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Al–Ti–B grain refiners via powder metallurgy processing of Al/K_2TiF_6/KBF_4 powder blends

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ABSTRACT

The response to thermal exposure of ball-milled Al/K_2TiF_6/KBF_4 powder blends was investigated to explore the potential of PM processing for the manufacture of Al–Ti–B alloys. K_2TiF_6 starts to be reduced by aluminium as early as 220 °C when ball-milled Al/K_2TiF_6/KBF_4 powder blends are heated. The reaction of KBF_4 with aluminium follows soon after. The Ti and B thus produced are both solutionized in aluminium before precipitating out as Al_3Ti and TiB_2. All these reactions take place below the melting point of aluminium. The ball-milled Al/K_2TiF_6/KBF_4 powder blends heat treated at approximately 525 °C can be compacted to produce Al–Ti–B pellets with in situ formed Al_3Ti and TiB_2 particles. These pellets are shown to be adequate grain refiners for aluminium alloys.

1. Introduction

Grain refinement has become a standard melt treatment practice in aluminium foundries owing to its highly attractive technical and economical features [1,2]. The vast majority of grain refining applications employ Al–Ti–B alloys which typically contain 2–10 wt% Ti and 0.1–2 wt% B [2–16]. Of the several processes employed to manufacture Al–Ti–B alloys [2,17–21] that which involves the addition of K_2TiF_6 and KBF_4 to a stirred body of molten aluminium is the most popular [2]. K_2TiF_6 and KBF_4 are readily reduced to Ti and B, producing a melt with a dispersion of soluble Al_3Ti and insoluble TiB_2 particles, subsequently cast either as a billet for extruding into a rod or directly as a rod with a continous rod caster.

Powder metallurgy (PM) processes were also investigated to manufacture grain refiners based on the Al–Ti–C system in recent years [22–24]. Such a process was recently employed to synthesize binary Al–Ti and Al–B alloys with in situ formed Al_3Ti and AlB_2 particles, respectively [25,26]. This solid-state process offers a very fine dispersion of aluminides and ensures rapid dissociation and dissolution into the melt. The master alloy tablets thus produced could be used for rapid adjustment of Ti and B levels in aluminium melts for grain refinining and/or removal of transition elements. The response to thermal exposure of ball-milled Al/K_2TiF_6/KBF_4 powder blends was investigated in the present work to explore the potential of PM processing for the manufacture of Al–Ti–B grain refiners. The sequence of reactions between K_2TiF_6, KBF_4 and aluminium was analyzed in a wide temperature range covering both the solid and liquid states of the latter.

2. Experimental procedures

Al/K_2TiF_6/KBF_4 powder mixture was prepared by mixing 5 g aluminium powder (wt% 99.9 Al, maximum particle size: 350 μm), 1.3 g commercial purity (~%98) K_2TiF_6 and 0.64 g commerial purity (~%98) KBF_4 salts. The amount of Ti and B thus made available in the ternary mixture is 5 and 1 wt% of the aluminium supply, respectively. Al/K_2TiF_6/KBF_4 powder mixture thus obtained was dry ball-milled for 1/2 h in a Spex 8000 laboratory mill using hardened steel vial and steel balls. Samples taken from the ball-milled powder blend thus obtained were heated in the differential scanning calorimetry (DSC) cell until 750 °C at a rate of 10 °C/min to investigate their response to thermal exposure. The DSC experiments were performed under flowing argon.

Larger volumes of ball-milled Al/K_2TiF_6/KBF_4 powder blends were heated in a tube furnace in the same manner as that employed in the DSC experiment, to selected temperatures. They were held at these temperatures for 1/2 h and then quenched to room temperature to retain the microstructural features introduced by these heat treatments. The heat treated powder blends were subsequently analyzed with X-ray diffraction (XRD), and metallographic techniques, in order to identify the reactions responsible for the DSC signals. XRD was conducted with Cu Kα radiation at a scan rate of 0.5 °/min in order to improve the counting frequency. Samples for metallographic analysis were prepared using conventional practices and were examined with an optical microscope. The experimental Al–Ti alloy pellets produced in the present work were assessed for their grain refining performance using the standard TP-1 [27]. As the purity of the aluminium to be inoculated with the experimental Al–5Ti–1B pellets was quite high (99.9 wt%) Ti addition level was selected to be 0.04 wt%.

3. Results and discussion

The response to thermal exposure of the ball milled binary Al/K_2TiF_6 and Al/KBF_4 powder blends are discussed in detail in

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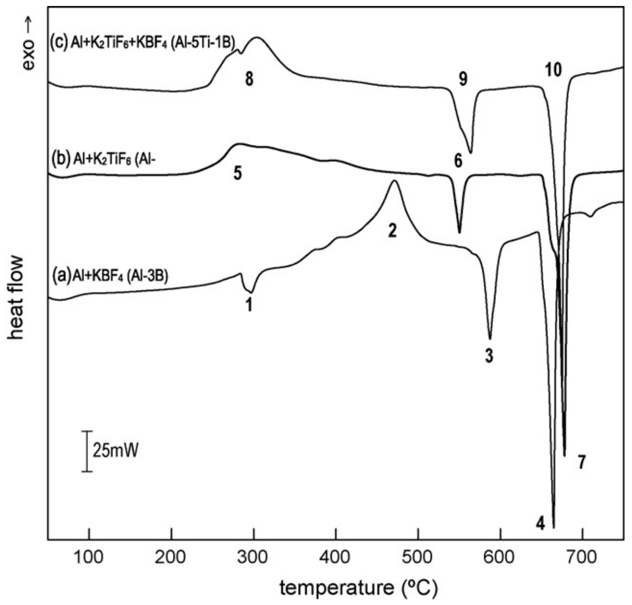

Fig. 1. DSC spectrums of ball-milled (a) Al/KBF_4, (b) Al/K_2TiF_6 and (c) Al/K_2TiF_6/KBF_4 powder blends.

[25,26]. So, only a brief summary is given here to help with the identification of the reaction sequence during thermal exposure of the ball milled ternary Al/K_2TiF_6/KBF_4 powder blend.

The small low-temperature endothermic signal (signal 1) in the DSC spectrum of the ball-milled Al/KBF_4 sample (Fig. 1) is linked with the polymorphic transformation of the KBF_4 salt [25]. The next exothermic signal was shown by XRD and metallographic analysis of samples heated at 525 °C to be produced by [25]:

$$2KBF_4 + 3Al \rightarrow AlB_2 + 2KAlF_4 \quad (1)$$

Signals 3 and 4 are due to the melting of $KAlF_4$ produced by the above reaction and aluminium, respectively.

The asymmetric exothermic signal (signal 5) in the DSC spectrum of the ball-milled Al/K_2TiF_6 powder blend starts as early as 220 °C and lasts until 500 °C after peaking at approximately 280 °C. The following consequent reactions:

$$3K_2TiF_6 + 4Al \rightarrow 3Ti + 3KAlF_4 + K_3AlF_6 \quad (2)$$

$$Ti + 3Al \rightarrow Al_3Ti \quad (3)$$

were shown by XRD and metallographic analysis of samples heated at 525 °C to be responsible for signal 5 [26]. K_2TiF_6 is reduced by aluminium, releasing Ti which is solutionized in aluminium. The solute Ti starts precipitating out as Al_3Ti particles as soon as its solubility limit in aluminium is exceeded. It is inferred from the shape of signal 5 that the precipitation of Al_3Ti particles lasts until 500 °C. The endothermic signals 6 and 7 are associated with the melting of the $KAlF_4$/K_3AlF_6 mixture produced by reaction (2) and with the melting of the Al–Ti solid solution, respectively.

The DSC spectrum of the ball-milled Al/K_2TiF_6/KBF_4 (Ti:B = 5:1) ternary powder blend is clearly not a simple superimposition of the individual Al/K_2TiF_6 and Al/KBF_4 scans (Fig. 1). A close look at the DSC curve suggests that the exothermic activities which start with signal 8 are not over until approximately 500 °C. The next two endothermic signals, signals 9 and 10, are readily identified from the DSC scan of the Al/K_2TiF_6 powder blend to be linked with the melting of the K–Al fluorides and of the aluminium matrix, respectively. With these features, the response to thermal exposure of the ternary powder blend is strikingly similar to that of the Al/K_2TiF_6 binary variety. This is not surprising since the K_2TiF_6 salt is the predominant ingredient of the ternary mixture with an intended nominal Ti:B ratio of 5:1.

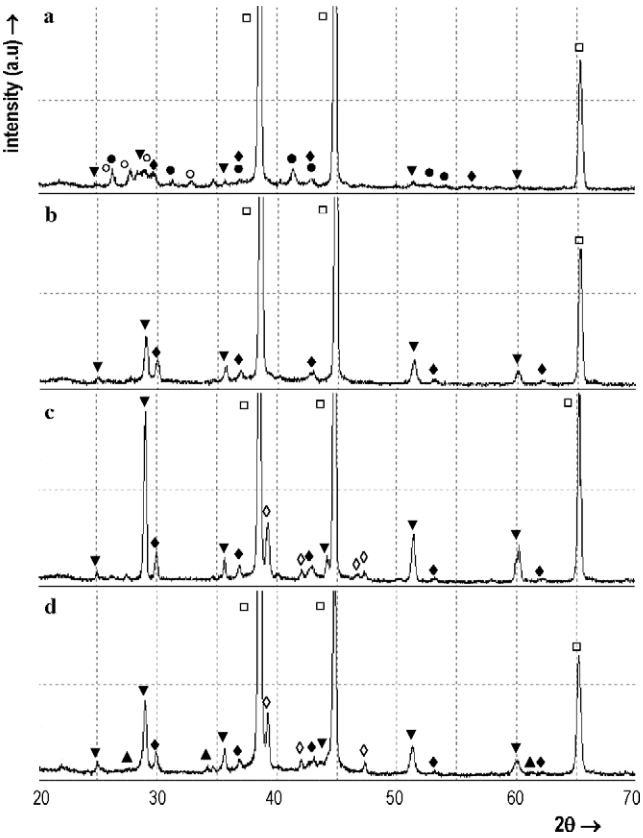

Fig. 2. XRD patterns of ball-milled Al/K_2TiF_6/KBF_4 powder blends heated to (a) 325 °C, (b) 425 °C, (c) 525 °C and (d) 625 °C and held at these temperatures for 1/2 h. ((□) α-Al; (●) K_2TiF_6; (○) KBF_4; (▼) $KAlF_4$; (◆) K_3AlF_6; (◇) Al_3Ti; (▲) TiB_2).

With a nearly identical start temperature, the exothermic signal 8 is claimed to involve the reduction of the K_2TiF_6 salt by aluminium (reaction (2)) as signal 5 in the DSC spectrum of the binary Al/K_2TiF_6 powder blend does. The depression on signal 8 coincides with signal 1 of the DSC spectrum of the Al/KBF_4 powder blend and is thus accounted for by the polymorphic transformation of the KBF_4 salt. This endothermic effect is now much smaller, however, due to the relatively smaller fraction of the KBF_4 salt in the ternary mixture. The XRD analysis of ball milled powder blend heated at 325 °C, right after the endothermic depression, reveals reflections of K_2TiF_6 and KBF_4 as well as of $KAlF_4$ and K_3AlF_6 (Fig. 2a). The coexistence of these fluorides implies that the reaction with aluminium of K_2TiF_6, and possibly of KBF_4, has started. It is not possible, however, to conclude from the XRD analysis whether KBF_4, in addition to K_2TiF_6, is reacting with aluminium at these temperatures since reaction (2) suffices to generate both $KAlF_4$ and K_3AlF_6. Evidence for K-Al fluorides wihout any sign of Al_3Ti suggests that the Ti produced by reaction (2) is not yet precipitating.

K_2TiF_6 and KBF_4 reflections are both missing in the XRD spectrum of the ball milled ternary powder blend heated at 425 °C which now reveals only $KAlF_4$ and K_3AlF_6 lines (Fig. 2b). Both K_2TiF_6 and KBF_4 must have been reduced completely by aluminium until 425 °C. The relative increase in the intensity of the $KAlF_4$ reflections suggests that the reaction of KBF_4 with aluminium:

$$KBF_4 + Al \rightarrow B + KAlF_4 \quad (4)$$

which produces only the $KAlF_4$ salt, predominates between 325 °C and 425 °C. Lack of evidence for Al_3Ti and TiB_2 (or AlB_2) seems to imply that both Ti and B are still in solution. The possibility that the

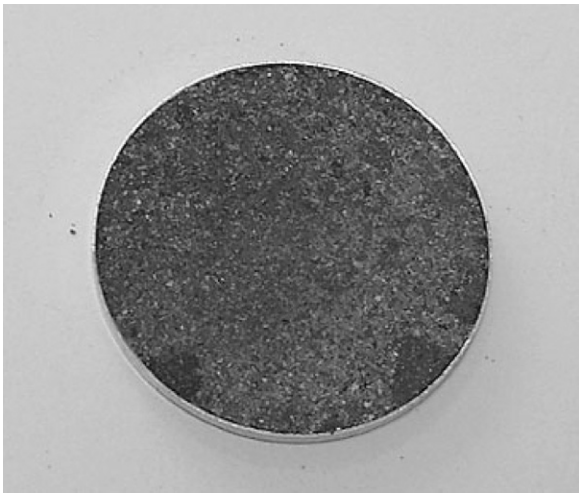

Fig. 3. Experimental Al–Ti–B alloy pellet produced in the present work.

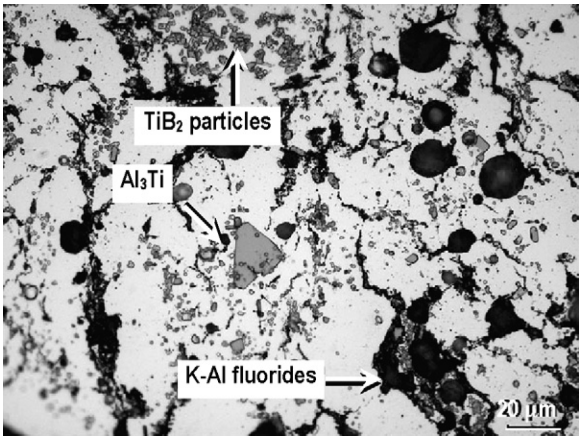

Fig. 4. Microstructure of the Al–Ti–B alloy pellet produced in the present work.

size and the volume fraction of the precipitating phases are yet too small to generate Bragg reflections shall not be overlooked either. Finally, the XRD spectrum of the ternary powder blend heated at 525 °C reveals Al_3Ti reflections for the first time (Fig. 2c). It is thus concluded that Al_3Ti precipitates extensively nearer to the end of signal 8. Samples held at 525 °C longer or at slightly higher temperatures additionally reveal TiB_2 reflections (Fig. 2d).

The following account is thus offered to explain the response to thermal exposure of the ball-milled ternary $Al/K_2TiF_6/KBF_4$ powder blend with a consideration of XRD and metallographic analysis of heat treated samples. K_2TiF_6 is reduced by aluminium, releasing Ti starting at approximately 220 °C. Likewise, KBF_4 starts to be reduced by aluminium a while later, possibly after its polymorphic transformation from orthorombic to cubic structure is over. Both Ti and B thus produced are initially solutionized in aluminium. Al_3Ti particles start to precipitate as as soon as the solubility limit of Ti in aluminium is exceeded. A portion of the solute Ti combines with solute B to form TiB_2:

$$\mathrm{Ti} + \mathrm{B} \rightarrow \mathrm{TiB_2} \tag{5}$$

The formation of Al_3Ti is favored as the solute Ti enjoys an unlimited access to aluminium while reaction (5) suffers from a rather heterogeneous distribution of solute B inside aluminium grains and is thus somewhat delayed. It is inferred from the DSC scan that the reactions (2) and (4) occur rather fast leading to a temporary solute Ti and B build up in aluminium while the precipitation of Al_3Ti and TiB_2 particles occurs nearer to the end of signal 8.

KBF_4 salt which generates AlB_2 particles when processed with aluminium alone [25], is clearly engaged in TiB_2 formation when K_2TiF_6 salt is added in the mixture. TiB_2 is more stable than AlB_2 and will eventually form when Ti is available [14]. On the other hand, TiB_2 fails to form under exactly the same processing conditions when Ti is supplied in the form of Al_3Ti particles rather than K_2TiF_6 salt. Al_3Ti particles survived the heat treatment at 525 °C of a ball-milled Al–10Ti/KBF_4 powder blend with no evidence of TiB_2 formation. Lack of a measurable reaction between B and Al_3Ti, confirmed also in a previous study [14], implies that Ti has to be available as solute to react with B.

Ball-milled $Al/K_2TiF_6/KBF_4$ powder blends with a Ti:B ratio of 5:1, heat treated at 525 °C for 1/2 h were compacted into 5 g pellets in a laboratory press (Fig. 3). These small pellets contained fine Al_3Ti and TiB_2 particles inside aluminium grains and additionally $KAlF_4/K_3AlF_6$ spent salts entrapped inside the aluminium grains (Fig. 4). The K–Al fluorides are expected to improve the wetting of the particles incorporated into the aluminium melt and are thus added intentionally in most master alloy hardeners used in aluminium foundries. These pellets were tested for their grain refining performance and were found to be fast acting grain refiners with an adequate efficiency (Fig. 5). Complete conversion of coarse columnar grains to fine equiaxed ones occurred within 2 min of inoculation. Inoculation with Al–Ti–B pelets has produced a fine equiaxed grain structure across the entire section of the grain refining test sample which was more or less retained for holding times upto 60 min. It is thus concluded that the PM process described in the present work can be employed to manufacture Al–Ti–B alloy tablets for grain refining aluminium alloys.

4. Conclusions

K_2TiF_6 starts to be reduced by aluminium as early as 220 °C when ball-milled $Al/K_2TiF_6/KBF_4$ powder blends are heated. The reaction of KBF_4 with aluminium follows soon after. The Ti and B thus produced are both solutionized in aluminium before precipitating out as Al_3Ti and TiB_2. All these reactions take place below the melting point of aluminium. The ball-milled $Al/K_2TiF_6/KBF_4$ powder blends heat treated at approximately 525 °C can be compacted to produce Al–Ti–B pellets with in situ formed Al_3Ti and TiB_2 particles. These pellets are shown to be adequate grain refiners for aluminium alloys.

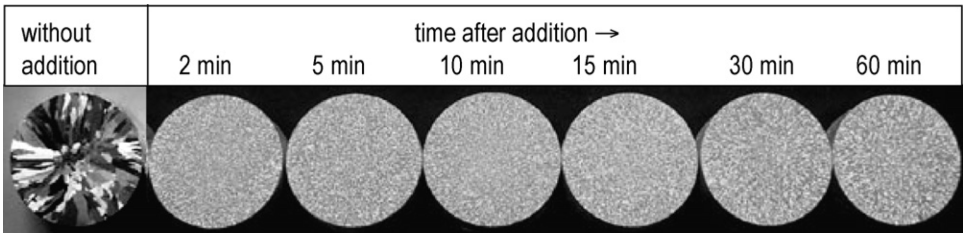

Fig. 5. Grain refining performance of the Al–Ti–B alloy pellet produced in the present work.

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