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AN IN-SITU TECHNIQUE FOR PREPARING Al-TiB_2 AND Al-Al_3Ti COMPOSITES

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Abstract

A novel technique for preparing in-situ Al-TiB_2 and Al-Al_3Ti composites by electroslag remelting (ESR) process was developed in this paper. The microstructure and phases of the composites were investigated by SEM and XRD. The aim of present work was to verify the feasibility of in-situ synthesis of Al-TiB_2 and Al-Al_3Ti composites by ESR process which had unique advantages in promoting fluoride salt-metal reaction efficiency. The reactant concentration and reactant contact area was improved greatly in the metal molten pool during ESR process leading to a totally complete reaction. The experiment results demonstrate that TiB_2 and Al_3Ti particulates disperse uniformly in the aluminum matrix and the mean particle size becomes much smaller compared with the conventional casting method.

Introduction

It is known that the metal matrix composites (MMCs) have been widely concerned because of their excellent characteristics such as high specific tensile strength, high modulus, high wear resistance as well as high temperature properties. Their unique outstanding performance makes them promising potential candidates for applications in automobile and aerospace industries [1-3]. Considerable efforts have been devoted to the development of particulate reinforced aluminum MMCs mainly in the preparation technology and many fabrication process have been developed during the last decades. Traditionally, Al based MMCs have mainly been produced via power metallurgy, spray deposition, casting method and perform infiltration, etc. Those ex-situ methods can not overcome the inherent defects such as poor wettability of the reinforcement, reaction of matrix-reinforcement interface and high processing cost. The in-situ fabrication processes have been developed offering significant advantages over the conventional processing both in technical and economic standpoints. Some of these technologies have been widely used, such as exothermic dispersion (XD), directed melt/metal oxidation (DIMOX), self-propagating high-temperature synthesis (SHS), vapor-liquid-solid (VLS), flux-assisted synthesis (FAS) and mechanical alloying (MA) [4-11].

Since 1993, J.V. Wood [12] has successfully synthesized A356/TiB_2 composites via a mixed salt route technique involving K_2TiF_6 and KBF_4, the mixed fluoride salts reaction method known as LSM has been investigated by many researchers because of the low cost and simple preparation process. Adding Ti-and B-bearing potassium fluoride salts into the high temperature aluminum melts, the Ti and B could transfer from the salts to molten aluminum, where the atoms dissolve in the melt and precipitate as TiB_2, then the Al based composite reinforced with TiB_2 particles is fabricated. However, there are several drawbacks in this technology need to be overcome. (1) It usually takes over 60 minutes for aluminum melt to mix and react with fluoride salts.(2) During the long time high temperature reaction procedure, the TiB_2 particles are easily to grow up, as a result, the particle size is almost1μm [13]. (3) Moreover, the mechanical stirring technique which is always applied in this process to promote the reaction can result in serious inspiration which impair the mechanical property of the composite. (4) Another critical problem is that it is hard to remove the salt slag in the the melt because they always mix with the Al melts and TiB_2 particles. By the same steps, X.Wang also fabricated the reinforcing phase of Al_3Ti particles via the molten aluminum and hexaflurotitanate (K_2TiF_6) but the size of Al_3Ti particles is as large as 30μm which is apparently not suitable for reinforcement [1].

The electroslag remelting (ESR) technology has now been in use for more than 50 years and is the standard production process for high-quality complex-alloy steel and alloys. It's known that the purpose of ESR is for purification because this technique has great advantages in removing impurity elements and inclusions in alloys. Generally, the ESR process includes the following parts, melting of slag cored, metal droplet entering into slag pool and reacting with large quantity of slag, solidification of the remelted molten metal. Some researchers [14] have studied the effects of ESR technique on the TiC particles appearance in the steel based composites and found the distribution of TiC particles was uniform, which enhanced the wear resistance of the composites. However, up to now, it has not been reported that ESR technique was applied to fabricate aluminum matrix composites.

In the traditional LSM process, mixed salts were poured into the molten aluminum while the ESR process imports the metal droplets gradually into the fluoric-salt system. The purpose of this work reported here is to introduce a new in-situ method of synthesizing Al-based metal matrix composites reinforced by TiB_2 and Al_3Ti particles through a comprehensive process combining the ESR with LSM technique and discuss the feasibility and advantages of the synthesis of Al based composites by ESR technique. The preliminary results were expected to be significant promotion of the development of in-situ technique for fabricating aluminum matrix composites.

Experimental

Materials and equipments

Figure 1 shows the schematic diagram of the ESR experimental arrangement for the preparing of Al-TiB_2 and Al-Al_3Ti composites. During the process of ESR, the solid electrode was polarized with a low voltage high current power supply and the copper mould served as the other pole. The two poles were connected by the slag cored presented in the mould. The raw materials used in this process were commercial pure aluminum (0.11wt%Fe; 0.04wt%Si; 0.0126wt%Ga; 0.0023wt%Mg, 0.0027wt%Zn; balance Al) and potassium hexafluorotitanate (K_2TiF_6) and potassium tetrafluoroborate (KBF_4) which were heated to 250℃ for 4 hours and thoroughly mixed together for 40 min to obtain a blended mixture. The basic fluxes composition for ESR was carefully selected based on the following mixture ratio, 47wt% KCl+ 30wt% NaCl+ 23wt% Na_3AlF_6, which was proved a proper ratio for ESR of aluminum. After the fluxes were dehumidified in a desiccator for 4 hours, K_2TiF_6 and KBF_4 then blended sufficiently with them and the whole mixtures weighing 1kg were used as the slag cored. The electrode of 2kg for the present study was made of pure commercial aluminum which was melted in the electric resistance furnace and casted into ingots of Φ40mm×700mm. The preparation process of Al-Al_3Ti composites is almost the same as Al-TiB_2 composites and the raw materials are pure commercial aluminum and hexaflurotitanate (K_2TiF_6).

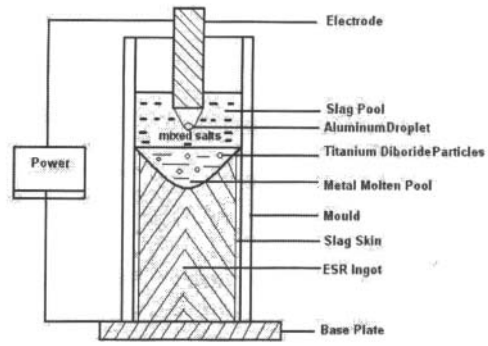

Figure 1.Schematic diagram of the ESR equipment

Experimental procedures

Initially, the power was applied, striking arc between the aluminum electrode and the pad material at the bottom of the mould. The slag powder was poured into the furnace and soon became molten. Then the electrode was fed into slag pool and the heat melted the tip of the electrode gradually by droplet which dropped through the slag pool. Reaction between the aluminum and the fluoride molten salt occurred both at the electrode surface and within the slag pool. Then TiB_2 and Al_3Ti particles were obtained during this process. Because of the full exposure of aluminum to fluoride molten salt, the in-situ reaction efficiency was enhanced greatly without mechanical stirring compared with traditional LSM method. When most of the electrode was melted, the power was turned off and the mould became cool in air. The slag generated in the reaction mostly on top of the ingot was easily removed after solidification and the Al-TiB_2 and Al-Al_3Ti composites ingots were prepared. The arc starting voltage was 50～55V while the remelting voltage was 20～25V.

The microstructure and phases of the composites were investigated by Field Emission Scanning Electron Microscope (SEM) (FEI SIRION 200/INCA OXFORD, USA) as well as X-ray diffraction (XRD) (BRUKER-AXS, German).

Results and discussion

The XRD pattern of the as-cast specimen is presented in Figure 2, which clearly shows the presence of TiB_2 peaks in Al based composites. It obviously can be seen that TiB_2 particles have been produced during the reaction and the equation of fluoride salt-metal reactions can be expressed as follows [15]:

$$3K_2TiF_6+6KBF_4+10Al \rightarrow 3TiB_2+9KAlF_4+K_3AlF_4 \quad (1)$$

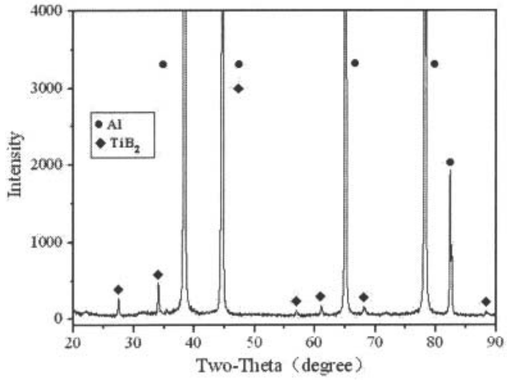

Figure 2.XRD pattern of Al-TiB_2 composites produced by ESR

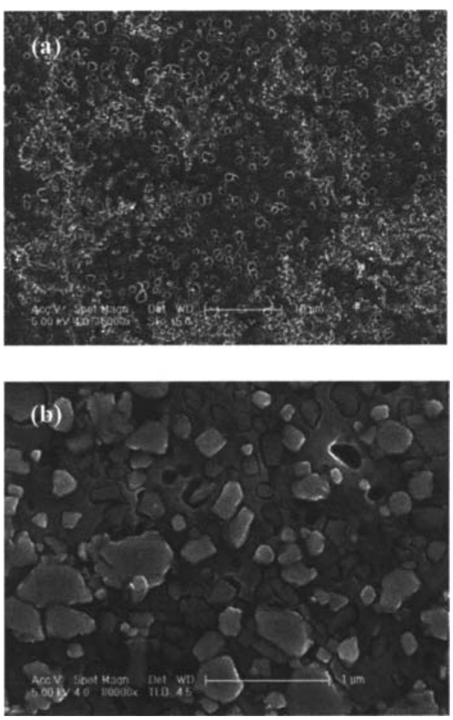

Figure 3.Microstructure of Al-TiB_2 composites produced by ESR

Since the nominal weight of the in-situ formed particles in the composites is just 2%, the intensity of the XRD patterns of TiB_2 is not much high. But we can confirm that the TiB_2 particles were obtained by ESR technique. When the working voltage retained 20～24 volt, the temperature in the mould could reach above 800℃ which was thermodynamicly feasible for the mixed salts reaction.

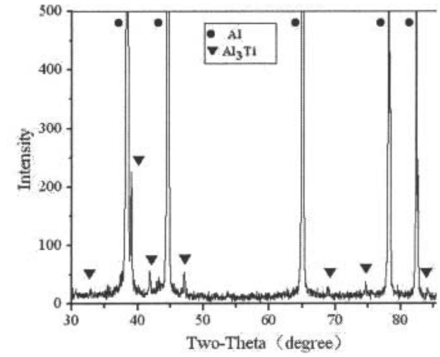

Figure 4.XRD pattern of Al-Al_3Ti composites produced by ESR

Figure 3 shows the SEM microstructure of the composites with 2wt% of the TiB_2 particles. The extremely fine particles are dispersing separately in aluminum matrix and the mean size of the particles is around 250nm which is much smaller than that produced via the conventional LSM method. We know that during the traditional process, the system temperature is higher than 850℃ and the reaction usually lasts nearly 60min. Under such condition, TiB_2 particles are more likely to aggregate and grow up to reduce the specific surface energy with the reaction procedure. As a result, the size of the agglomeration is usually controlled around 1μm. While in this experiment, the TiB_2 particles were produced as the aluminum droplet entered the slag pool where the reaction of K_2TiF_6 and KBF_4 with aluminum occurred immediately. Since the density of the particles is higher than the slag, TiB_2 particles were easy to move to the aluminum molten pool where temperature was lower than the slag pool because of the water cooling circulating system. It's a consecutive process and particles were obtained gradually.

Generally, chemical reaction efficiency is influenced by the following factors: system temperature, catalyst, reactant concentration, reactant contact area. With the higher reactant concentration and larger contact area, the reaction will speed up faster and the process will be more thoroughly. During the ESR experiment, the reaction began when the aluminum droplet immersed in the molten fluoride slag pool completely because of its bigger density than the fluoride salt. Therefore, the contact area between the aluminum and salt is at most and definitely gains higher reaction efficiency. By contrast, in the traditional LSM process, it's hard to keep the fluoride salt inside the molten aluminum and mechanical agitation must be used to disperse the salt so as to disperse the fluoride slag and increase the contact area, which will cause serious inspiration at the same time. The improved reaction efficiency by ESR dramatically shortens the time required for preparation to 15min while the average time in the conventional LSM process is about 60min which is enough for particulates to aggregate together [16].

Figure 3 and Figure 4 show the XRD pattern and SEM microstructures of Al-Al_3Ti composites fabricated by ESR technique. The presence of Al_3Ti particulates is confirmed by XRD analysis and also evidenced by the blocky and flaky morphologies shown in the SEM micrograph. The flux-metal reaction demonstrating the formation of Al_3Ti can be described as follows [17]:

$$3K_2TiF_6+13Al \rightarrow 3Al_3Ti+3KAlF_4+k_3AlF_6 \qquad (2)$$

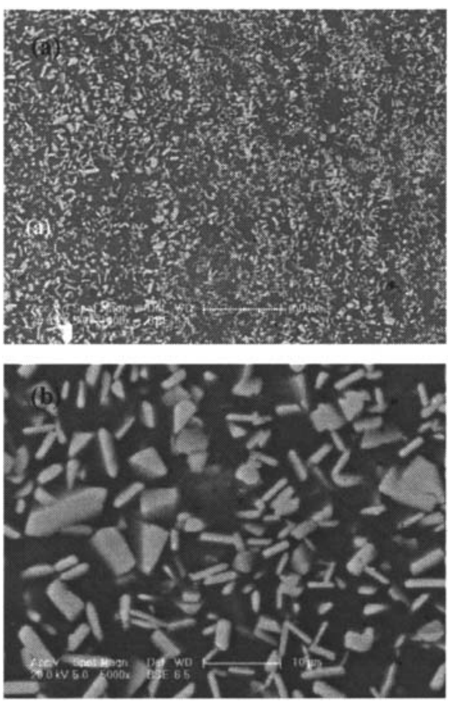

Figure 5.Microstructure of Al-Al_3Ti composites produced by ESR

Figure 5.a is the low SEM magnification image showing the homogeneous dispersion of the in-situ Al_3Ti particulates while Figure 5.b is the high magnification SEM image showing in-situ Al_3Ti particulates of different morphologies. It has been reported [1] that the in-situ Al_3Ti particulates produced by conventional casting method were either needle-like or blocky and the size was 30μm on average. As candidate reinforcement, the in-situ Al_3Ti particles offer lighter weight and stronger bonding with Al-alloy matrix compared with in-situ TiB_2 particles. The disadvantage is that Al_3Ti particles are very easy to grow up at high temperature and have a large aspect ratio which is not well qualified for reinforcement. V.Auradi [17] found that the mean Al_3Ti particles size increased from 11.9 to 23.3μm with increase in reaction temperature from 800 to 1000℃. In ESR process, the initial reaction temperature was controlled at 800℃, as the reaction efficiency was greatly enhanced because of the improved reactant concentration and large contact area, the reaction would be completed within 15min and the Al_3Ti particles size was much smaller and the mean size was 5μm as shown in Figure 5. b.

Conclusions

The new method utilizing ESR process to fabricate the in-situ aluminum composites was developed and the in-situ Al-TiB_2 and Al-Al_3Ti composites were successfully synthesized. The ESR technique could promote the reaction efficiency greatly by increase the reactant concentration and reactant contact area. The particulates produced by ESR technique were much finer and more homogeneous compared with the conventional LSM process. This ESR technology provided a novel approach to prepare in-situ MMCs and had advantages of improving the reaction efficiency and casting quality.

Acknowledgements

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