

Behavior of CeO₂ additive in in-situ TiB₂ particles reinforced 2014 Al alloy composite

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Abstract: In-situ TiB₂ particles reinforced 2014 aluminum alloy composite was prepared using an exothermic reaction process with K₂TiF₆ and KBF₄ salts. The effects of CeO₂ additive on the microstructure and properties of in-situ TiB₂/2014 composite were investigated. The results showed that CeO₂ at high temperature exhibits the same function as Ce. When 0.5% (mass fraction) CeO₂ additive was added, the dispersion of TiB₂ particles in the matrix is improved significantly, and particles have no obvious settlement. The dispersing mechanism of TiB₂ particles in 2014 Al alloy matrix was explained. Compared with the composite without CeO₂, the hardness, tensile strength, yield strength and elongation of the composite with CeO₂ addition are greatly increased in as-cast condition.

Key words: 2014 Al alloy; TiB₂; composites; CeO₂

1 Introduction

Particles reinforced aluminum alloy matrix composites have emerged as potential alternatives to conventional Al alloy due to their high strength, hardness, modulus, wear resistance and fatigue resistance [1–6]. Among various Al matrix composites, the in-situ TiB₂ particles reinforced Al alloy composite prepared using an exothermic reaction process with K₂TiF₆ and KBF₄ salts has been the highlight of research interests in recent years, since the interfaces between TiB₂ particles and Al matrix alloy are clear and well bonded, and reaction products are easy to remove [7–12]. 2014 Al alloy is high strength and hardness (including high temperature) alloy, which is generally used in the aerospace industry for making structural components. In order to further increase the mechanical properties of 2014 Al alloy, in-situ TiB₂/2014 composite was prepared. However, a common problem associated with the TiB₂/Al composites is particles agglomeration [13–17], which has deleterious effects on the properties of the composite [18]. So, the dispersion of TiB₂ particles in 2014 Al alloy matrix plays an importance role in achieving the desired properties in the material.

Some reports showed that surface active additive

can improve the dispersion of TiB₂ particles in Al alloy matrix, such as Mg and Zr [19,20]. In addition, conventional secondary deformation processing methods (rolling or extrusion) were also used to improve the distribution homogeneity of the particles [16,21]. However, the report on effect of rare earth as additive on the dispersion of TiB₂ particles is relatively few. We previously reported the advantages of CeO₂ as additive during the preparation of in-situ TiB₂/Al composite [22]. In this study, in-situ TiB₂ particles reinforced 2014 Al alloy composite was successfully fabricated when 0.5% CeO₂ was added, and the behavior of CeO₂ additive in the composite was studied.

2 Experimental

In the present study, in-situ 5% (volume fraction) TiB₂/2014 composites with and without CeO₂ were prepared. Appropriate amount of commercial purity (CP) Al was melted in a medium frequency furnace, and a pre-weighed mixture of K₂TiF₆, KBF₄, CeO₂ powders (0.5%, mass fraction) and Na₃AlF₆ cosolvent (2%, mass fraction) was inserted in batches into molten CP aluminum by bell at 870 °C. Then the melt was stirred for 30 min using a graphite stirrer and held for 30 min until the reaction completed. The dross which floated on

the top of the melt was decanted. When the melt temperature reached as low as 800 °C, high purity copper, Al–Mn alloy and Al–Si alloy were added into the melt, and the melt was held for 30 min until the alloys were thoroughly melted. Then the melt was stirred for 10 min and degassed using C_2Cl_6 at 730 °C. Mg was added to the melt at 730 °C. Finally, the composite melt was cast into graphite mould at room temperature.

The samples were sectioned from the same height of the cast rods with and without CeO_2 to compare the dispersion of TiB_2 particles; and the top and bottom chemical compositions of the composite melt with CeO_2 were analyzed to study the settlement of TiB_2 particles in the preparation. The composites were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) equipped with energy dispersive X-ray (EDX) microanalysis. Chemical composition was analyzed by inductively coupled mass spectrometry (ICP-MS). The hardness was tested using Vickers hardness tester at 50 N load (hence the hardness is represented as HV50). Each hardness value presented was an average of at least ten symmetrical indentations. The tensile properties were evaluated at room temperature using Zwick/Roell test machine. The tensile properties reported were the average of four tests at the same condition.

3 Results and discussion

3.1 Synthesis of $TiB_2/2014$ composite

The chemical compositions of the 2014 Al alloy and 5% $TiB_2/2014$ composite prepared in this work are given in Table 1. It can be seen that the absorption rates of Ti and B are both higher. Figure 1 shows the XRD pattern of the 5% $TiB_2/2014$ composite with CeO_2 , which clearly indicates that the phases in the sample include mainly $\theta-CuAl_2$, TiB_2 and $\alpha(Al)$, and no other discernible diffraction peaks appear. The SEM microstructures of the 5% $TiB_2/2014$ composite with CeO_2 are shown in Figs. 2(b) and (d). It can be observed that the particle morphology is nearly spherical and its size is less than

Table 1 Chemical compositions of 2014 Al alloy and 5% $TiB_2/2014$ composite (mass fraction, %)

Alloy	Cu	Si	Mn	Mg	Ti	B	Ce	Fe	Al
2014	4.80	0.78	0.88	0.74	–	–	–	0.11	Bal.
5% $TiB_2/2014$	4.88	0.77	0.85	0.75	5.32	2.61	–	0.16	Bal.
5% $TiB_2/2014+$ 0.5% CeO_2	4.85	0.75	0.91	0.79	5.27	2.52	0.41	0.12	Bal.

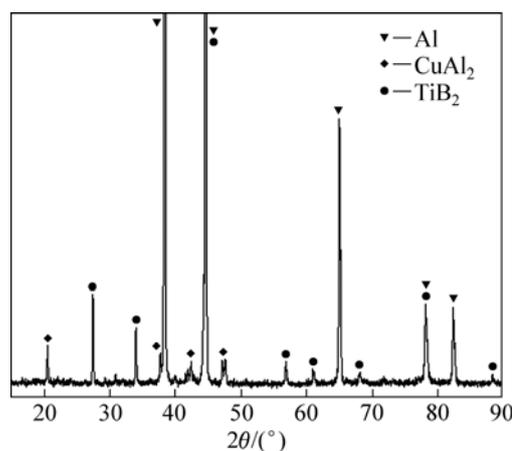


Fig. 1 XRD pattern of 5% $TiB_2/2014+0.5\%CeO_2$ composite

2 μm . The results suggest that $TiB_2/2014$ composite can be fabricated successfully when CeO_2 additive is added.

3.2 Effect of CeO_2 on dispersion of TiB_2 particles

Figure 2 shows the microstructures of the 5% $TiB_2/2014$ composites with and without CeO_2 . From Fig. 2(a), it can be observed that $\theta-CuAl_2$ phases with needle-shape in the composite without CeO_2 distribute uniformly in the form of semi-continuous network in the matrix, and TiB_2 particles distribute along the grain boundary in coral-like form and interweave with $CuAl_2$ phases. There are few scattering particles inside matrix dendrites. Figure 2(b) shows the TiB_2 particle morphology at grain boundary in the composite without CeO_2 . Most of the particles have no clear profile and exist in the form of agglomerations, which is in accordance with the previous findings [11–15]. However, when CeO_2 additive is added, the microstructures of composite have obvious change. TiB_2 particles disperse from grain boundary to inner grain gradually, and a large number of scattering particles inside matrix dendrites can be observed despite a small number of agglomerations still exist, as shown in Fig. 2(c). Using image processing program in MATLAB to count the particles with the same grayscale value in Figs. 2(a) and (c), the result indicates that the coverage area of the particles in matrix is increased by 76.4% compared with that of the composite without CeO_2 . Figure 2(d) shows the TiB_2 particle morphology in the composite with CeO_2 . Compared with Fig. 2(b), most of the TiB_2 particles exist in isolation, and particles with clear profile are close to spherical with less than 2 μm in size. In addition, the interfaces between TiB_2 particles and Al 2014 matrix alloy are clear and clean.

The microstructures of the composite without CeO_2 indicate that TiB_2 particles prepared using in-situ

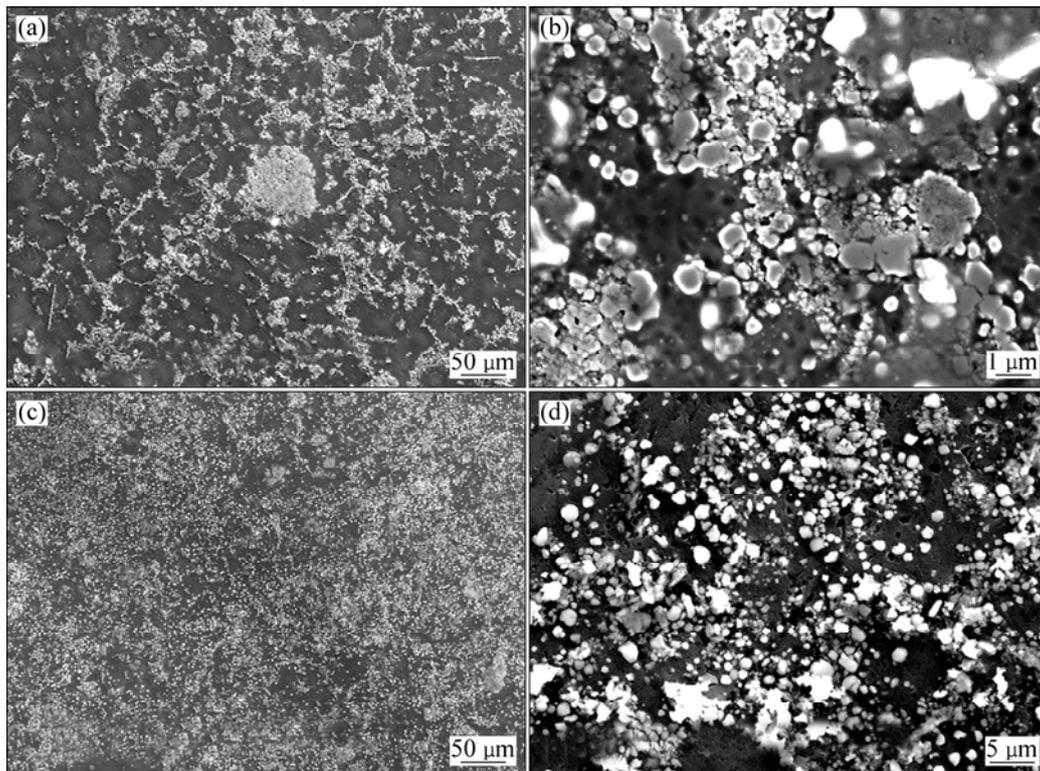


Fig. 2 SEM microstructures of 5%TiB₂/2014 composite: (a, b) Without CeO₂; (c, d) With 0.5%CeO₂

reaction have higher surface energy and the energy is easy to decrease for the agglomeration of TiB₂ particles [23]. When CeO₂ additive is added, CeO₂ is reduced to Ce by aluminum. Rare earth Ce is a kind of surface active element, which can reduce the surface tension of Al alloy melt and be adsorbed easily at phase boundary [24,25]. Therefore, in the TiB₂/2014 composite with CeO₂, the surface tension of 2014 Al alloy melt is reduced, which increases the wettability and surface-spread coefficient of TiB₂ particles in alloy melt. Ce is adsorbed at phase boundaries between TiB₂ particles and matrix alloy, which not only fills the interface defects but also decreases the interfacial energy. Finally, TiB₂ particles disperse uniformly in the 2014 Al alloy melt. During the solidification, the single TiB₂ particle with smaller moving velocity in 2014 Al alloy melt [22] can be captured by matrix grain, which makes the TiB₂ particles distribute dispersedly almost in the whole 2014 Al matrix alloy except a slight segregation is observed. Figure 3 shows the result of element area scanning of the TiB₂/2014 composite with CeO₂. As shown in Fig. 3, Ce mainly distributes at phase boundaries between TiB₂ particles and 2014 Al alloy matrix, and agglomerative TiB₂ particles are dispersed gradually, which is consistent with the above analysis.

Figure 4 shows the crystal morphology and SAED pattern of TiB₂ particles in the 5%TiB₂/2014+ 0.5% CeO₂ composite. It can be seen that the CeO₂ additive

does not affect the formation of TiB₂ particles, and Ce element is only absorbed at the interfaces between TiB₂ particles and Al matrix and does not combine with TiB₂ particles to form a new phase.

3.3 Settlement of TiB₂ particles in composite with CeO₂

Figure 5 shows the SEM microstructures of the top and bottom of the composite melt with CeO₂. The TiB₂ particles have good dispersion in 2014 Al alloy whether on the top or bottom of the sample, and most of TiB₂ particles can break away from the agglomerations at grain boundary and disperse gradually to inner grain. However, it can be observed that the number of TiB₂ particles in the bottom sample seems to be more than that in the top sample. Table 2 lists the chemical compositions of top and bottom samples. The result shows that the contents of Ti and B in the top sample are slightly lower than those in the bottom sample, which indicates that TiB₂ particles have slightly settled in the preparation of the composite. But the number of sedimental TiB₂ particles accounts only for 2.1% of the total particles, which can be ignored in the preparation of in-situ TiB₂ particles reinforced metal matrix composite. So, the TiB₂/2014 composite with good particle dispersion is prepared successfully when CeO₂ additive is added.

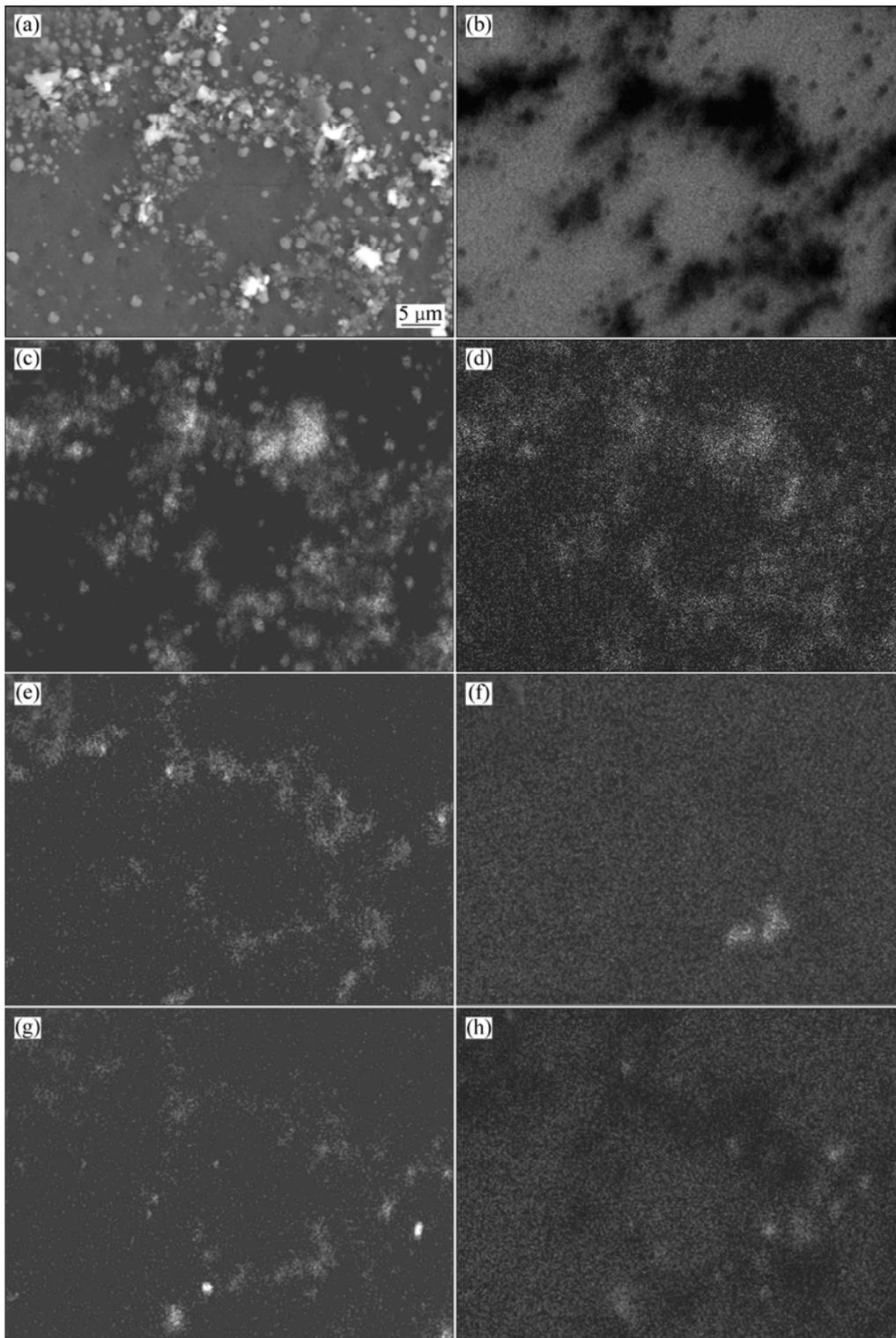


Fig. 3 SEM image (a) and elemental mapping of Al (b), Ti (c), Ce (d), Cu (e), Mn (f), Si (g) and Mg (h) in 5%TiB₂/2014+0.5% CeO₂ composite

Table 2 Chemical composition of 5%TiB₂/2014+0.5%CeO₂ composite at different parts (mass fraction, %)

Location	Cu	Si	Mn	Mg	Ti	B	Ce	Fe	Al
Top	4.87	0.75	0.91	0.79	5.23	2.48	0.41	0.12	Bal.
Bottom	4.82	0.77	0.91	0.76	5.45	2.62	0.4	0.13	Bal.

3.4 Mechanical properties

The mechanical properties in as-cast condition, such as hardness, tensile strength, yield strength and elongation of both the alloy and composites are compiled in Table 3. The values of hardness (HV₅₀), tensile strength and yield strength of 5%TiB₂/2014 composite

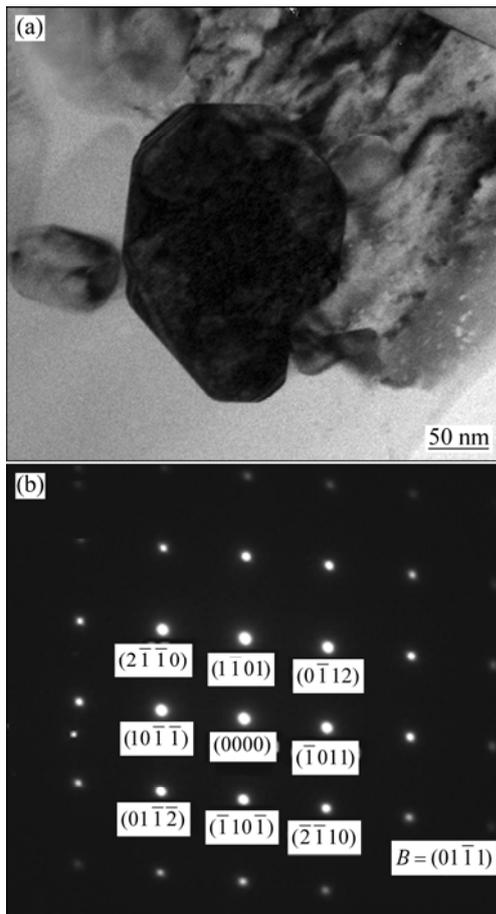


Fig. 4 Crystal morphology (a) and SAED pattern (b) of TiB_2 particles in 5% TiB_2 /2014+0.5% CeO_2 composite

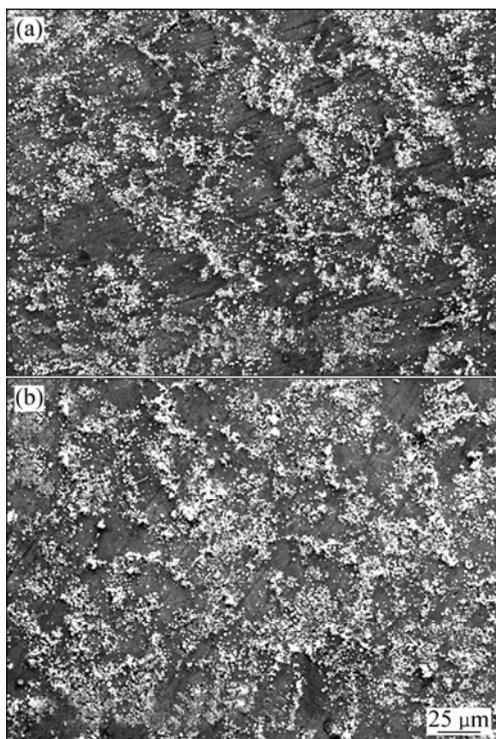


Fig. 5 SEM microstructures of 5% TiB_2 /2014+0.5% CeO_2 composite at different parts: (a) Top; (b) Bottom

without CeO_2 are 52.1%, 20.3% and 21.4% higher than those of the 2014 Al matrix alloy, and the elongation is not decreased. When CeO_2 is added, the hardness, tensile strength, yield strength and elongation of the composite are 62.0%, 31.1%, 31.0% and 38.9% higher than those of the 2014 Al matrix alloy. The strengthening reasons of 2014 Al alloy matrix composite are due to some factors, such as the size, morphology and dispersion of TiB_2 reinforcement particles, the matrix grain refinement and the interfacial bonding between TiB_2 reinforcement particles and matrix. When TiB_2 particles are introduced into a molten 2014 Al alloy by in-site synthesis, the differences in the thermal expansion coefficient between TiB_2 particles and Al alloy matrix will make the dislocation density within the composite increase. Al alloy matrix grain can be refined due to the accumulation of particles in the liquid between the growing dendrites, which seems to inhibit continued dendritic growth. However, when CeO_2 is added, the dispersion of TiB_2 particles is improved obviously, which is equal to increasing the amount of TiB_2 particles and reducing the stress concentration arising from the TiB_2 particle agglomerations. In addition, the special behaviors of Ce in Al alloy such as refinement, purification and degassing also can improve the mechanical properties [25], especially elongation.

Table 3 Mechanical properties of composites

Composite	Hardness (HV ₅₀)	Tensile strength/MPa	Yield strength/MPa	Elongation/%
2014 alloy	71	212	126	3.6
5% TiB_2 /2014	108	255	153	3.8
5% TiB_2 /2014 +0.5% CeO_2	115	278	165	5.0

4 Conclusions

In-situ TiB_2 particles reinforced 2014 Al alloy composite is successfully prepared. When CeO_2 additive is added, the dispersion of TiB_2 particles in the matrix is improved greatly, and particles have no obvious settlement. The hardness, tensile strength and yield strength of 5% TiB_2 /2014 without CeO_2 composite are 52.1%, 20.3% and 21.4% higher than those of the 2014 Al alloy and the elongation is not decreased. When CeO_2 is added, the hardness, tensile strength, yield strength and elongation of 5% TiB_2 /2014 composite are 62.0%, 31.1%, 31.0% and 38.9% higher than those of the Al 2014 alloy.

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CeO₂ 添加剂在原位 TiB₂ 颗粒增强 2014 铝合金复合材料中的作用

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摘要: 将 K_2TiF_6 和 KBF_4 混合盐与铝合金熔体通过放热反应法制备原位 TiB_2 颗粒增强 2014 铝合金基复合材料。研究 CeO_2 添加剂对原位 $\text{TiB}_2/2014$ 铝基复合材料显微组织和力学性能的影响。结果表明, 在高温时添加 CeO_2 与添加 Ce 的作用相同; 当添加 0.5% CeO_2 时, TiB_2 颗粒在基体中的分散性大幅度提高, 颗粒与基体的界面清晰, 在复合材料制备过程中颗粒没有明显的沉降现象。解释了 TiB_2 颗粒在 2014 铝合金基体中的分散机理。加入 CeO_2 的复合材料, 其铸态硬度、抗拉强度、屈服强度和伸长率有较大提高。

关键词: 2014 铝合金; TiB_2 ; 复合材料; CeO_2

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