precipitates both in 2014Al alloy and the composite becomes larger, and the former is 3 times larger than the latter, as shown in Fig. 6(e), (f). Figure 7 gives the sizes of precipitates for 2014Al alloy and the composite aged at 443 K for different periods. It is obvious that the existence of TiB\(_2\) particles suppresses the growth of precipitates.

It can be seen from Fig. 6(f) that TiB\(_2\) particles with discoid shape distribute relatively homogeneous in the composite, while in microscopic view, there are still some dense and rare particle region. Figure 8 shows TEM micrographs of the rare and dense particle regions in the composite aged at 443 K for 64 h. It is obvious that the density of precipitates in rare particle region is higher than that of dense particle region.

3.4 Effect of TiB\(_2\) particles on the aging behavior

Earlier studies\(^1,3,7\) found that for most of ex-situ micro-particle reinforced composites, the addition of particles accelerates aging kinetics of the matrix alloy in composite. Most of researchers considered that the major reason for aging acceleration is a higher dislocation density in the composite due to the introduction of particles into matrix alloy. Many dislocations may act as nucleation sites for precipitates as well as provide solute atom diffusion alleyway, thus accelerating nucleation and growth of the precipitates.

However, the effect of TiB\(_2\) particles on the aging response
of 2014Al alloy matrix in the composite is obviously different from that of micro-particle on matrix alloy in the ex-situ micro-particle reinforced composites. Although the introduction of TiB\textsubscript{2} particles accelerates aging kinetics of 2014Al alloy matrix in composite, the age-hardness efficiency of the composites is lower than that of 2014Al alloy at the same aging temperature. In addition, the number and size of precipitates in the composite are relatively less and smaller compared with that in 2014Al alloy. In the composite the size of in-situ formed TiB\textsubscript{2} particles is smaller and about 50 nm in the composite are relatively less and smaller compared with that in 2014Al alloy. In the composite the size of in-situ formed TiB\textsubscript{2} particles is smaller and about 50 nm compared with that of 2014Al alloy. In addition, the morphology of TiB\textsubscript{2} particle has also effect on the aging precipitation behavior of 2014Al alloy matrix. Earlier studies show\textsuperscript{25} that for micro-particles with sharp corner reinforced Al matrix composite, a high dislocation density is formed in the matrix alloy due to the bigger thermal mismatch stress between particles and matrix. While, when the particle size reduces to submicron or nanometer, the thermal mismatch stress is so weak that it is difficult to form dislocation structure. In the in-situ TiB\textsubscript{2}/2014Al composite the morphology of TiB\textsubscript{2} particle is near discoid shape and its size is small (50 nm \textasciitilde 1 \textmu m). So, the thermal mismatch stress between particle and alloy matrix is lower, and it is difficult to form dislocation in the alloy matrix. The lower dislocation density in the composite can't provide solute atoms diffusion alleyway, which inhibits precipitate nucleating and growing up. In the meantime, the lack of G.P. zones has also a considerable effect on the later stages of aging process. The suppression of G.P. zone formation during the early aging stage means that no nuclei are produced for \texttheta' formation until a considerably later stage of the aging process. Therefore aging precipitation phases in the composite are less in number and finer in shape compared with that of 2014Al alloy.

### 4. Conclusions

The age-hardening behavior in-situ TiB\textsubscript{2}/2014Al composite and effect of in-situ formed TiB\textsubscript{2} particles on the aging characteristics of TiB\textsubscript{2}/2014Al composite are investigated. The main conclusions are:

1. The time to achieve peak hardness in the composite is shorter than that in 2014Al alloy at three aging temperatures.
2. The age-hardening efficiency of composite is lower than that of 2014Al alloy. The reason is believed to be due to the suppression of G.P. zone and \texttheta' phase formation in the 2014Al alloy matrix of composite.
3. Aging temperature has a great effect on the aging hardening process. With the increasing of temperature, the precip-
itation process is accelerated, and the time to reach peak hardness is shortened.

For the composite and 2014Al alloy, the aging temperatures with maximum hardness value are both 443 K.

(4) The existence of TiB$_2$ particles in 2014Al alloy matrix suppresses the formation of G.P. zones since the introduction of vast particle-matrix interfaces acts as a sink for vacancies and soaks up vacancies during quenching. Moreover, due to the presence of TiB$_2$ particles the thermal-diffusion activation energy of $\theta'$ phase is increased during aging process, which makes the precipitation of $\theta'$ phase more difficult. This may be attributed to the introduction of vast particle-matrix interfaces, lower dislocation density and suppression of G.P. zone formation in the composite compared with that in 2014 Al alloy. The number and size of precipitates in the composite are relatively less and smaller.

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REFERENCES