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Effects of CeO_2 additive on the microstructure and mechanical properties of in situ TiB_2/Al composite

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ABSTRACT

In this paper, CeO_2 was investigated as an additive for in situ preparation of TiB_2/Al composite using an exothermic reaction process via K_2TiF_6 and KBF_4 salts. Experimental results indicated that when 0.5 wt.% CeO_2 additive was added, the dispersion of TiB_2 particles was improved significantly. Meanwhile, α-Al matrix grain was further refined. Compared with the composite without CeO_2, the ultimate tensile strength, yield strength, elastic modulus and tensile elongation increased by 8%, 7%, 26% and 14%, respectively in as-cast condition, and the tensile fracture behavior of the composite with CeO_2 belonged to a typical ductile fracture with microvoid coalescence.

1. Introduction

TiB_2 is portrayed to be a good potential reinforcing candidate in an aluminum matrix because it is a refractory compound that exhibits outstanding features such as high melting point (2790 °C), high hardness (86 HRA or 960 HV), high modulus (530×10^3 GPa) and its resistance to plastic deformation even at high temperatures [1,2]. At present, although advantages of the TiB_2/Al composite produced using in situ method on mechanical properties and abrasive resistance have been widely reported in many literatures [3–11], when the composite with high volume fraction TiB_2 is produced, TiB_2 particle agglomeration is formed easily, and most of the agglomerations segregate in the grain boundary [12–17], which not only weakens the advantages of TiB_2 particles as reinforcing phase but also has detrimental factors to the properties of TiB_2/Al composite [18]. Besides, the agglomeration of TiB_2 particles makes it much easier to produce settlement, which would result in non-uniformity distribution of the particles in matrix. Fundamentally, the agglomeration and settlement of TiB_2 particles are related to the dispersion of particles. So, the control of the dispersion of TiB_2 particles in aluminum matrix is of an engineering importance for producing TiB_2/Al composite with high specific modulus and strength via casting technique. At present, the reports on the dispersion of TiB_2 particles in aluminum matrix are relatively few.

There have been some reports [19–21] on the effects of Mg and Zr as the surface active additives on the dispersion of TiB_2 particles in aluminum matrix. However, none has mentioned rare earth as the additive. Research shows [22,23] that rare earth is a kind of surface active element with the special behaviors in aluminum alloy such as refinement, purification and modification, which to some extent, can improve the mechanical properties, physical properties, processing performance and comprehensive usability. Therefore, in this paper, the effects of CeO_2 as an active additive on the dispersion of TiB_2 particles, matrix grain refinement and mechanical properties of the TiB_2/Al composite produced using in situ synthesis technology were discussed.

2. Experimental procedures

Experimental materials included commercial purity (CP) aluminum (99.7 wt.% purity), commercial KBF_4 (98.0 wt.% purity), commercial K_2TiF_6 (99.0 wt.% purity), high purity CeO_2 powder and chemical purity Na_3AlF_6 (99.5 wt.% purity).

A mixture of K_2TiF_6, KBF_4, CeO_2 powder (0.5 wt.%) and Na_3AlF_6 cosolvent (2 wt.%) were mixed in ball mill for 30 min. The mixture was wrapped using aluminum foil and set aside. Melting of CP aluminum was carried out in a graphite crucible that has been repeatedly brush-coated with alcohol-based zirconium oxide. A medium frequency furnace operating under normal atmospheric condition was used to do the heating. The mixture above was preheated at 300 °C for 2 h and inserted in batches into molten CP aluminum by bell at 850 °C. Then the melt was stirred for 20 min using a graphite stirrer and held for 15 min until the reaction completed. Molten slag was scooped away from the melt surface. Finally, the composite melt was degassed by using C_2Cl_6 at 730 °C, then cast into graphite mould at room temperature.

The casting rods with and without CeO_2 were prepared, sampled from the same height section respectively to compare the dispersion of TiB_2 particles; Casting rods were cut open from the same height cross-sectional, polished, corroded to observe the macrostructural features; In order to give further investigation on the effect of

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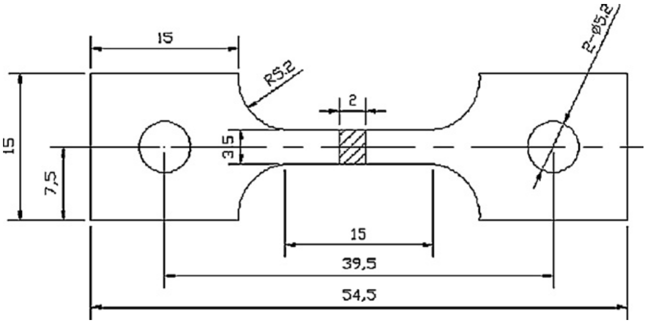

Fig. 1. Sizes of the specimens for mechanical properties testing.

CeO_2 on the dispersion and settlement of TiB_2 particles, the casting rods above were remelted in Al_2O_3 crucible with ϕ30 mm, H100 mm and held for 60 min at 780 °C in 5 kW electrical furnace, then the crucible was removed from the furnace and cooled in the air, and each remelting rod was sampled from the upper and under part, respectively to compare the dispersion and settlement of particles. Chemical composition was analyzed by ICP-MS. X-ray diffractometer (XRD) was used to determine the phase component while field emission scanning electron microscopy (SEM) was used to analyze microstructural features and tensile fracture surfaces. Tensile properties were tested at room temperature by zwick/roell test machine. Each value of the tensile properties reported was the average of four tests at the same condition. The sizes of the specimens for mechanical properties testing were shown in Fig. 1.

3. Results and discussion

3.1. Preparation of TiB_2/Al composite with CeO_2

Table 1 shows the chemical compositions of 5 vol.% TiB_2/Al composite. It can be seen from Table 1 that the contents of Ti and B in the composites with and without CeO_2 are both slightly higher than nominal values, which is attributed to aluminum oxidation loss during preparation of the composite. In addition, the contents of Ti and B in the composite with CeO_2 are almost the same as that without CeO_2, which indicates that the absorption rates of Ti and B are not influenced when 0.5 wt.% CeO_2 additive was added. XRD analysis, as shown in Fig. 2, indicates that only TiB_2 and α-Al phases are detected, and rare earth phase is not found. The SEM microstructure of the composite with 0.5 wt.% CeO_2 is shown in Fig. 3(c, d and e), it can be seen clearly that the particle morphology displays a hexagonal shape, which is the characteristic of TiB_2, and its size is less than 2 μm. Also clean interface between TiB_2 particle reinforcement and aluminum matrix is observed. Evidences mentioned above verify strongly that TiB_2 particle reinforced aluminum matrix composite is produced successfully in present study when 0.5 wt.% CeO_2 additive is added.

3.2. Effect of CeO_2 on the dispersion of TiB_2 particles

The SEM microstructures of 5 vol.% TiB_2/Al composite with and without CeO_2 are shown in Fig. 3. It reveals the effect of CeO_2 additive on the dispersion of TiB_2 particles in the CP aluminum matrix. TiB_2 particles in the composite without CeO_2 are found to be distributed along the grain boundary regions in coral-like form, and most of the particles with unclear profile adhere to each other and exist in the microstructure in the form of agglomerations. The distribution of TiB_2 particles along the grain boundary regions indicates that particle segregation at the solid/liquid interface during solidification still exists, despite TiB_2 particles being formed in situ in the melt. However, significant changes can be found in the microstructure of the composite with CeO_2, as shown in Fig. 3(c and d). The number of the TiB_2 particle agglomerations is reduced greatly, and the particles are distributed dispersedly almost in the whole view. Using image processing program in MATLAB to count the particles with the same grayscale value in Fig. 3(a and c), the result indicates that the coverage area of the particles in matrix is increased by 139% compared with the composite without CeO_2. In addition, it can be seen from Fig. 3(d and e) that the shape of TiB_2 particles with clear profile is regular polygon, and most of the particles exist in isolation. Clean interface between TiB_2 particle reinforcement and aluminum matrix is observed. The dispersive distribution of TiB_2 particles in the CP aluminum matrix indicates that the particles are captured by matrix grains during solidification.

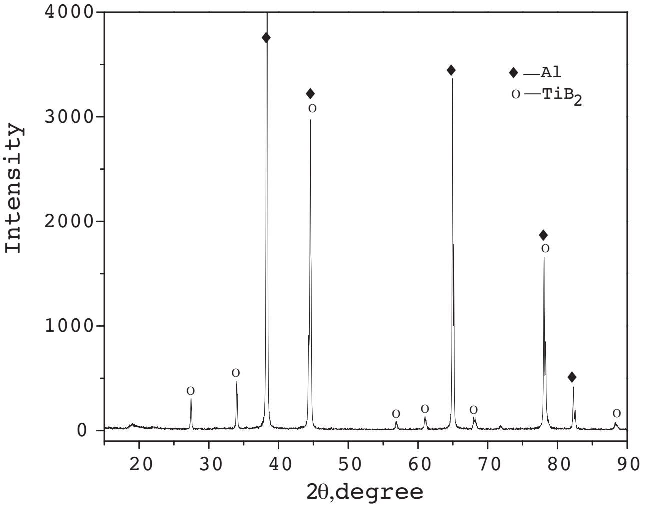

Fig. 2. XRD pattern of 5 vol.% TiB_2/Al + 0.5 wt.% CeO_2 composite.

The result above is attributed primarily to high surface energy of TiB_2 particles produced using in situ reaction in aluminum melt, and the energy is easy to be decreased by the agglomeration of TiB_2 particles. Luo reported [23] that CeO_2 was decomposed into [Ce] and [O] when the temperature was higher than 750 °C. So, in this work, CeO_2 exhibits the same function as Ce. Rare earth Ce is a kind of surface active element, which can reduce surface tension of aluminum melt and enhance its fluidity. In the preparation of the TiB_2/Al composite with 0.5 wt.% CeO_2, the surface tension of melt is weakened, which results in the corresponding increase of the wettability of TiB_2 particle in aluminum melt and increase of surface-spread coefficient of TiB_2 particles. Besides, the solid solubility of Ce is very low in aluminum, and Ce is adsorbed easily in phase boundary, which not only fills the interface defects but also decreases the interfacial energy between TiB_2 particle and aluminum melt. Consequently, relatively dispersive TiB_2 particles are formed in the CP aluminum melt. However, the distribution of particles in matrix depends ultimately on the moving velocity of the particle in the matrix melt and the solidification rate of the matrix melt. When the solidification rate of the matrix melt is more than

Table 1
Chemical compositions of 5 vol.% TiB_2/Al composite (wt.%).

Element	Al	B	Fe	Si	Ti	V	Ce
Nominal	Bal.	2.52	0.11	0.04	5.57	–	–
Without CeO_2	Bal.	2.61	0.18	0.20	5.78	0.15	–
With 0.5 wt.% CeO_2	Bal.	2.58	0.13	0.07	5.75	0.14	0.29

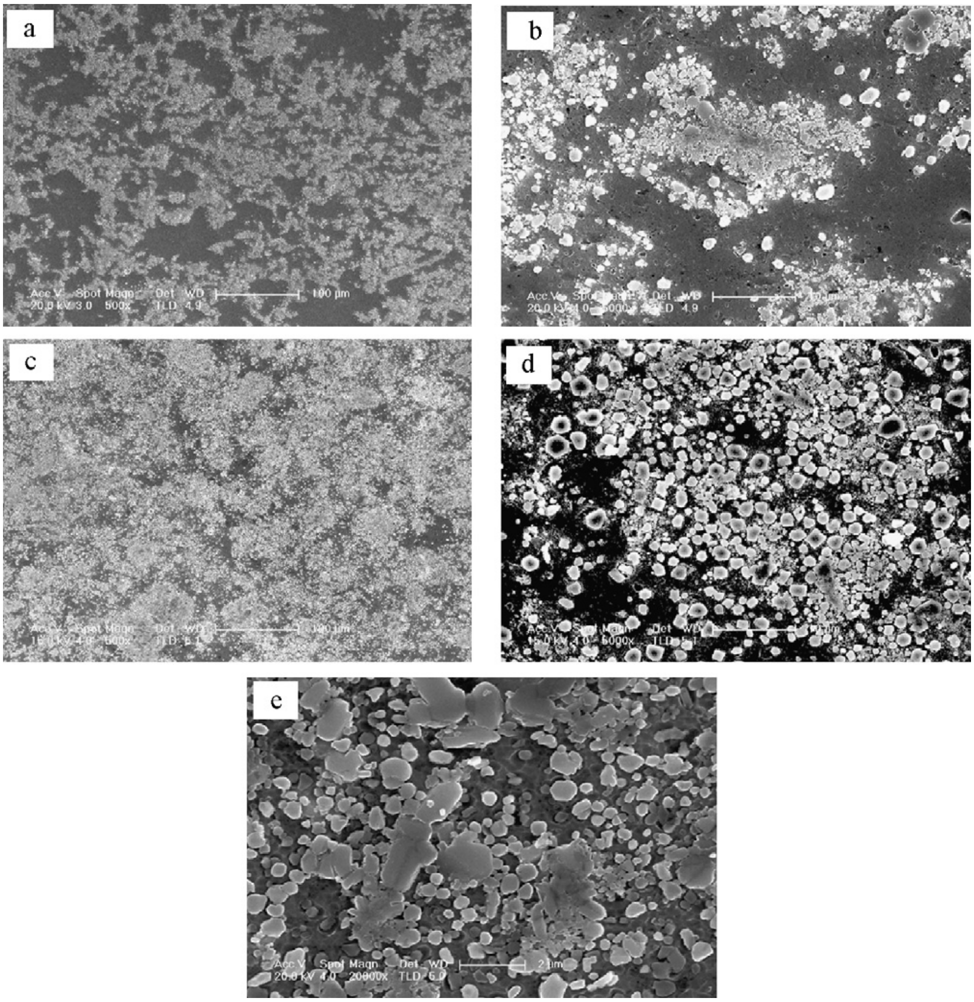

Fig. 3. SEM microstructures of 5 vol.% TiB_2/Al composite: (a) and (b) without CeO_2; (c) (d) and (e) with 0.5 wt.% CeO_2.

the moving velocity of particle in the matrix melt, the particles are captured easily by the matrix grains and distribute dispersedly throughout the matrix. On the contrary, the particles are pushed by the advancing solidification front and eventually trapped in the grain boundary in the form of agglomerations. According to the formula of stokes on the moving velocity of particle [24]:

$$v = \frac{1}{18}(\rho_p - \rho_m)\frac{gd^2}{\eta}$$

where η is the viscosity of liquid-metal (Pa s), d is the diameter of reinforcing particle (m), g is the gravity acceleration (9.8 m s^{-2}), ρ_m is the density of molten metal (kg m^{-3}), ρ_p is the density of particle (kg m^{-3}).

According to the formula above, it can be obtained that the moving velocity of particle in melt decreases as its size is reduced. So, in the composite melt with CeO_2, the moving velocity of the single TiB_2 particle is far smaller than that of the TiB_2 particle agglomeration and can meet the condition that the moving velocity of particle in matrix melt is less than the solidification rate of the matrix melt. As a result, TiB_2 particles are captured by matrix grain and distributed dispersedly almost in the whole aluminum matrix except a slight segregation of particles is observed.

3.3. *Effect of CeO_2 on the settlement of TiB_2 particles*

Fig. 4 shows the SEM microstructures of 5 vol.% TiB_2/Al composite with and without CeO_2 after remelting. It can been seen that TiB_2 particles are still found to be distributed along the grain boundary regions in coral-like form in the composite without CeO_2, and most of the particles with unclear profile adhere to each other. It is evident that the particles under part of remelting rod are denser than that in the upper. Comparing Fig. 3(a and b) and Fig. 4(a, b and e), it can be seen clearly that the size of TiB_2 particle agglomerations is increased after remelting. However, in the composite with CeO_2, TiB_2 particles distribute uniformly both in the upper and under part of remelting rod, and there is no obvious settlement and agglomeration, as shown in Fig. 4(c and d). It is found from Fig. 4(f) that every TiB_2 particle still exists in isolation, and clean interface between TiB_2 particle reinforcement and aluminum matrix is still observed. It is mainly that TiB_2 particles exist in the form of agglomerations in the composite without CeO_2 before remelting, and the size of the agglomerations is increasing during remelting. According to the formula of stokes above, the settlement velocity of TiB_2 particle during remelting and the moving velocity of the particle during solidification are both increased. As a result, the particles under part of remelting rod is more than that in the upper, and under part the phenomena of particle segregation in the grain boundary is very serious, as is illustrated in the Fig. 4(a and b). While CeO_2 additive is added, due to the improvement of the dispersion of TiB_2 particles in aluminum melt, no obvious settlement and segregation are formed, as shown in Fig. 4(c and d).

From Fig. 4(c, d and f), it can be seen that TiB_2 particles distribute uniformly in aluminum matrix without obvious settlement even in the lower solidification rate, which indicates the moving

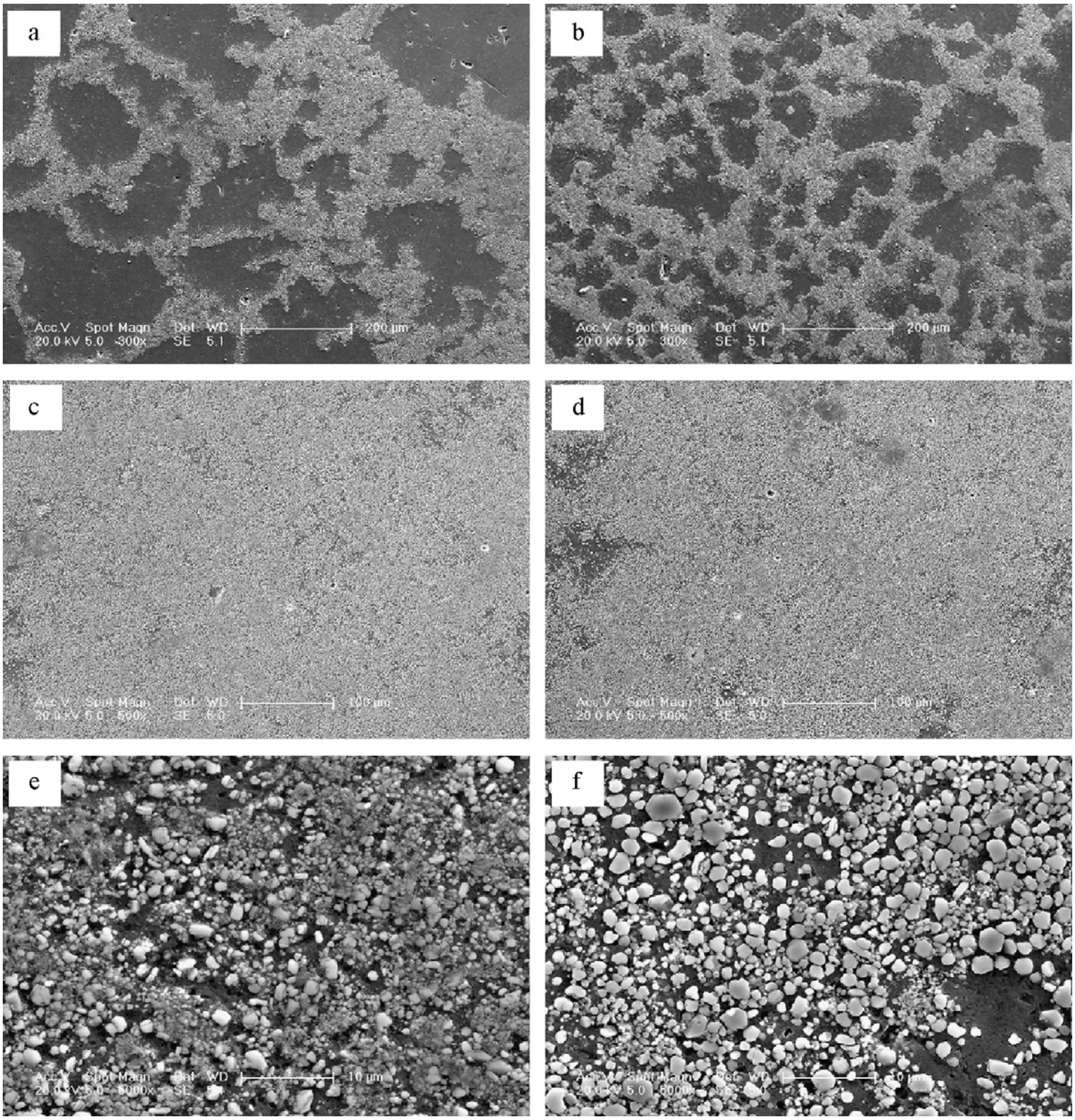

Fig. 4. SEM microstructures of 5 vol.% TiB_2/Al composite after remelting: (a) the upper without CeO_2; (b) and (e) the under part without CeO_2; (c) the upper with 0.5 wt.% CeO_2; (d) and (f) the under part with 0.5 wt.% CeO_2.

velocity of single particle is small enough to meet the condition that the moving velocity of particle in matrix melt is less than the solidification rate of the matrix melt under the general solidification condition. The result is that TiB_2 particles are captured easily by matrix grain and distribute uniformly in the matrix. Therefore, the dispersion of TiB_2 particles in aluminum melt is the key to solve on the segregation and settlement of particles.

3.4. *Effect of CeO_2 on matrix grain refinement*

Fig. 5 presents the macrostructures of 5 vol.% TiB_2/Al composite with and without CeO_2 in as-cast condition. It can be seen obviously that matrix grain size of the composite with CeO_2 is smaller than that of the composite without CeO_2.

The widely accepted explanation on the refinement of the TiB_2/Al composite matrix grain is that the accumulation of particles in the liquid between the growing grains to inhibit continued grain growth [15,21,25,26]. However, compared with the composite without CeO_2, the matrix grain size of the composite with CeO_2 is reduced greatly even the improvement of the TiB_2 particles dispersion in melt weakens its function of hindering matrix grain growth, which verifies strongly that Ce promotes matrix grain refinement.

3.5. *Effect of CeO_2 on mechanical properties*

Fig. 6 presents the mechanical properties have the CP aluminum and 5 vol.% TiB_2/Al composite with and without CeO_2 in as-cast condition. Comparison has been made with the unreinforced CP aluminum that had been melted and held at 750 °C for 15 min before casting in a similar way as for the composite. The result shows that 5 vol.% TiB_2/Al composite without CeO_2 yields 88% and 83% increase in the ultimate tensile and yield strengths, respectively and 14% in elastic modulus, but tensile elongation is decreased by 32%. However, When 0.5 wt.% CeO_2 is added, the ultimate tensile strength, yield strength, elastic modulus, and tensile elongation are 8%, 7%, 26% and 14% higher than the composite without CeO_2, respectively. The strengthening micromechanics of the matrix is influenced by the TiB_2 reinforcing particles. When particle

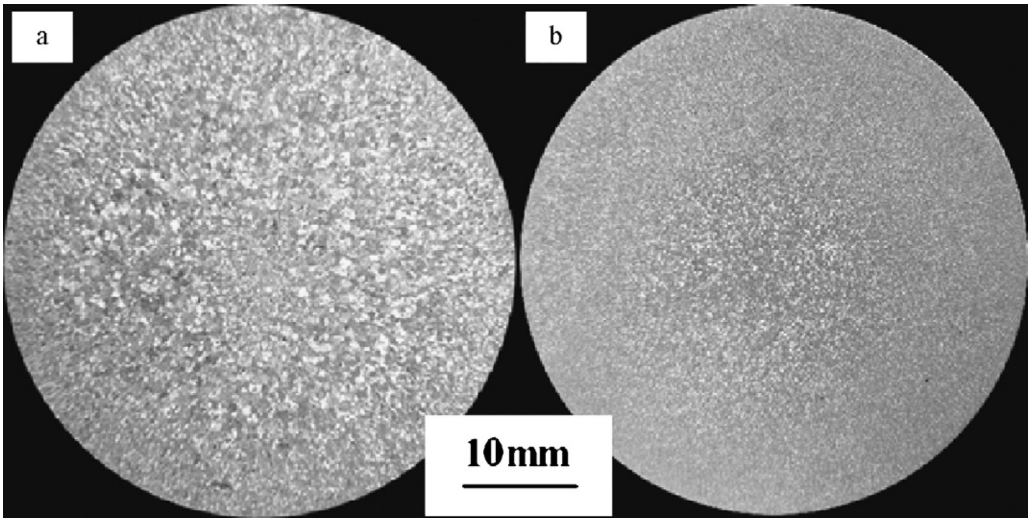

Fig. 5. Macrostructures of 5 vol.% TiB_2/Al composite: (a) without CeO_2; (b) with 0.5 wt.% CeO_2.

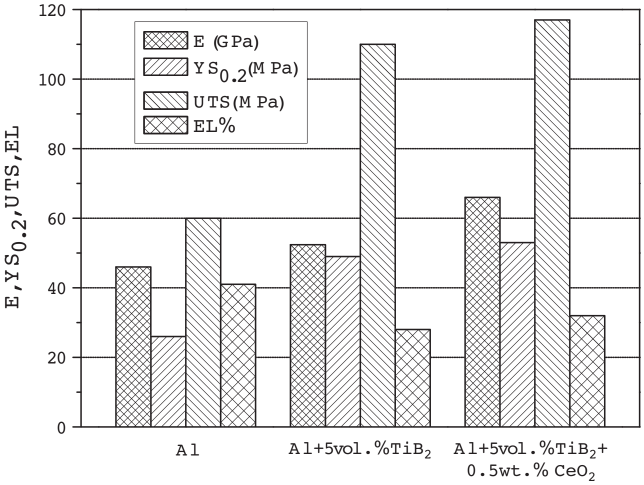

Fig. 6. Mechanical properties of the CP aluminum and 5 vol.% TiB_2/Al composite.

reinforcement is introduced into a molten aluminum matrix, there is usually a significant increase in the dislocation density within the composite due to differences in the value of the coefficients of thermal expansion between CP aluminum matrix and TiB_2 particle reinforcement. In this work, obviously, when CeO_2 additive is added, the dispersion of TiB_2 particles is improved significantly, which is equal to increasing the amount of TiB_2 reinforcing particles and reducing the size of TiB_2 particles; meanwhile, the matrix grain of the composite with CeO_2 is smaller than that of the composite without CeO_2, as shown in Fig. 5. All these would cause increased dislocation density, resistance of the dislocation motion and interaction between dislocations and the reinforcing particles, resulting in increased strain hardening and tensile strength. The increased tensile elongation may be attributed to the reduced matrix grain size and the improvement of the TiB_2 particle dispersion.

Research indicated [23] that rare earth with high chemical activity had a strong affinity with impurity elements in CP aluminum melt such as H_2, Fe and Si, and rare earth could form compounds with these impurity elements to eliminate their harmful effects on aluminum matrix. So the increases of strength and tensile elongation can be partly attributed to the function of degassing and purification of Ce in aluminum melt.

Fig. 7 shows SEM images of the tensile fracture surface of 5 vol.% TiB_2/Al composite with and without CeO_2. A lot of larger ductile dimples can be seen from Fig. 7(a), while the small and dispersive ductile dimples are formed in Fig. 7(b). It is because TiB_2 particle fracture in itself would not be caused owing to the properties of the particle produced using in situ reaction such as fine, a good integrality and breaking strength. As a result, crack initiation is mainly in the interface between particle and matrix, and the crack in interface is increasing, gathering and growing up with the load increasing, which results in debonding at the interface between particle and matrix. In the composite without CeO_2, the larger

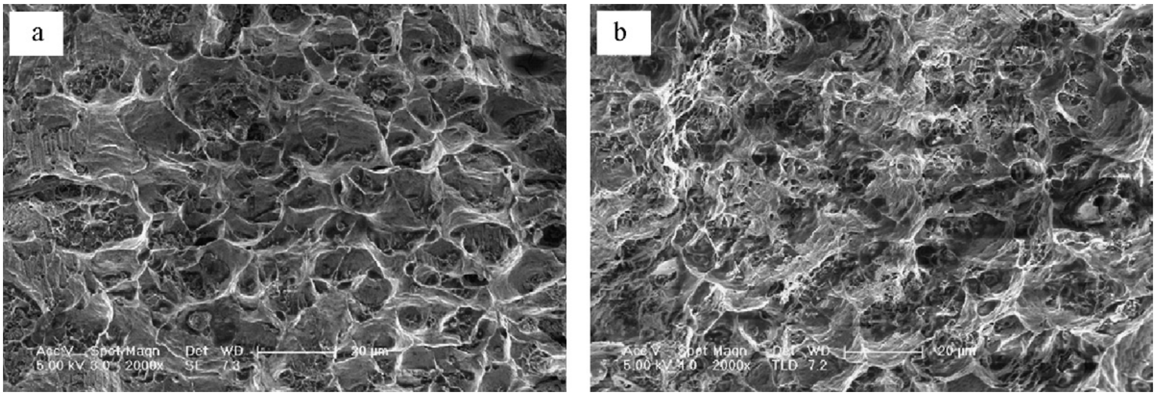

Fig. 7. SEM images of the tensile fracture surface of 5 vol.% TiB_2/Al composite: (a) without CeO_2; (b) with 0.5 wt.% CeO_2.

ductile dimples are formed due to the debonding of the interface between the matrix and the TiB_2 agglomerations. When CeO_2 is added, the dispersion of TiB_2 particles is improved significantly, which is equal to decreasing the size of TiB_2 particles and increasing the bonding strength between TiB_2 particle and aluminum matrix. Consequently, micron ductile dimples generated by the debonding of single TiB_2 particle and aluminum matrix distribute dispersedly in the fracture surface, which belongs to a typical ductile fracture with microvoid coalescence.

4. Conclusions

TiB_2 particle reinforced aluminum matrix composite is produced successfully in present study when 0.5 wt.% CeO_2 additive is added. When CeO_2 is added, the dispersion of TiB_2 particles in the aluminum melt is improved. As a result, under the general solidification condition, the moving velocity of single TiB_2 particle in the aluminum melt is far smaller than the solidification rate of the aluminum melt. Finally, TiB_2 particles are captured by aluminum matrix grain and distribute uniformly in the matrix. At the same time, the α-Al matrix grain of the composite with 0.5 wt.% CeO_2 is further refined. In addition, the settlement of TiB_2 particles during the remelting of the composite with CeO_2 has been alleviated greatly. The ultimate tensile strength, yield strength, elastic modulus, and tensile elongation of 5 vol.% TiB_2/Al + 0.5 wt.% CeO_2 composite increased by 8%, 7%, 26%, and 14%, respectively in as-cast condition in comparison with the composite without CeO_2, and the tensile fracture behavior of the composite with CeO_2 belongs to a typical ductile fracture with microvoid coalescence.

Acknowledgment

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