Grain refining performance of Al–Ti($C_{0.7}$, $N_{0.3}$) master alloy and its effect on mechanical properties for commercial pure aluminium

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A new Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy with a uniform microstructure was successfully prepared by casting method. Grain refining test indicates that Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy exhibits an excellent grain refining performance on commercial pure aluminium and the average grain size of pure Al can be effectively refined to 130 µm from about 3000 µm after adding 0.1 wt.% Ti($C_{0.7}$, $N_{0.3}$) particles by Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy. The tensile strength and elongation are increased by about 20.5% from 55 to 66.3 and 14.9% from 39 to 44.8 due to the grain refinement by adding Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy. Compared with Al–5Ti–1B master alloy, Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy has a slightly better ability in improving the mechanical properties of pure aluminium due to the better grain refining performance.

1. Introduction: Grain refinement of Al and its alloys by addition of ultra-fine ceramic particles which can act as substrates for heterogeneous nucleation into melt is considered to be a very effective melt treatment way to achieve a fine equiaxed grain structure with improved mechanical properties, machinability and cosmetic properties [1–6]. Nowadays, Al–Ti–C and Al–Ti–B master alloys exhibit a good grain refining performance on pure Al and its alloys and some of them have been widely used in modern Al and its alloys industry. However, the intrinsic instability of TiC particles in aluminium melt result in the serious fading behaviour and limit the further development of Al–Ti–C master alloys [7]. TiB_2 particles in Al–Ti–B master alloys are fairly coarse and have a tendency to agglomerate and precipitate, reducing the grain refining efficiency and leading to many problems such as porosity and streak in aluminium foils, scratch-like linear surface defects in litho and bright-anodised sheet and internal cracking in extrusion billets [8–10]. In addition, Al–Ti–B master alloys have obvious fading behaviour due to the poisoning effect of some elements such as Zr, Cr, V [7, 11] etc. Therefore, it is necessary to find a new kind of grain refiners for pure Al and its alloys.

Transition metal carbides and nitrides have attracted increasing attention because of their specific physical and chemical properties such as high melting point, high hardness, low density, low coefficient of thermal expansion, good electrical and thermal conductivity as well as high chemical and thermal stability [12]. Moreover, they have been widely used in many fields such as cutting tools, advanced structure materials, catalysts, electric devices [12] etc. Recently, numerous investigations have indicated that transition metal carbides and nitrides can act as an effective grain refiners for cast irons, steels and Al and its alloys [3, 12, 13]. The addition of transition metal carbides and nitrides can significantly enhance the comprehensive mechanical properties and physical properties due to the grain refinement and sediment reinforcement. In the present Letter, a new Al–Ti($C_{0.7}$, $N_{0.3}$) master alloy was successfully prepared by casting method. Moreover, the grain refining performance of the prepared Al–Ti($C_{0.7}$, $N_{0.3}$) master alloy and its effect on mechanical properties of commercial pure aluminium were also studied.

2. Experimental methods: Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy was prepared by pure Al powder (99.7 wt.% in purity, ≤75 µm), commercial pure aluminium ingots (99.7 wt.% in purity) and homemade Ti($C_{0.7}$, $N_{0.3}$) powder (≤1.5 µm) using casting method in an electrical resistance furnace. First, Al powder and Ti($C_{0.7}$,$N_{0.3}$) particles in definite proportion were mixed by ball milling for 5 h, and then were hot-pressed into a cylindrical compact using a graphite die at 550 °C for 30 min under a pressure of 60–65 MPa in a vacuum atmosphere. Second, about 300 g pure Al ingot was melted in a graphite crucible using an electrical resistance furnace at 1100 °C. Subsequently, the cylindrical compact wrapped by Al foil was charged into the molten Al melt and held at the temperature until the compact was melted. Moreover, then the melt was stirred with a graphite stirrer for about 10 min to disperse the Ti($C_{0.7}$, $N_{0.3}$) ceramic particles uniformly in the Al matrix. Finally, the melt was poured into an iron mould pre-heated to 250 °C.

Grain refining tests were carried out by adding different Ti($C_{0.7}$, $N_{0.3}$) levels, 0.03, 0.05, 0.08 and 0.1 wt.%, and Al–5Ti–1B master alloy (0.1 wt.% Ti level) into the aluminium melt with the same procedures. At first, the aluminium ingots (99.7 wt.% in purity) were melted in a graphite crucible using an electrical resistance furnace at 720 ± 5 °C. Moreover, the Al–Ti($C_{0.7}$, $N_{0.3}$) master alloy or Al–5Ti–1B master alloy was added into the melt and stirred thoroughly. The melt was held for 5 min and then poured into a pre-heated (250 °C) KBI cylindrical steel mould (65 mm in diameter and 25 mm in height) on a fire brick. After solidification, the bottom surface of the refined samples in contact with the brick was ground and etched by a reagent [60% HCl + 30% HNO_3 + 5% hydrofluoric acid (HF) + 5% H_2O, vol.%]. The macrograph of each sample was taken by a digital camera and the average grain size was measured by the linear intercept method. Meanwhile, some of the melts were poured into an iron mould ($235 \times 35 \times 100\ mm^3$) pre-heated to 250 °C to gain tensile test bars after refining.

Mechanical properties of pure Al before and after refined by Al–Ti($C_{0.7}$, $N_{0.3}$) master alloy and Al–5Ti–1B master alloy were determined using a tensile testing machine (WDW-50E) with a cross-head speed of 2.0 mm/min at room temperature, according to the GB/T228-2002 standard. The tensile strength and elongation data of each alloy reported below are average values of three tensile specimens. Microstructure and phase analyses of the prepared Al–Ti ($C_{0.7}$,$N_{0.3}$) master alloy were investigated by using scanning electron microscopy (SEM, S-4800, Hitachi, Japan) equipped with an energy-dispersive spectrometer (EDS) and X-ray diffraction

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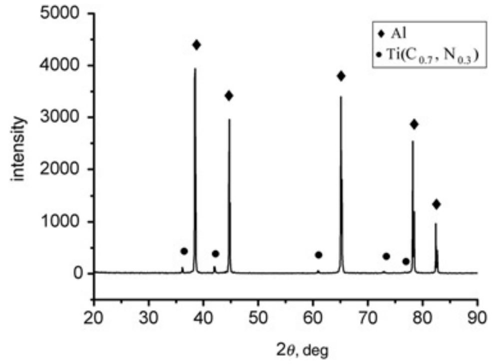

Fig. 1 *XRD pattern of Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy*

(XRD, DX-2700, Fangyuan, China). To study the grain refinement mechanism of Ti($C_{0.7}$, $N_{0.3}$) particles, the sample refined with 0.1 wt.% Ti($C_{0.7}$, $N_{0.3}$) particles was etched with a 0.5% vol.% HF solution after mechanical polishing and then analysed with an SEM equipped with an EDS.

3. Results and discussion: Fig. 1 shows the XRD pattern of the prepared Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy. It can be seen clearly that Ti($C_{0.7}$, $N_{0.3}$) is detected in the master alloy, which suggests that Ti($C_{0.7}$, $N_{0.3}$) particles were successfully added into Al melt by a hot-pressed cylindrical compact.

Fig. 2 shows the SEM images of the prepared Al–4.2 wt.% Ti ($C_{0.7}$, $N_{0.3}$) master alloy. It can be seen clearly that Ti($C_{0.7}$, $N_{0.3}$) particles are well distributed in the Al matrix as shown in (Fig. 2*a*). As illustrated in the magnified microstructure (Fig. 2*b*), Ti($C_{0.7}$, $N_{0.3}$) particles are disconnected with each other and dispersed uniformly in the Al matrix, which is beneficial for Ti($C_{0.7}$, $N_{0.3}$) particles to act as high efficient nucleating agent for α-Al.

Fig. 3 shows the macrostructures of commercial pure aluminium before and after refined with Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy and Al–5Ti–1B master alloy after 5 min holding. It was observed that the macrostructure of unrefined commercial pure aluminium (Fig. 3*a*) is composed of outer columnar grains and centric coarse equiaxed grains and its average grain size is about 3000 µm. Compared with the commercial pure aluminium without adding Ti ($C_{0.7}$, $N_{0.3}$) grain refiner (Fig. 3*a*), the macrostructures of commercial pure aluminium refined with different contents Ti($C_{0.7}$, $N_{0.3}$) grain refiner (Figs. 3*b–e*) and Al–5Ti–1B master alloy (Fig. 3*f*) exhibit a finer equiaxed grains and their average grain sizes are about 485, 215, 142, 130 and 154 µm. Compared with Al–5Ti–1B master alloy, Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy exhibits a slightly better grain refining performance. It also can be seen that the effect of grain refinement is more significant with the increase of Ti($C_{0.7}$, $N_{0.3}$) particles as shown in Figs. 3*b–d*. Moreover, the increase of grain refining efficiency is most efficient at low content of Ti($C_{0.7}$, $N_{0.3}$) particles (about 0.08 wt.%), whereas further increase of the Ti($C_{0.7}$, $N_{0.3}$) particles up to 0.1 wt.% does not lead to the further significant improvement of grain refinement.

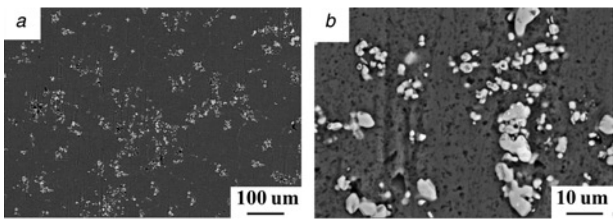

Fig. 2 *Microstructure of Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy*
a Low magnification of the Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy
b High magnification of the Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy

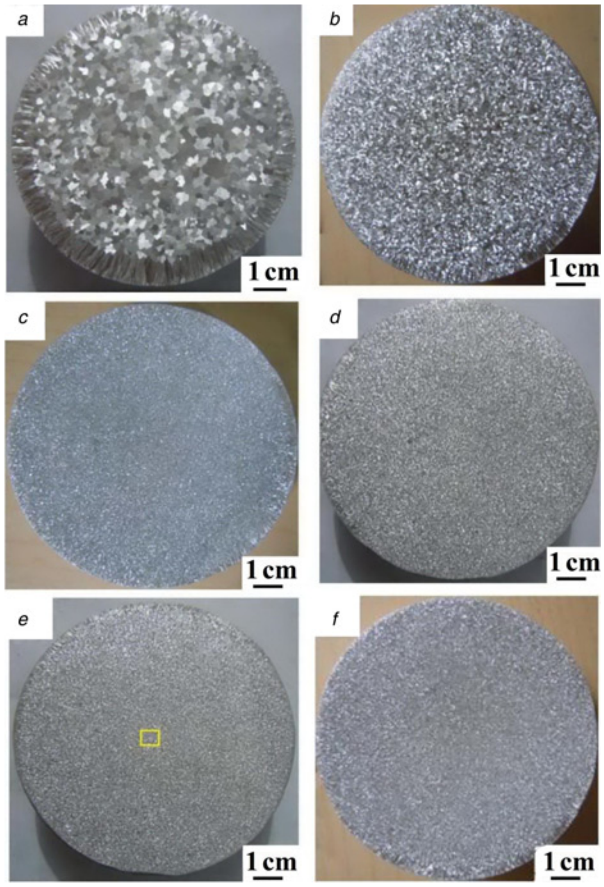

Fig. 3 *Macrostructure of pure Al before and after refined with different grain refiners*
a Pure Al
b–e Refined with 0.03, 0.05, 0.08 and 0.1% Ti($C_{0.7}$, $N_{0.3}$) particles by Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy
f Refined with Al–5Ti–1B (0.1 wt.% Ti)

Notably, with 0.1 wt.% addition of Ti($C_{0.7}$, $N_{0.3}$) particles, the average grain size of pure Al is only about 130 µm and the grains is homogeneous with a fine equiaxed grains as shown in Fig. 4.

It is well known that when master alloys are added into molten aluminium, the aluminium matrix will dissolve and release a large number of potential heterogeneous nuclei into the Al melt, which will nucleate α-Al during solidification. In this Letter,

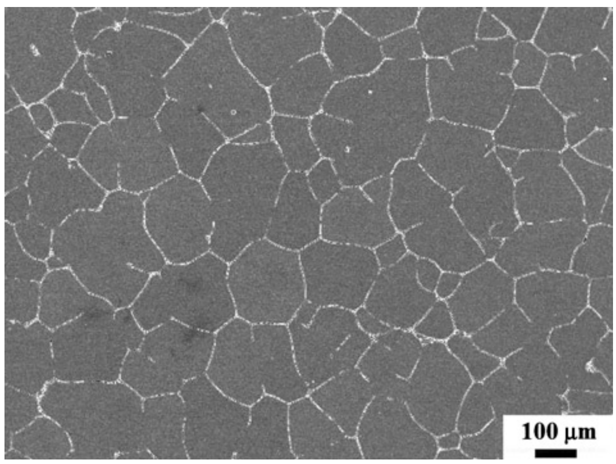

Fig. 4 *SEM image of pure Al refined with 0.1% Ti($C_{0.7}$, $N_{0.3}$) particles by Al–4.2 wt.% Ti($C_{0.7}$, $N_{0.3}$) master alloy*

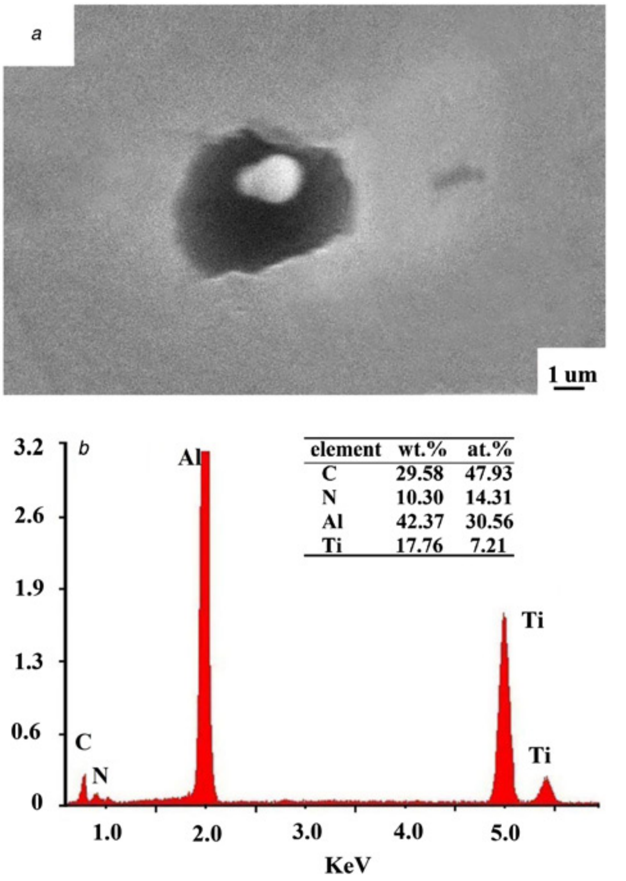

Fig. 5 *SEM image and the analysis results*
a SEM image
b EDS results of the crystallisation centre in pure Al grain refined with 0.1% $Ti(C_{0.7}, N_{0.3})$ particles by Al–$Ti(C_{0.7}, N_{0.3})$ master alloy

Al–4.2 wt.% $Ti(C_{0.7}, N_{0.3})$ master alloy will dissolve and release a large number of $Ti(C_{0.7}, N_{0.3})$ particles when it was added into the Al melt. The melting point of $Ti(C_{0.7}, N_{0.3})$ particles is much higher than that of aluminium and it has a good stability in the molten aluminium. Moreover, the crystal structures of $Ti(C_{0.7}, N_{0.3})$ (a = 0.4297 nm) and α-Al (a = 0.4049 nm) are both face centred cubic type structure making the nucleation of α-Al on $Ti(C_{0.7}, N_{0.3})$ particles favourable. Therefore, it provides original heterogeneous nuclei for α-Al to nucleate and grow. According to the planar disregistry model of two-dimensional lattices proposed by Bramfitt, the lattice disregistry (δ) between $Ti(C_{0.7}, N_{0.3})$ and α-Al is 5.77% [14], which much less than the critical value (15%) for the nucleant particles to act as heterogeneous nuclei [14]. Hence, $Ti(C_{0.7}, N_{0.3})$ particles can act as the efficient heterogeneous nuclei for pure Al. Meanwhile, $Ti(C_{0.7}, N_{0.3})$ keeps a good coherent relation with α-Al crystal due to the small lattice disregistry and this makes it more easy for aluminium atoms to nucleate directly on $Ti(C_{0.7}, N_{0.3})$ particles due to the small strain energy. On the other hand, the nitrogen element can improve the wettability effectively between the $Ti(C_{0.7}, N_{0.3})$ and Al and enhance the structural stability to some extent [12, 15], which eventually result in the high grain refining performance on pure aluminium. Finally, the uniform dispersion of $Ti(C_{0.7}, N_{0.3})$ particles in Al–4.2 wt.% $Ti(C_{0.7}, N_{0.3})$ master alloy and multilayer absorption [12] between $Ti(C_{0.7}, N_{0.3})$ particles and Al atoms may make an extra contribution to the high grain refinement performance. Therefore, the excellent grain refining efficiency on pure aluminium is obtained.

Fig. 5 shows the SEM image and the analysis results of the crystallisation centre in pure Al refined with 0.1 wt.% $Ti(C_{0.7}, N_{0.3})$ particles. It can be seen that one particle about 1.5 μm in size located at the grain centre as shown in Fig. 5*a*. The EDS analysis of this particle (Fig. 5*b*) indicates that the particle mainly contain Al, Ti, C and N elements, while Al is from the matrix. It is indicated that the particle at the grain centre is $Ti(C_{0.7}, N_{0.3})$, which further confirmed that $Ti(C_{0.7}, N_{0.3})$ particles are an efficient heterogeneous nuclei for commercial pure aluminium.

The mechanical properties of commercial pure aluminium before and after refined with $Ti(C_{0.7}, N_{0.3})$ particles and Al–5Ti–1B master alloy at room temperature after holding 5 min are also investigated in this Letter, and the average value of three samples is shown in Table 1. The tensile strength and elongation of the unrefined pure aluminium are 55 MPa and 39%. After the addition of Al–5Ti–1B master alloy (0.1 wt.% Ti) and 0.1 wt.% $Ti(C_{0.7}, N_{0.3})$ particles, the tensile strength and elongation are increased to 65.2 and 66.3 MPa, 43.5 and 44.8%, respectively. Compared with pure aluminium, the tensile strength and elongation are increased by about 18.5 and 20.5%, 11.5 and 14.9%, respectively. The results indicate that the grain refinement has resulted in a significant enhancement both in tensile strength and elongation of commercial pure aluminium. It is also indicated that Al–4.2 wt.% $Ti(C_{0.7}, N_{0.3})$ master alloy has a slightly better ability in improving the mechanical properties of pure aluminium than Al–5Ti–1B master alloy due to the better grain refining performance. Moreover, the successful usage of Al–4.2 wt.% $Ti(C_{0.7}, N_{0.3})$ master alloy offered a new direction to fabricate efficient grain refiner for Al and its alloys.

Table 1 Mechanical properties of pure Al before and after refined by Al–5Ti–1B and $Ti(C_{0.7}, N_{0.3})$ particles master alloy at room temperature

Specimens	Tensile strength, MPa	Elongation, %
pure Al	55	39
pure Al + Al–5Ti–1B	65.2	43.5
pure Al + 0.1 wt.% $Ti(C_{0.7}, N_{0.3})$	66.3	44.8

4. Conclusion: A new Al–4.2 wt.% $Ti(C_{0.7}, N_{0.3})$ master alloy with a uniform microstructure was successfully prepared by casting method. It is shown that Al–4.2 wt.% $Ti(C_{0.7}, N_{0.3})$ master alloy exhibits an excellent grain refining performance and the grain refinement effect is more significant with the increase of $Ti(C_{0.7}, N_{0.3})$ content. With addition of 0.1 wt.% $Ti(C_{0.7}, N_{0.3})$ particles by Al–4.2 wt.% $Ti(C_{0.7}, N_{0.3})$ master alloy, the average grain size of α-Al can be effectively refined to 130 μm from about 3000 μm and the tensile strength and elongation are increased by about 20.5 and 14.9% due to the grain refinement. It is also considered that the $Ti(C_{0.7}, N_{0.3})$ particles found at the grain centre are the effective nucleating substrates for α-Al during solidification, which accounts for the good grain refining performance of Al–4.2 wt.% $Ti(C_{0.7}, N_{0.3})$ master alloy. Compared with Al–5Ti–1B master alloy, Al–4.2 wt.% $Ti(C_{0.7}, N_{0.3})$ master alloy has a slightly better ability in improving the mechanical properties of pure aluminium due to the better grain refining performance.

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