Research Article

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Study on the fabrication of in-situ TiB_2/Al composite by electroslag melting

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Abstract: In-situ TiB_2 particles can be synthesized via the salts-Al reaction by adding mixed K_2TiF_6 and KBF_4 ($\text{Ti/B}=1/2$) salts into Al melt. In this research, a novel electroslag melting technology was proposed to synthesize TiB_2 particles by the salts-Al reaction in order to reduce the reaction time period and purify the melt of composite. The effects of current of electroslag melting on the synthesis of TiB_2 particles and mechanical properties of composite were investigated. The results showed that TiB_2 particles could be in-situ synthesized by electroslag melting at 600 A for 15min. Compared with 60 min at 850°C of traditional LSM method, the efficiency of preparation was greatly improved. In addition, the dispersion of TiB_2 particles in the composite prepared by electroslag melting was improved, meanwhile the non-metallic inclusions in the composite was reduced. The values of YS, UTS and El pct of composite prepared by electroslag melting were higher than that of the composite prepared by traditional LSM method.

Keywords: In-situ composites, Electroslag melting; TiB_2

1 Introduction

In-situ particles reinforced Al matrix composites have attracted a great deal of attentions in the automotive and aerospace industries due to their good performances, such as high specific strength, low weight, excellent wear resistance [1, 2]. In recent years, in-situ TiB_2/Al composite was widely investigated since the fine particles ($<1\ \mu\text{m}$), clean interface and strong interfacial bonding between particle and matrix, and better mechanical properties [3]. It

is well known that the in-situ TiB_2 particle can be synthesized via a salts-Al exothermic reaction by adding K_2TiF_6 and KBF_4 mixed salts into Al melt, and the method is relatively simple. Because the method was first proposed by London Scandinavian Metallurgical Co., Ltd. [4], it is called the LSM method. Figure 1 shows a schematic illustration of LSM method. Plenty of researchers [5–9] have fabricated in-situ TiB_2/Al composites via the traditional LSM method. Studies showed that a total synthesis period of in-situ TiB_2 particles by the traditional LSM method needed 60 min at 850°C , and the TiB_2 particles existed in the matrix in the form of aggregation. In addition, the slag produced by the salts-Al reaction was difficult to remove completely. This not only limits the preparation efficiency of composite, but also makes it difficult to give full play to the strengthening effect of TiB_2 particles.

At present, in order to solve the problems encountered in traditional LSM method, many works have been done. Agrawal *et al.* [10] synthesized in-situ TiB_2 for 60 min at 850°C and employed a rotary electromagnetic stirring during solidification of composites to improve the distribution of TiB_2 particles. The result showed that the distribution of particles is almost homogenous only near the surface of the solidified castings. Wang *et al.* [11] introduced a blade paddle mixer during the salts-Al reaction to reduce the reaction time and improve the dispersion of particles. The

Figure 1: A schematic illustration of mixed salts in-situ reaction process (LSM method).

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results indicated that TiB_2 particles could be synthesized at 850°C for 30 min, but the dispersion of particles was not changed significantly. Researches indicated that the TiB_2 particle clusters in composites took the adverse effect on the mechanical strength of composites. These effects can cause the practical mechanical properties severely deviated from the theoretical prediction. Liu *et al.* [12] introduced a high-intensity ultrasound into melt for 5 minutes after the salts-Al reaction was completed. Although the dispersion of TiB_2 particles was improved, most of particles still distributed in the grain boundaries. Chen *et al.* [13] also introduced the impeller during salts-Al reaction to stir the salts/Al interface and a total synthesis period was still at 860°C for 60 min. The results showed that proper stirring intensity and duration were helpful to suppress the formation of severe agglomeration. Previous studies showed that the additional melt treatment device can improve the dispersion of in-situ TiB_2 particles to some extent, but the preparation process was complex. In addition, the efficiency of preparation was low, and more non-metallic inclusions was introduced in preparation process. Xue *et al.* [14] prepared the in-situ TiB_2/Al composites at 860°C for 60 min by adding CeO_2 during the salts-Al reaction. Good results have been achieved on the dispersion of particles, refine matrix grains and purify the melt, but the preparation efficiency was still low.

Electroslag melting is a secondary refining process, which has already been well established for producing steels and other high performance alloys [15, 16]. In the process of electroslag melting, the metal consumable electrode melts layer by layer along the surface, and reacts with molten slag in the form of droplet, which results in the high contact area between metal melt and molten slag. Researches [17] showed that the current density of tip of metal consumable electrode in the slag pool is 10 times higher than that of the inner wall of slag pool, which led to the formation of concentrated high temperature region in slag pool, and accelerated the reaction process between metal melt and molten slag. At present, the electroslag refining of Al has been studied. Chen *et al.* [18–20] investigated the effects of electroslag refining on removals of iron impurity and alumina inclusion from aluminum using $\text{KCl-NaCl-Na}_3\text{AlF}_6$ slag containing $\text{Na}_2\text{B}_4\text{O}_7$. The results indicated that Fe could be removed effectively due to the effective chemical reaction between Fe in Al melt and $\text{Na}_2\text{B}_4\text{O}_7$ in

molten slag. In addition, alumina inclusion in Al was also removed effectively. Therefore, Al melt can interact sufficiently with molten slag during the electroslag melting of Al.

In view of the advantages of electroslag melting, in this work, we attempt to prepare in-situ TiB_2/Al composite by the electroslag melting technology to improve preparation efficiency and microstructures and refine composite melt, thereby increasing the mechanical properties of composite. During electroslag melting, melting current has a direct effect on the melting rate of consumptive electrode and the temperature distribution of slag pool. Thus, it is one of the key parameters in the preparation of TiB_2/Al composites by electroslag melting. In this paper, the effect of melting current on the synthesis of TiB_2 particle is explored. The microstructures and mechanical properties of composite prepared by electroslag melting are investigated.

2 Experimental procedures

2.1 Raw materials and preparation

The slag agent of electroslag melting used for the preparation of in-situ TiB_2/Al composite was a mixture of K_2TiF_6 , KBF_4 used to synthesize TiB_2 and the basic slag agent used to refine Al melt. The K_2TiF_6 and KBF_4 were mixed with a molar ratio of $\text{Ti/B}=1/2$, and the amount added in slag agent corresponded to form 5wt % TiB_2/Al composite. Basic slag agent was common refining agent that contained 47% KCl , 30% NaCl and 23% Na_3AlF_6 (mass fraction). The slag agent

Figure 2: The photograph of Al consumable electrode.

Table 1: Composition of commercial purity aluminum (wt.%).

Fe	Si	Cu	Ga	Mg	Zn	Na	K	B	Al
0.120	0.110	0.002	0.014	0.003	0.003	0.016	0.009	0.004	Balance

was dried in drying oven at 300°C for 2 h and mixed in ball mill at 300 rpm for 30 min, and then were poured out and sealed. Commercial purity aluminum (CP) was cast to consumable electrodes with size of $\Phi 40\text{mm} \times 800\text{mm}$, as shown in Figure 2. The composition of CP is listed in Table 1.

2.2 Composite preparation

The electroslag melting experiments were carried out in a 60 kVA single phase AC unit. The apparatus is shown in Figure 3. The principle of electroslag melting is shown in Figure 4. The CP Al consumable electrode was clamped in electrode clamp. The solid starting technique was used through the arc striking agent. An appropriate amount of arc striking agent was placed in the center of bottom of crystallizer, and was ignited at 50 V. Then, the slag agent was added into crystallizer, and melted to form a slag pool.

Figure 3: The apparatus of experiment (a) and the size of crystallizer (b).

The consumable electrode was immersed in slag pool, and subjected to electroslag melting to obtain composite ingots with size of $\Phi 70\text{mm} \times (250 \sim 300)\text{mm}$ under a voltage of 15V, a current of 400~700A and a descending speed of 26~126mm/min.

Figure 4: Principle of the electroslag melting.

For comparison, in-situ 5wt.% TiB_2/Al composite was prepared by conventional LSM method. CP Al ingot was melted in a graphite crucible in an electrical resistance furnace. Mixed fluoride salts of K_2TiF_6 and KBF_4 was wrapped and inserted in batches into Al melt by bell at 850°C , then the melt was hold for 60 min. Periodic stirring was carried out to ensure complete reaction between salts and Al melt. Molten slag was scooped away from the melt surface. Finally, the composite melt was refined by using C_2Cl_6 at 730°C , then cast into graphite mould at room temperature.

2.3 Sample analysis

The test samples of composite were taken from the middle of ingots. Chemical composition was analysed by using inductively coupled plasma mass spectrometry (ICP-MS). The phase compositions of composite were detected by X-ray diffraction (XRD, D/MAX 2550 VB/PC) using $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA and scan rate of $5^\circ/\text{min}$. The slag crust on the surface of ingot of electroslag melting was also analyzed by XRD to examine the composition of slag after reaction.

The microstructures of samples etched using 0.5% HF solution were analyzed by field emission scanning electron microscopy (SEM, Sirion 200) equipped with an energy dispersive spectroscope (EDS) device for identifying the components in samples. Tensile properties were tested at room temperature by zwick/roell test machine at a crosshead

speed of 1mm/min. Each value of the tensile properties reported was the average of three tests at the same condition. The size of specimen for mechanical properties testing was shown in Figure 5. The tensile fracture surfaces were also analyzed using SEM.

Figure 5: Dimension of the tensile specimen (in mm).

3 Results and discussion

3.1 Effect of melting current on the synthesis of in-situ TiB_2 particles

The electrical parameters of electroslag melting mainly include melting current and voltage, which controls the melting process, including the size and rate of formation of metal droplets, the size and temperature of slag pool, and the depth and volume of metal pool etc. In this work, the melting voltage was constant of 15 V, and different melting currents were set to study on the effect of currents on the formation of in-situ TiB_2 particles. In-situ 5 wt% TiB_2/Al composite was prepared at different melting currents. In the preparation of composites, the corresponding melting time and slag pool temperature were measured, as shown in Table 2. It is found that with increasing melting currents, the melting time decreases and the temperature of slag pool increases. Figure 6 is appearance of 5wt% TiB_2/Al ingot prepared at 600A. A thin layer of slag crust is found on the surface of the ingot, which indicates that the slag agent can play an important role of insulation during electroslag melting. Moreover, some gases were also generated during electroslag melting due to the direct dissociation of the salts which may occur as follows [20]:

Figure 6: Appearance of 5 wt.% TiB_2/Al ingots prepared at 600A.

Table 2: Melting times and slag pool temperatures in preparation of composite at different melting currents.

	I	II	III	IV
Melting current I/A	400	500	600	700
Melting time t/min	20	18	15	9
Slag pool temperature T/°C	735	778	820	905

Figure 7: XRD pattern of slag crust on the surface of 5 wt% TiB_2/Al ingot prepared at 600A.

Figure 7 shows XRD patterns of slag crust on the surface of 5 wt.% TiB_2/Al composite ingot prepared at 600 A. It can be seen that the slag crust mainly contains NaCl , KCl , KAlF_4 and K_3AlF_6 phases. Among them, the phases of NaCl and KCl are basic slag agent, while the phases of KAlF_4 and K_3AlF_6 are reaction products between K_2TiF_6 , KBF_4 and Al melt. Figure 8 shows XRD patterns of the ingot sample prepared at 600 A. The existence of obvious diffraction peaks of TiB_2 phase indicates that TiB_2 phase was in-situ

Figure 8: XRD pattern of the composite prepared at 600A.

formed in the ingot prepared by electroslag melting at 600A. Based on the XRD result of slag crust and ingot sample, the formation of TiB₂ phase can be follow the reaction below:

Previous studies [22, 23] also proposed that the reaction formula to describe the synthesis of TiB₂ phase was as follows:

In both formula (1) and (2), TiB₂ phase was the only product that was kept in the matrix. However, in this work, the formula (1) might be more suitable to describe the formation of TiB₂ particles in the reaction. The result is in accordance with previous reports [13, 22]. In addition, the XRD results prove that TiB₂ particles can be synthesized by the method of electroslag melting.

Figure 9 shows the typical microstructures of 5 wt.% TiB₂/Al composites prepared by electroslag melting at different melting currents. It is clear that melting current has a significant effect on the microstructures. Agglomerations with a size beyond 10 μm are formed in the composite prepared at 400 A, a few blocky particles scatter around the agglomerations, as shown in Figure 9(a). EDS analysis is performed on the agglomerations in Figure 9(a), and the result is shown in Figure 10. It is found that a certain amount of F and K elements exists in the agglomeration. Early researches [2, 4, 12–14] have shown that the molten slag produced by the reaction of Al melt and K₂TiF₆, KBF₄ salts could be decanted in the process of preparing the composite by traditional LSM method, and TiB₂ phase was the only product that was kept in the matrix. So, it can be concluded that the reaction between Al melt and K₂TiF₆, KBF₄ salts used to synthesize TiB₂ was not complete in process of

electroslag melting at 400 A. It can be seen from Table 2 that the slag pool temperature is 735°C at 400 A. Chen *et al.* [24] reported that a complete reaction between Al melt and K₂TiF₆, KBF₄ salts was hard to be achieved at 750°C. Higher reaction temperature could increase the reactivity, which was beneficial for the formation of TiB₂ phase. Liu

Figure 9: Effect of melting current on the microstructures of TiB₂/Al composites.

Element	Weight%	Atomic%
C K	1.99	4.00
F K	36.27	46.00
Na K	2.72	2.85
Al K	41.24	36.82
K K	12.82	7.90
Ti K	4.07	2.05
Fe K	0.87	0.38
Totals	100.0	

Figure 10: EDS spectrum and micro-area components of the agglomeration in composite prepared at 400A

et al. [22] also indicted that temperature played a key factor in the reaction of Al and K_2TiF_6 , KBF_4 salts. When the temperature was low, the transfer of Ti and B from molten salts to Al melt was hindered, leading to a limitation of the synthesis of TiB_2 phase. Therefore, the above analysis indicates that the Al-salts reaction used to synthesize TiB_2 was not complete in process of electrosag melting at 400 A, the low slag pool temperature hindered the synthesis of TiB_2 phase.

Figure 9(b) shows the microstructural features of composite prepared at 500 A. A large number of cellular adhesions is found. And a small amount of particles exists in isolation around them. However, a significant change in microstructure of composite can be observed when the current increases to 600 A, as shown in Figure 9(c). It is clear that cellular adhesions disappear, and many particles with polygon exist in isolation except for a few particle adhesions. And the size of particle is less than $1\ \mu m$. In addition, clean interfaces of Al/particles can be observed. From Figure 8, it is clear that only Al and TiB_2 phases are detected in sample at 600 A, which indicates that the particles in Figure 9(c) is TiB_2 phase, and the Al-salts reaction used to synthesize TiB_2 is complete in process of electrosag melting at 600 A. When current increases to 700 A, as shown in Figure 9(d), the particles with a size beyond $1\ \mu m$ are observed, and their morphologies are hexagonal and rectangular. In addition,

small particle adhesions at the interfaces of Al/particles is observed.

As mentioned above, the melting current has a significant effect on the synthesis of in-situ TiB_2 phase via Al-salts reaction during electrosag melting. At low current, the Al-salts reaction is not complete due to low slag pool temperature. At the beginning of melting, Al consumable electrode immersed the slag pool. The first melting Al entered the slag pool and reacted with K_2TiF_6 , KBF_4 salts to form TiB_2 particles. These particles mingled with the intermediates of subsequent reaction and unreacted salts to form large agglomerations. The slag pool temperature increased with current increasing, which facilitates the reaction of Al-salts. The large agglomerations formed at low current gradually disintegrated into cellular adhesions. When the current was increased to 600 A, the slag pool temperature was $820^\circ C$, which is enough to ensure that the Al melt could react fully with salt melts at optimal reaction temperature, melting rate and droplet size of Al consumable electrode. Finally, the in-situ TiB_2 /Al composite can be successfully prepared in only 15 min. Early researches [2, 10, 13, 14] indicated it took 60 min to synthesize in-situ TiB_2 particles by traditional SLM method. It is visible that the preparation efficiency of composite is greatly improved by electrosag melting. When the current reached to 700 A, the slag pool temperature increased to $900^\circ C$, which resulted in the growth of preferentially synthesized TiB_2 particles. In addition, melting time of Al consumable electrode decreased from 15 min of 600 A to 9 min of 700 A, which led to the Al melt has not sufficient time to react with molten salts. Therefore, unreacted salts particles adhered to the interfaces between TiB_2 particles and Al matrix, as shown in Figure 9(d).

In the present research, it is demonstrated that the electrosag melting technology can promote effectively the synthesis of in-situ TiB_2 particles via the Al-salts reaction at 600 A. Many earlier researches [22, 25] suggested that the salts-metal reaction of K_2TiF_6 - KBF_4 -Al system is complex. After the mixed salts is added into the Al melt in the traditional LSM method, Ti and B released from the molten salts can diffuse into Al melt across the salts/Al interface to form rather small sized $TiAl_3$, AlB_2 by reduction reaction. These two phases can dissolve in the Al melt immediately. At a certain temperature, when the solutes Ti and B in Al melt reach saturation, TiB_2 is formed since TiB_2 is the most thermodynamically stable phase due to its lowest free energy formation among these three compounds. Thereby, the final formation of TiB_2 phase is controlled by the transfer of Ti and B from molten salts to liquid Al and the transformation from $TiAl_3$, AlB_2 to TiB_2 phase [22, 26]. In the electrosag melting process, on the one hand, the Al

melt reacts with molten salts in the form of droplet, which results in hundreds of times more contact area between them than that of LSM method, therefore accelerating the transfer of Ti and B from molten salts to Al melt. On the other hand, in the process of electroslag melting consumable electrode tip is the high temperature region and the Al-salts reaction mainly occurs in the region near Al consumable electrode tip, which accelerates the diffusion rates of Ti and B, leading to a faster saturation of Ti and B in the Al melt. Consequently, TiB_2 nuclei can be formed more easily. In addition, the molten salts flow continuously to high temperature region due to the vigorous movement of molten slag under electromagnetic action, which makes the interface of Al-salts renewed continuously, consequently fully reacting.

3.2 Microstructural features of composites

Table 3 is chemical composition of 5 wt% TiB_2/Al composites prepared by electroslag melting and traditional LSM method. It can be seen that the absorption rates of Ti and B in Al melt in the process of electroslag melting are almost the same as that of the LSM method. Figure 11 shows the microstructures of composites prepared by two different methods. It is found that the TiB_2 particles in the composite prepared by LSM method distribute along the boundaries of $\alpha\text{-Al}$ grains in coral-like form, and few particles exist within $\alpha\text{-Al}$ grains, as shown in Figure 11(a). A more detailed view of the area of grain boundary is shown in Figure 11(c). Most of the TiB_2 particles adhere to each other and exist in the form of clusters. Only the particles at the edge of clusters exist in isolation. However, the significant changes in microstructure can be observed in the composite prepared by electroslag melting, as shown in Figure 11(b)(d). The dispersion of TiB_2 particles is improved significantly although most of particles still tend to distribute in the boundaries of $\alpha\text{-Al}$ grains. Compared the composite prepared by LSM method, the particles more loose, that is, TiB_2 particles tend to distribute from the grain boundaries to interior of $\alpha\text{-Al}$ grains, as shown in Figure 11(b). High magnification microstructure in the grain boundary areas, as shown in Figure 11(d), it is found that most of the particles exist in isolation, and the size is smaller than $1\text{ }\mu\text{m}$. Clean interfaces between TiB_2 particles and Al matrix are observed. In addition, compared with the composite prepared by traditional LSM method, the size of $\alpha\text{-Al}$ grains is decreased in the composite prepared by electroslag melting, as shown in Figure 11(d).

The distribution of TiB_2 particles in Al matrix mainly depends on the dispersion of particles in Al melt and so-

Figure 11: Microstructures of composites prepared by (a)(c) LSM method and (b)(d) electroslag melting.

Table 3: Chemical compositions of 5 wt% TiB_2/Al composites prepared by different processes (wt.%).

Element	Al	B	Ti	Si	Fe
LSM	Bal.	1.56	3.42	0.15	0.14
Electroslag melting	Bal.	1.52	3.36	0.11	0.12

lidification rate. In the composite prepared by electrosag melting the dispersion of TiB_2 particles is improved, which mainly is attributed to the shorter Al-salts reaction time, faster solidification rate in water-cooled crystallizer.

3.3 Mechanical properties

Figure 12 presents the mechanical properties of CP aluminum and 5 wt% TiB_2/Al composites prepared by LSM method and electrosag melting. Comparison with the unreinforced CP aluminum has been made. It can be seen that the average values of yield strength (YS) and ultimate tensile strength (UTS) of composite prepared by LSM method are 40 MPa and 94 MPa, which are 53.8% and 56.7% higher than that of CP aluminum, but the elongation (EI) is 32% and decreases by 22%. However, the average values of YS and UTS of composite prepared by electrosag melting are 45 MPa and 99 MPa, which are 73.1% and 65.0% higher than that of CP aluminum, and the elongation (EI) is 36% and decreases by only 12.2%. It is visible that the YS, UTS and EI of composite prepared by electrosag melting are further improved, and are 12.5%, 5.3% and 12.5% higher than the composite prepared by LSM method, respectively. Figure 13 shows the tensile fracture morphology of 5 wt.% TiB_2/Al composite. It is found that some large inclusions exist in the composite prepared by LSM, as shown in Figure 13(a)(b). However, the tensile fracture of composite prepared by electrosag melting is clean and no obvious inclusion is observed, as shown in Figure 13(c)(d). This is mainly attributed to the function of basic slag agent used to refine Al melt. In the process of electrosag melting, the contact area between Al melt and slag agent was hundreds of times more than that of the conventional stirring method, and

the slag pool is stirred strongly due to electromagnetic action. Therefore, the non-metallic inclusions in Al melt were adsorbed fully by the refining agent, and automatically migrated to the slag pool.

Previous studies have shown that the strength mechanism of in-situ TiB_2/Al composite was mainly attributed

Figure 12: Mechanical properties of 5 wt.% TiB_2/Al composites prepared by different processes.

Figure 13: The tensile fractures of TiB_2/Al composites prepared by (a)(b) LSM and (c)(d) electrosag melting.

to the load-bearing strengthening ($\Delta\sigma_{Load}$), the coefficient of thermal expansion (CTE) mismatch strengthening ($\Delta\sigma_{CTE}$), and the orowan strengthening ($\Delta\sigma_{Orowan}$). And the strengthening effect mainly depended on the dispersion of TiB₂ particles in the matrix [11, 12]. In this research, the dispersion of TiB₂ particles is further improved in the composite prepared by electrosag melting, that is, the effective TiB₂ particle volume fraction increases, which leads to increases in $\Delta\sigma_{Load}$, $\Delta\sigma_{CTE}$ and $\Delta\sigma_{Orowan}$, thereby increasing the YS of composite. In addition, the reduction of non-metallic inclusions and improvement of dispersion of TiB₂ particles in the composite prepared by electrosag melting decrease crack initiation and propagation during tensile test, thereby increasing UTS and El.

4 Conclusions

In this research, the in-situ TiB₂/Al composites were successfully prepared via the reaction of Al-K₂TiF₆-KBF₄ by electrosag melting. The effects of electrosag melting process on the formation of TiB₂ particles, and the microstructures and mechanical properties of composites were investigated. The following conclusions are drawn.

1. In the process of electrosag melting, the melting current has a significant effect on the formation of TiB₂ particles. The Al-salts reaction is not complete at both too low current and too high current. TiB₂ particles can be in-situ synthesized successfully at 600 A for 15min. Compared with 850°C for 60 min of LSM method, the preparation efficiency is greatly improved.
2. The dispersion of TiB₂ particles is improved in the composite prepared by electrosag melting. TiB₂ particles tend to distribute from the grain boundaries to interior of α -Al grains, and most of the particles exist in isolation. This mainly is attributed to the shorter Al-salts reaction time and faster solidification rate in water-cooled crystallizer. In addition, the size of α -Al grains is decreased due to faster solidification rate in electrosag melting.
3. The non-metallic inclusions are significantly reduced in the TiB₂/Al composite prepared by electrosag melting. The values of YS, UTS and El pct of composite prepared by electrosag melting are 12.5%, 5.3% and 12.5% higher than that of the composite prepared by LSM method.

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