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Influence of zirconium on grain refining efficiency of Al–Ti–C master alloys

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Abstract The influence of Zirconium on the grain refinement performance of Al–Ti–C master alloys and the effect mechanism has been studied in this paper. The experimental results show that Zr not only results in poisoning the Al–Ti–B master alloy, but also poisons the Al–Ti–C master alloys. The poisoning effect is more obvious at higher melting temperature. When 0.12%Zr is added into the melt, the grain refinement performance of Al–5Ti–0.4C refiner with 0.2% addition level absolutely disappears at 800 °C. The experimental results also show that it is difficult to refine the commercial purity Al containing 0.15%Zr by Al–5Ti–0.4C master alloy. Further experiments show that the Zr element can interact with both $TiAl_3$ and TiC phases. If both of them are present, Zr preferentially reacts with $TiAl_3$ phase.

Introduction

The Al–Ti–B master alloys are widely used as the refiner of purity Al and its alloys after realizing industrialized production in the 1960s [1]. They are very effective as the refiners of Al alloys, but they also have some problems during almost the half century application. One of them is that the Al–Ti–B master alloys will be poisoned when the Al alloys contain some Zr, Cr or V element [2–6].

Several attempts have been made to explain the effect of Zr on Al–Ti–B master alloys. Mats. Johnsson [2] thinks that a deterioration occurs only when the content of Zr exceeds the hyperperitectic concentration and then some Ti will dissolve in the $ZrAl_3$ phase to form mixed aluminized phase $(Ti_{1-x}Zr_x)Al_3$ which removes dissolved Ti from the melt. Abdel-Hamid [3] agrees that ternary phases precipitate but claims that the negative effect of Zr is due to the change in the lattice parameters of $TiAl_3$ and TiB_2. G.P. Jones and J. Pearson [4] suggest that the fading mechanism is mainly due to the formation of a thin layer of ZrB_2 on TiB_2 particles in the melt. They claim that the nucleation is on TiB_2 particles adsorbing of Ti, when Zr element is present, the titanium borides will be covered with a monolayer of zirconium borides preventing the dissolved Ti from being adsorbed. A. M. Bunn, P. Schumacher et al. [5] consider that Zr can interfere with both the aluminide and the boride phase during holding in the melt. They added 0.1%Zr into Al–Ti–B mater alloys and found that when both phases are present, zirconium preferentially substitutes in the aluminide phase (Fig. 1).

In recent years, the Al–Ti–C master alloys are used more and more as the development of the manufacture technology. They are also good refiners of Al alloys and many researchers think they cannot be poisoned by Zr, Cr or V [7–13]. In this paper the authors have examined the influence of Zr on the grain refining efficiency of Al–Ti–C master alloys and analyzed the mechanism.

Experimental procedure

Commercial purity aluminum (99.7%) was used in the experiments and the refiner was Al–5Ti–0.4C master alloy. The Al–10Ti and Al–5Ti–1.25C master alloys also were used. The Zr element was added in the form of Al–6Zr master alloy.

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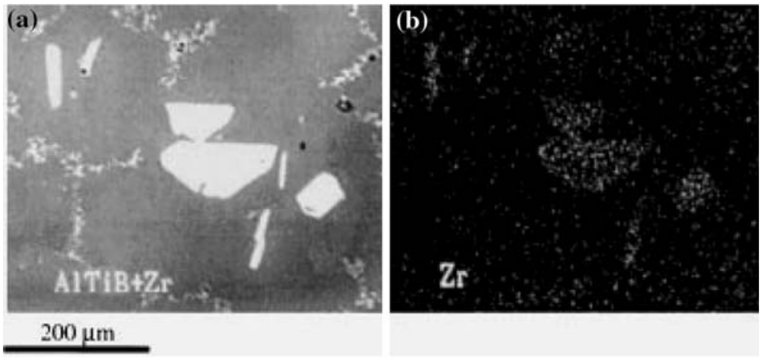


Fig. 1 Examination by SEM of a polished cross-section of Al–5Ti–1B refiner doped with 0.1%Zr [5]. (**a**) Backscattered electron image; (**b**) EDS composition map for Zr

In the first experimental series, about 800 g commercial purity Al was melted and 0.2%Al–5Ti–0.4C master alloy was added into it at 730 °C, then kept the adding level of Al–5Ti–0.4C refiner constant and varied the concentration of Zr by addition of Al–6Zr master alloy.

In the second experimental series, the melting temperature was up to 800 °C, the other procedures were the same with the first.

In order to make sure how the temperature and holding time affect the efficiency of Al–5Ti–0.4C master alloy, we also do an additional experiment that refining the Al without Zr used 0.2%Al–5Ti–0.4C master alloy and held different time at 800 °C. And then kept the content of Zr element constant in the purity Al and varied the adding amount of Al–5Ti–0.4C master alloy at 730 °C.

In the next experimental series, changed the master alloy into Al–10Ti or Al–5Ti–1.25C refiner and repeated the first experimental series at 730 °C. Then added 0.2%Zr into commercial purity Al and varied the adding amount of Al–10Ti or Al–5Ti–1.25C refiner to examine the mutual effects between them.

In order to analyze the effect mechanism of Zr on Al–Ti–C master alloys, 0.5%Zr was added into Al–5Ti–0.4C master alloy. The sample was taken and analyzed by electron probe microanalysis.

In each experiment, the melt was stirred for 3 s by a graphite stick before being sampled to minimize the influence of particle sedimentation. There was 10 min interval during each sample and the cooling rate is about 6 °C/s in all the experiments. Each experiment series has been repeated at least three times.

Results and discussion

The effect of Zr on the grain refinement of the commercial purity Al is shown in Fig. 2. It is obvious that the grains of Al samples refined by 0.2%Al–5Ti–0.4C master alloy are coarse after adding Zr element at 730 °C, especially when the content of Zr increases from 0.06 to 0.12%. When the concentration of Zr is 0.12%, the grain size achieves to about 1500 µm and some columnar crystals appear. This poisoning effect also becomes severe by rising the melting temperature. When temperature is 800 °C, only 0.06%Zr can make the grain size coarse to about 1600 µm and 0.12%Zr can make 0.2%Al–5Ti–0.4C master alloy absolutely poisoned. Figure 3 illustrates the change of the grain size with the increase of Zr content. In addition, an additional experiment has also been done to clarify the effect of higher temperature on the stability of Al–5Ti–0.4C master alloy. The result is shown in Fig. 4. It is found that the efficiency of Al–5Ti–0.4C is very good when holding time is less than 15 min. When prolonging to 30 min, the grains grow up to about 600 µm. It is concluded that although the

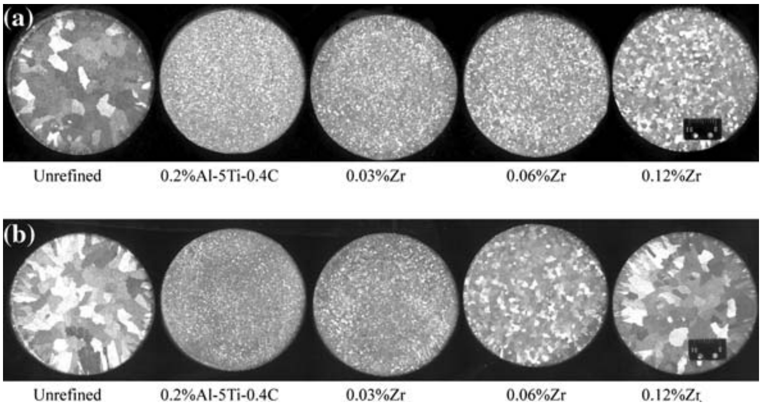


Fig. 2 Macrostructures of samples refined with 0.2%Al–5Ti–0.4C for different content of Zr. (**a**) The commercial purity Al melted at 730 °C; (**b**) The commercial purity Al melted at 800 °C

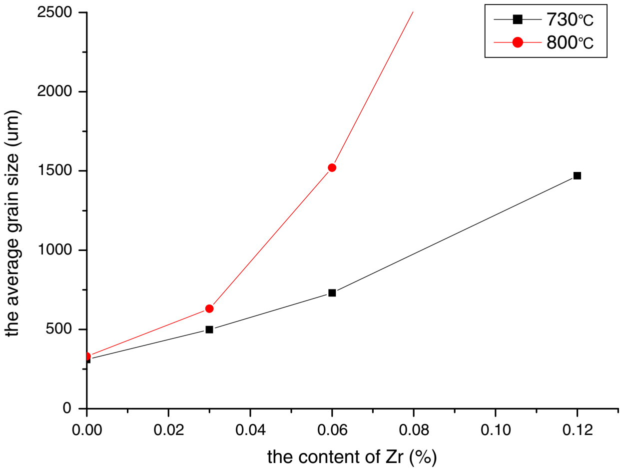


Fig. 3 Influence of Zr on the grain size of commercial-purity Al refined with 0.2%Al–5Ti–0.4C

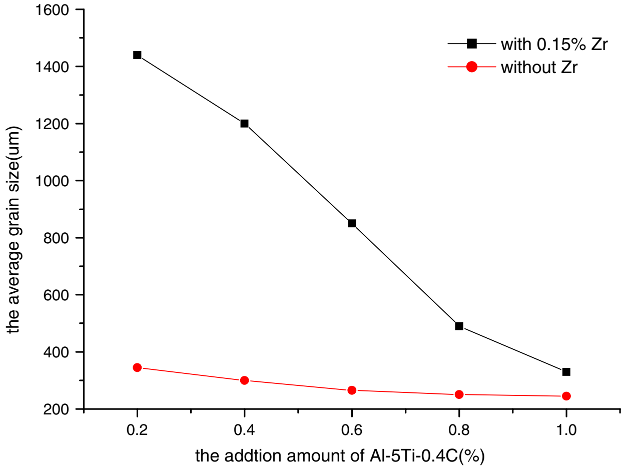


Fig. 6 The grain size of Al with 0.15%Zr vs. the addition amount of Al–5Ti–0.4C

temperature and holding time have some affect on the efficiency of Al–5Ti–0.4C, the main reason for the fading effect in Fig. 2b is the influence of Zr.

The grain refinement performance for different amount of Al–5Ti–0.4C master alloy in the presence of 0.15%Zr is shown in Figs. 5 and 6. It is found that at least 1%Al–5Ti–0.4C master alloy is needed in order to refine the commercial purity Al containing 0.15%Zr, but only 0.2%Al–5Ti–0.4C can do that for the commercial purity Al without Zr (Fig. 5b). The result indicates it needs much more Al–5Ti–0.4C master alloy to achieve satisfactory grain refinement efficiency when Zr is present.

In order to analyze the poisoning mechanism of Zr on the Al–Ti–C master alloy, we also have examined the effects between Zr and the Al–10Ti which only contains the intermediate phase of $TiAl_3$ or Al–5Ti–1.25C master alloys which mainly contains the phase of TiC. Figure 7 shows the interaction effect between Zr and Al–10Ti master alloy. Figure 8a and b are that between Zr and Al–5Ti–1.25C master alloy. It can be seen from Fig. 7a that grains of the sample refined by 0.2%Al–10Ti master alloy are coarse and the grain becomes coarser with increasing the Zr level. The effect of Al–10Ti on the samples refined by Zr is also obvious and only 0.01%Ti can

Fig. 4 Macrostructures of samples refined with only 0.2%Al–5Ti–0.4C at 800 °C for different holding time

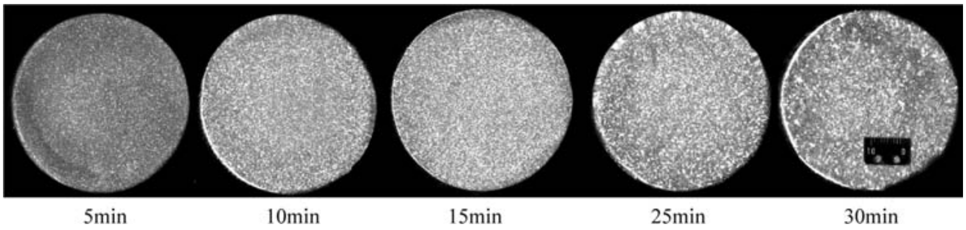
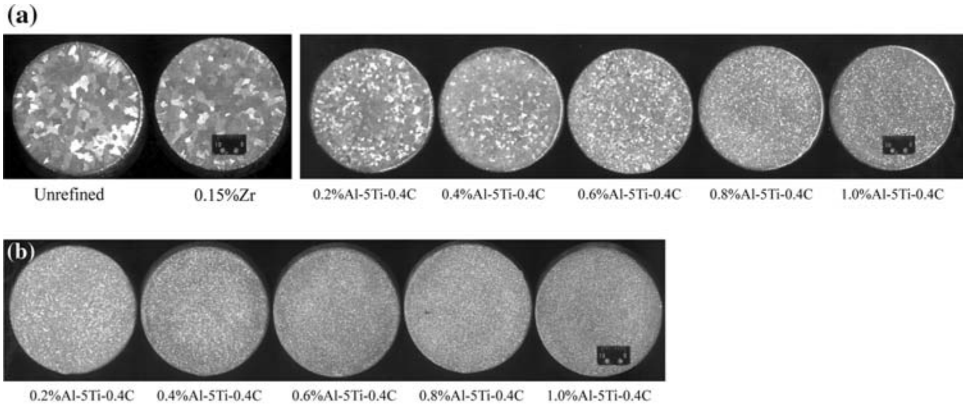
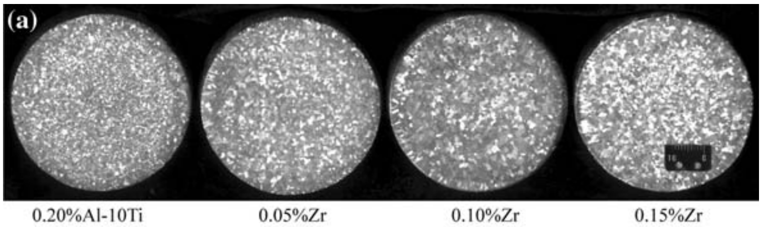


Fig. 5 The effect of Zr on the refining efficiency of Al–5Ti–0.4C master Alloy. (**a**) Grain structures for different amount of Al–5Ti–0.4C in the presence of 0.15%Zr. (**b**) The refining efficiency of Al–5Ti–0.4C master Alloy without Zr





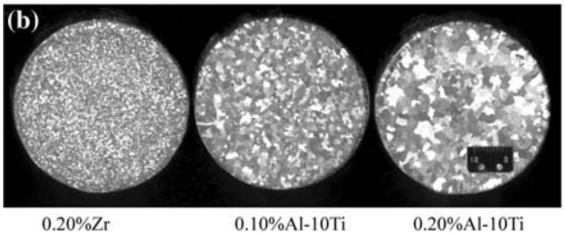


Fig. 7 The interaction between Zr and Al–10Ti master alloy. (**a**) The effect of Zr on refinement efficiency of Al–10Ti master alloy; (**b**) The effect of Ti on refinement efficiency of Zr element

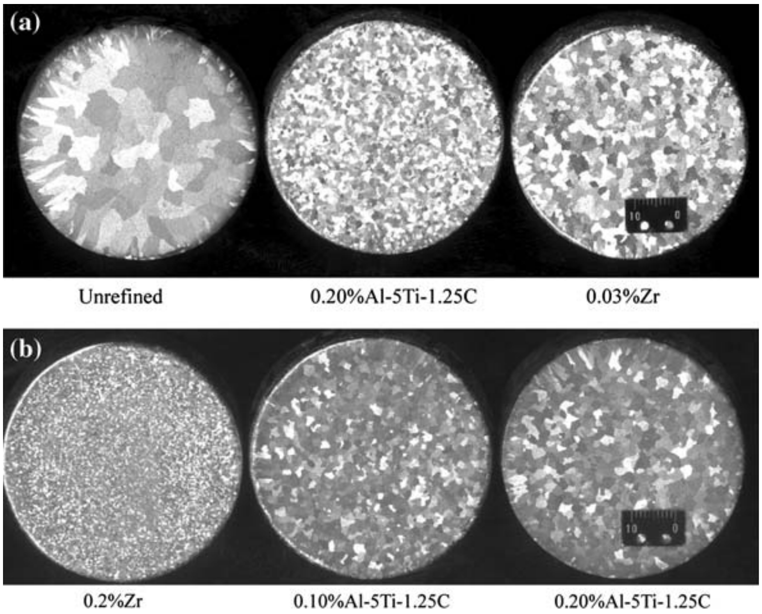


Fig. 8 The interaction between Zr and Al–5Ti–1.25C master alloy. (**a**) The effect of Zr on refinement efficiency of Al–5Ti–1.25C master alloy; (**b**) The effect of TiC on refinement efficiency of Zr

make the grains coarse seriously (Fig. 7b). From Fig. 8a it is found that Al–5Ti–1.25C master alloy also can refine the purity Al but the refining efficiency isn't as good as Al–5Ti–0.4C refiner, which is the same with some researcher's results [13]. After adding 0.03%Zr element, the refining effect of Al–5Ti–1.25C master alloy is poisoned seriously. In the other hand, only 0.1%Al–5Ti–1.25C master alloy also can make the refinement of 0.2%Zr weak drastically as shown in Fig. 8b.

Because the intermediate phase is $TiAl_3$ or TiC in Al–10Ti or Al–5Ti–1.25C master alloy, we assume that both $TiAl_3$ and TiC phases can interact with Zr element during holding in the melt. In order to confirm that, we added 0.5%Zr into Al–5Ti–0.4C master alloy and studied the sample by EPMA. Figure 9 shows the results of that experiment. It is found that there are two different morphology phases in aluminium matrix. One phase contains a lot of Ti and Zr elements besides α-Al. But it seems that the TiC phase isn't affected by Zr. This isn't agreement with the suggestion which the authors have made according to the result of the effects between Zr element and the Al–5Ti–1.25C master alloy. So it is considered that when both $TiAl_3$ and TiC phases are present, Zr preferentially reacts with TiAl3 phase as A. M. Bunn, P. Schumacher et al. [5] have suggested respect to the poisoning mechanism of Zr on Al–Ti–B master alloy.

According to the research of Yu Lina. et al. [14], the dissolved Ti will distribute around the TiC particles and then evolve into the Ti transition layer on the interface between TiC and aluminum melt. This Ti transition layer is important for the refinement. Considering the influence of melting temperature and the level of Zr addition, it is

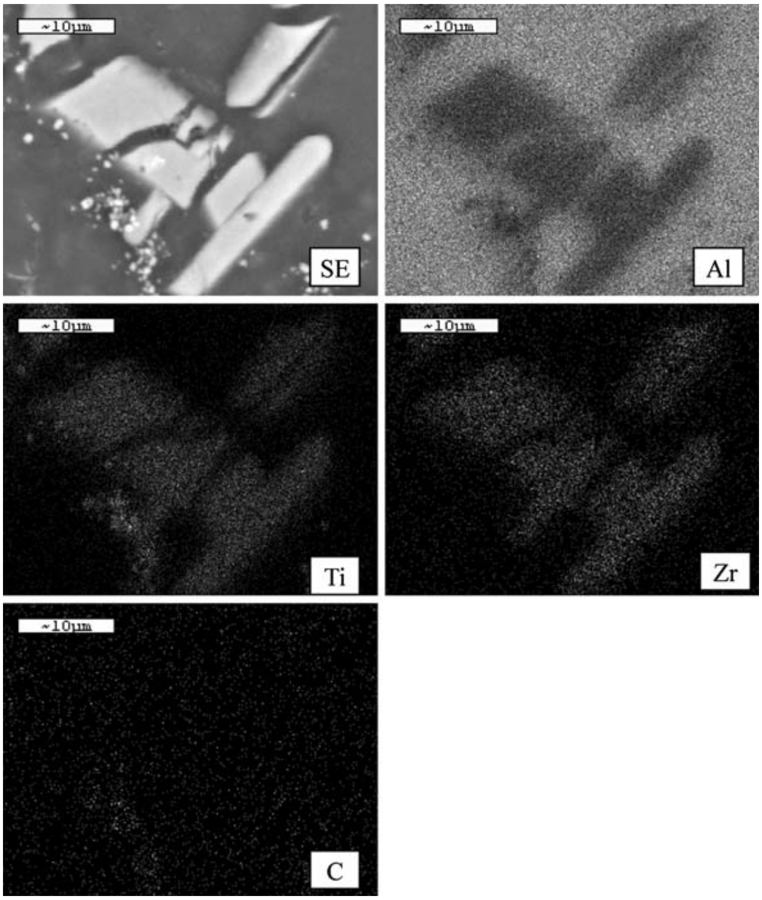


Fig. 9 EPMA analysis of Al–5Ti–0.4C + Zr

deduced that zirconium substitution in this Ti transition layer may be mainly responsible for the poisoning of Al–Ti–C when the melting temperature is low and the amount of Zr is a little. After increasing the melting temperature and the concentration of Zr, some Zr will react with TiC phase which can seriously deteriorate the refinement efficiency of the Al–Ti–C master alloy. So when the temperature and the content of Zr are high, the poisoning effect is due to the interaction between Zr and both of $TiAl_3$ and TiC phases.

Conclusions

The following conclusions have been drawn regarding the influence of Zr on Grain-refining Efficiency of Al–Ti–C master alloy.

1. The grain refinement efficiency of Al–Ti–C master alloys can be poisoned by Zr and the poisoning effect is more obvious when the melting temperature is higher.
2. The reason for the poisoning effect may be that the interaction between Zr and TiC phase and the effect of Zr on the Ti transition layer.

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