In-situ preparation of Al matrix composites reinforced by TiB_2 particles and sub-micron ZrB_2

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Particulate-reinforced metal-matrix composites (PRMMCs) are of particular interest due to their ease of fabrication, low costs and isotropic [1]. The selection of a compatible reinforcement is very important for PRMMCs. Among various reinforcements used in the PRMMCs such as TiC, TiB_2, Al_2O_3, SiC, ZrB_2 and BN, TiB_2 and ZrB_2 are excellent reinforcements. This is due to the fact that TiB_2 and ZrB_2 are stiff, hard and more importantly, do not react with aluminum to form any reaction products [2]. There are many reports about the fabrications and mechanical behaviors about TiB_2/Al composites [3–6]; however, information related to the synthesis of composites with combined *in-situ* TiB_2 and ZrB_2 is very limited. In this paper, a novel Al matrix composite reinforced with TiB_2 and ZrB_2 was fabricated by the mixing salts reaction method and the microstructures of the composites were investigated with scanning electron microscope (SEM) and transmission electron microscope (TEM). X-ray diffraction (XRD) was used to identify the phases in the composites.

The composites were fabricated by mixing salts reaction process at 860 °C with KBF_4, K_2ZrF_6 and K_2TiF_6 salts used. The 99.85% commercial pure Al was first melted in clay-graphite crucible using an intermediate frequency furnace at 800 °C, after which a preweighted mixture of KBF_4, K_2ZrF_6 and K_2TiF_6 (the weight ratio of KBF_4:K_2ZrF_6:K_2TiF_6:Al is 7:12:8:73) was added into the molten metal using the stirring method at 860 °C. Then the melt was stirred for 10–15 min and *in-situ* TiB_2 and ZrB_2 particles were formed in the melt as the resultants of chemical reactions among the three salts and Al. After pouring out the liquid slag (fluoride), the melt was cast into the rods of 25 mm diameter. The samples for microstructure observations and XRD analysis were cut from the bulk of ingots. The samples were metallographically prepared using conventional grinding and mechanical polishing techniques. The TEM samples were initially polished to 100 μm in thickness using the SiC paper. Then 3 mm disc samples were punched from these thinned samples and ground to a thickness of 20 μm. Finally, the disc samples were thinned by argon ion milling (Gatan) with an incident angle of 10 ° until a perforation occurred.

The formations of TiB_2 and ZrB_2 reinforcements via the potassium fluoride molten salts mixture are thermodynamically favorable. The overall reaction is divided into two steps: (a) the reactions among KBF_4, K_2ZrF_6, K_2TiF_6 salts and Al; (b) resultants of former reaction continue to react to produce the TiB_2 and ZrB_2 phases. Table I shows the values of the Gibbs free energy of all

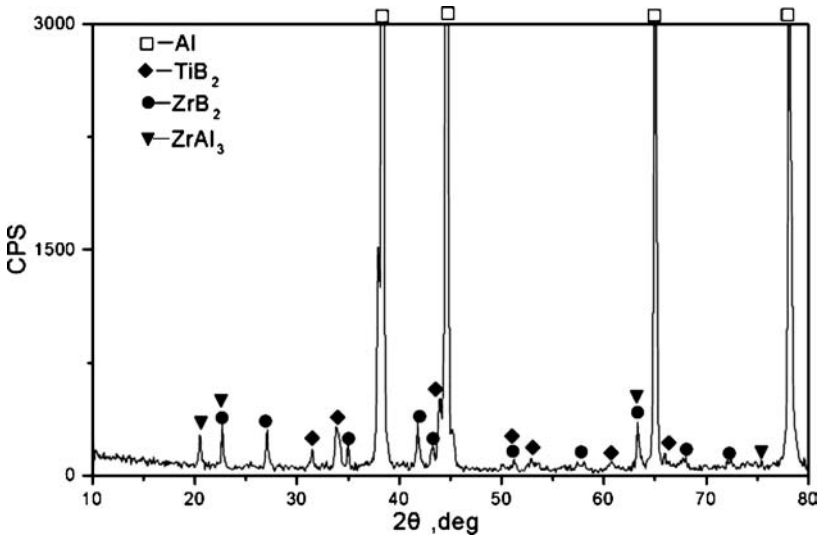

Figure 1 X-ray diffraction patterns of (TiB_2 + ZrB_2)/Al composites.

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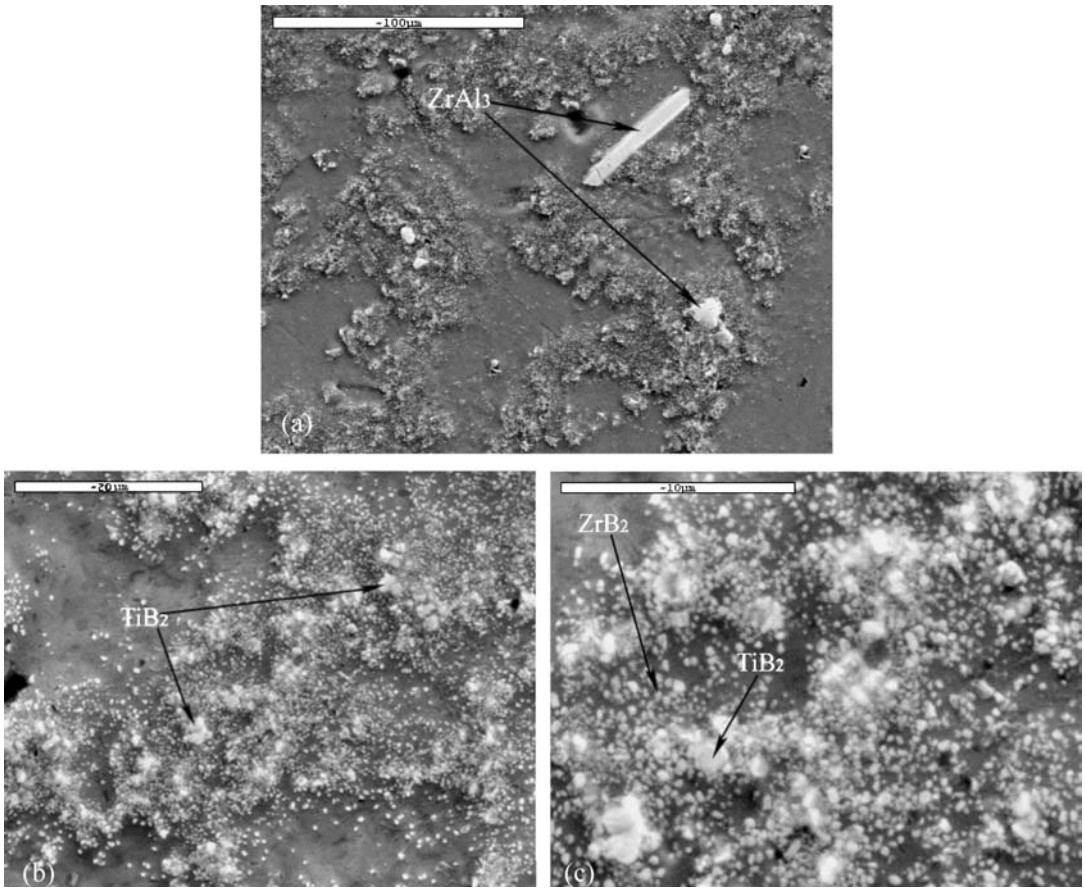

Figure 2 (a, b) SEM micrograph of the ($TiB_2 + ZrB_2$)/Al composites (c) enlarged graph corresponding to (b).

reactions at 1000 K [7]. The overall reactions showing the formations of TiB_2 and ZrB_2 can be written as:

$$K_2TiF_6 + 2KBF_4 + 10/3Al = TiB_2 + 10/3AlF_3 + 4KF \quad (1)$$

$$K_2ZrF_6 + 2KBF_4 + 10/3Al = ZrB_2 + 10/3AlF_3 + 4KF \quad (2)$$

From the reactions shown in Table I, the Gibbs free energy values of reaction (1) and (2) are −860.08 and −758.53 KJ/mol, respectively. Both of them are exothermic reactions and are favorable at about 1000 K.

Fig. 1 shows the XRD (using Cu-Kα radiation and operating at 40 kV and 100 mA) patterns of (ZrB_2 + TiB_2)/Al composites. It indicates that the present phases in the composite are α-Al, TiB_2, ZrB_2, and $ZrAl_3$. The result of the XRD analysis confirms that Al matrix composites reinforced with TiB_2 and ZrB_2 particles can be fabricated by the mixing salts reaction process. SEM micrographs of (ZrB_2 + TiB_2)/Al composite are presented in Fig. 2. From the Fig. 2a and b it can be seen

TABLE I The reactions and the standard Gibbs free energy values at 1000 K

Recations	ΔG° (KJ/mol) 1000 K
(i) $2KBF_4 + 3Al = AlB_2 + 2AlF_3 + 2KF$	−404.31
(ii) $K_2TiF_6 + 13/3Al = TiAl_3 + 4/3AlF_3 + 2KF$	−354.65
(iii) $K_2ZrF_6 + 13/3Al = ZrAl_3 + 4/3AlF_3 + 2KF$	−276.24
(iv) $TiAl_3 + AlB_2 = TiB_2 + 4Al$	−101.12
(v) $ZrAl_3 + AlB_2 = ZrB_2 + 4Al$	−77.98

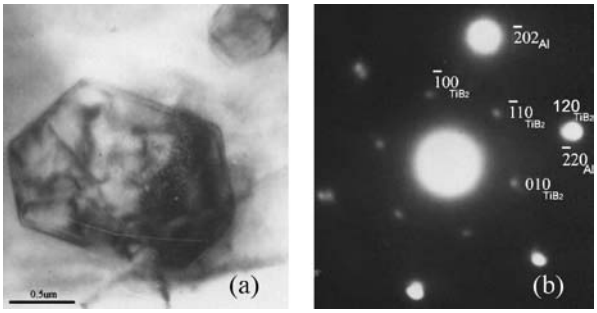

Figure 3 (a) TEM image of TiB_2 (b) composite electron diffraction patterns from TiB_2 crystal axis along [001] and Al along [111].

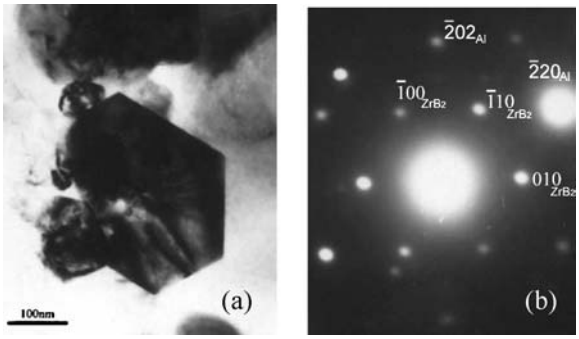

Figure 4 TEM image of ZrB_2 (b) composite electron diffraction patterns from ZrB_2 crystal axis along [001] and Al along [111].

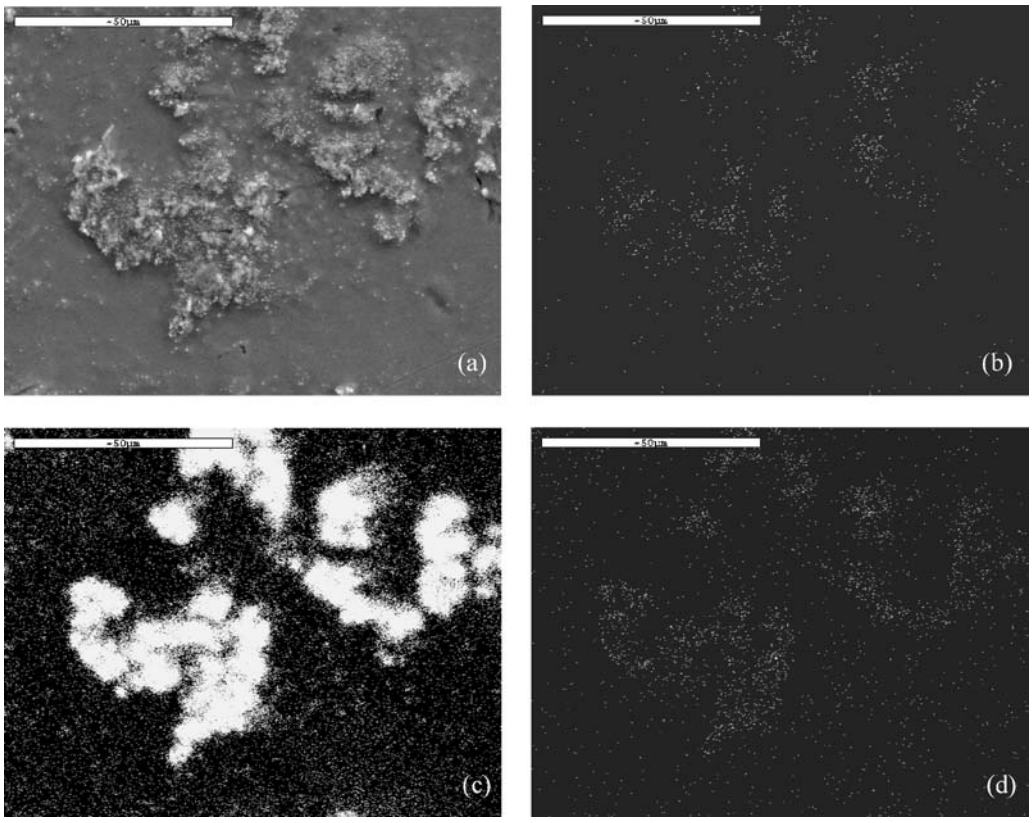

Figure 5 EPMA elemental of (TiB_2 + ZrB_2)/Al composites (a) SEM micrograph and X-ray dot maps of element; (b) B; (c) Ti; (d) Zr.

that most of the TiB_2 and ZrB_2 particles are distributed along the grain boundary regions and some agglomerations (clusters) of the particles are observed. The distribution of particles is not homogeneous in the Al matrix; however, the agglomerations or clusters, distribute uniformly. The average size of agglomerations (clusters) is 40–50 μm. The results of energy dispersion X-ray (EDX) spectrometer indicate the bigger reinforcements in Fig. 2c are TiB_2 particles, while the smaller ones are ZrB_2 phases. The ZrB_2 reinforcements distribute around the TiB_2 reinforcements. The main reason for agglomeration of particles is that the ratios of heat transfer coefficient between the particle reinforcements and matrix are less than 1. According to the theory of thermal conductivity in the process of solidification, the TiB_2 and ZrB_2 reinforcements are pushed by the solidification front. As a result, the TiB_2 and ZrB_2 particles agglomerate at the solid/liquid interface during solidification. In addition, it also can be found that there are some strip-shaped phase and near-spherical phase existing in the composites as shown in Fig. 2a. With the help of EDX, it can be concluded that they are all $ZrAl_3$ phases, which are also present in the XRD result. The main reason for the formation of $ZrAl_3$ phase is that chemical reaction (2) is incomplete. If the atomic ratio of Ti/2B and Zr/2B is controlled strictly and reaction holding time is longer, the $ZrAl_3$ phase will tend to decompose to form ZrB_2. The $TiAl_3$ phase is not observed because the atom ratio of Ti:B in the salts mixture is less than 1:2.

Figs 3 and 4 show the typical bright field TEM images of reinforcements and the composite electron diffraction patterns of reinforcements and matrix. It can be observed that the TiB_2 and ZrB_2 particles are hexangular and near-equiaxed shape, but TiB_2 particles are bigger than ZrB_2 particles in size. The average size of TiB_2 particle is 1–1.20 μm, while that of ZrB_2 particle belongs to sub-micron size and is about 0.30 μm. From Fig. 5a and d, which show the EPMA micrographs of agglomerations (clusters) in the composites and X-ray dot maps of elements B, Zr, Ti, it can be observed that the distributions of Ti, Zr and B elements are coincident on the whole.

The shape of the reinforcements is related to their crystal structures. TiB_2 or ZrB_2 particle has a C32-AlB_2 structure and MeB_2 type (TiB_2 with lattice parameters $a = 0.3029$ nm, $c = 0.3228$ nm; ZrB_2 with lattice parameters $a = 0.317$ nm, $c = 0.3513$ nm). The crystal structure of TiB_2 or ZrB_2 shows high geometrical symmetry for the chemical bond between the atoms Ti (or Zr) and B. This indicates that TiB_2 or ZrB_2 will grow almost at the same speed in each direction and form equiaxed or near equiaxed shape.

In conclusion, our results show that *in situ* (ZrB_2 + TiB_2)/Al composites were synthesized successfully through the mixing salts reaction among the KBF_4, K_2ZrF_6, K_2TiF_6 and Al. The agglomerations (clusters) of the particles distribute uniformly in the Al matrix. The TiB_2 and ZrB_2 particles are hexangular and near-equiaxed shape. The average size of TiB_2 particle is about 1 μm while that of ZrB_2 particle is about 0.30 μm.

Acknowledgments

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