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Crystallography and refining mechanism of (Ti, B)-contained salts in pure aluminum

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Abstract: It is shown from experiment that the pure B contained salt exhibits little refining effect, while the pure Ti contained salt, especially the salt containing 5Ti/1B, shows obvious refining effect on the pure aluminum. Crystallographic study indicates that Al_3Ti particle is a more suitable nucleation site for the aluminum matrix than (Ti, Al)B_2 type particles (TiB_2, AlB_2 and (Ti,Al)B_2), because there exist more coherent planes with aluminum matrix in the former. Thermodynamics estimation, X-ray diffraction (XRD) and SEM detection show that the refining mechanism of (Ti, B)-contained refiners is mainly contributed to the heterogeneous nuclei of fine Al_3Ti particles dispersed in the melting, which comes from the reaction between the Ti and aluminum. (Al, Ti)B_2 type particle shows little or no direct refining effect, but it will reduce the size of Al_3Ti since the Al_3Ti nucleates and grows along the (Al, Ti)B_2 type particle interface.

Key words: pure aluminum; crystallography; refining mechanism; microstructure

1 Introduction

Although techniques as electromagnetic stirring[1], supersonic vibrating[2] and rapid solidifying[3] have been developed, grain refiner is still the most useful method in improving the behavior of cast aluminum and its alloys as it is convenient and economical. The most commonly used commercial refiners are based on the Al-Ti-B system[4−7]. Up to now, many researches have discussed the refining mechanism of Al-Ti-B system, which contains (Al, Ti)B_2 type and Al_3Ti particles in melting. However, the role of (Al, Ti)B_2 type and Al_3Ti particles on refining aluminum is still unclear, and contrary arguments commonly exist[5, 7, 8−12]. Some authors persisted that the Al_3Ti particles should be the heterogeneous nucleation sites as they are a pro-peritectic phase, which is normally considered as the nucleation core during solidification, furthermore, it exhibits very good lattice matching with Al[8−12]. Others considered that (Al,Ti)B_2 particles are the nucleation sites as they are more stable in aluminum melts[5−7].

According to classic solidification theory, the interfacial energy between particles and solution phase heavily affects the nucleating potency of the particle. In order to minimize the interfacial energy, maximum atom matching at the interface is necessary. So, further study of the crystallography between the nucleation particle and Al matrix in grain refinement is important as well.

In this work, the effect of salts containing Ti and B elements on the pure aluminum was studied. Meanwhile, the refining mechanism was also investigated by XRD, SEM-EDAX, thermodynamics calculation and crystallography determination.

2 Experimental

Commercially pure aluminum (≥99.9%) and pure K_2TiF_6 and KBF_4 salt (≥99.9%) were prepared as experimental material and refiners, respectively.

Pure aluminum was molten in Al_2O_3 crucible of resistant furnace at 750 ℃. A quantity of refiners were added to the molten aluminum. After manual stirring, slag removing and soaking for different time, molten aluminum was then cast into samples. Iron mold was used and preheated to 200 ℃ before casting[8−12].

Samples were cut along transversal section and at location of 20 mm apart from the ingot bottom, and then ground, polished and etched in 5 mL 40%HF+75 mL 38% HCl+25 mL 68%HNO_3 solution. Macrostructure was recorded by Nikon L150 Optical Microscope. D/MAX

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X-ray diffractometer and JSM-6700F scanning electron microscope were used to observe the crystal structure, morphology and constitution of the reacted particle, which would become the heterogeneous nuclei for α(Al) grain. Thermodynamic calculation and crystallography were used to investigate the refining mechanism of Ti and B in pure aluminum castings.

3 Results and discussion

3.1 Effect of (Ti, B)-contained salts on macrostructure of pure aluminum castings

Fig.1 shows the typical macrostructure of the samples refined by salt containing Ti or B element, which was held at 750 ℃ for 30 min after being added to the melting.

It is clear from Fig.1 that the macrostructure of ingots refined by salt containing Ti, especially the 5Ti1B mixed, is much finer than that without refiner, but the B contained salt has a little or no refining effect. This indicates that Ti contained salt, especially the 5Ti1B contained salt, is the more effective refiner for the aluminum.

3.2 Thermodynamic analysis on resultants in refined aluminum melting

The following reactions (1)−(3) can be listed when the salts containing Ti and B elements were added into aluminum melting:

$$Ti+3Al = TiAl_3 \tag{1}$$

$$Ti+2B = TiB_2 \tag{2}$$

or

$$Al, Ti+2B = (Al, Ti)B_2 \tag{3}$$

When refiners containing 0.2%Ti or 0.2%Ti+ 0.009%B were added into aluminum melting at 750 ℃, the changes in Gibbs energy ($\Delta G^{\Theta}_{750\,℃}$) of reactions (1)−(3) calculated according to Refs.[8, 12] are all negative. This means reactions (1)−(3) can proceed spontaneously from left to right below 750 ℃, that is to say, the resultants of Al_3Ti and (Ti, Al)B_2 or TiB_2 are stable in molten aluminum below 750 ℃. It can be found from the XRD pattern of Al-4.12Ti-1.24B master alloy shown in Fig.2 that, there exist three phases, i.e., FCC structure of matrix α(Al) (a=0.404 94 nm), tetragonal structure of Al_3Ti particle (a=0.384 9 nm, c=0.861 0 nm) and hexagonal structure of both (Ti, Al) B_2 and TiB_2 (a = 0.302 8 nm, c= 0.322 8 nm).

3.3 Crystallographic study on atom match among Al_3Ti, (Ti, Al)B_2 type particle and aluminum matrix

Figs.3−5 show the atom configuration for Al, Al_3Ti and (Ti, Al)B_2 type phases. In order to present concise and intuitive sketches, all the circle diameters were drawn in the proportion of atomic diameters, while the distances between the atoms were enlarged by 4 times in relation to the atomic diameter.

Each unit cell of aluminum matrix contains four Al atoms and each of Al_3Ti contains two Ti atoms and six Al atoms. All the TiB2, AlB_2 and (Ti, Al)B_2 exhibit the same crystal structure and each hexagonal unit cell possesses three Ti or Al atoms and six B atoms. The atom positions in FCC unit, tetragonal unit and 1/3 the hexagonal cell are all listed in Table 1[13]. The mismatching of atoms in the close or nearly close packed directions located in possible coherent planes between Al_3Ti, (Ti, Al)B_2 and Al phases are calculated and listed in Table 2 and Table 3, respectively.

If atomic mismatching between directions is less than 5%, the related planes are supposed to coherent with each other. It is clear from Table 2 and Table 3 that there

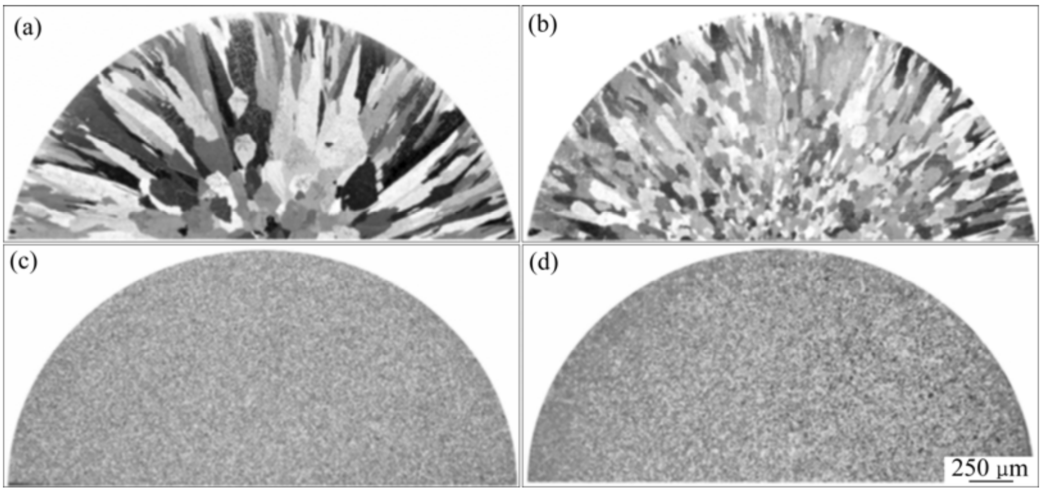

Fig.1 Typical macrostructures of pure aluminum castings with different mass fractions of Ti/B (30 min holding): (a) Without refiner; (b) 0.2%B; (c) 0.2% Ti+0.009%B; (d) 0.2%Ti

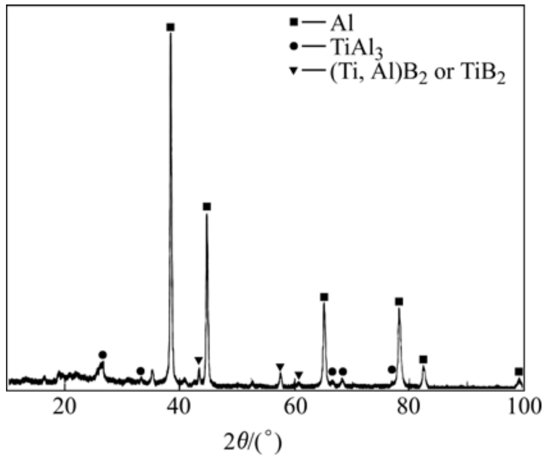

Fig.2 XRD pattern of Al-4.12Ti-1.24B master alloy

are three coherent planes between aluminum matrix and Al_3Ti particle. These coherent planes are as follows: $(012)_{Al}//(011)_{Al_3Ti}$[14], $[\bar{1}00]_{Al}//[\bar{1}00]_{Al_3Ti}$[14]. $(111)_{Al}//(112)_{Al_3Ti}$[15], $[\bar{1}10]_{Al}//[\bar{1}10]_{Al_3Ti}$[15] and $(001)_{Al}//(001)_{Al_3Ti}$[15], $[010]_{Al}//[010]_{Al_3Ti}$[15]. However, there are only one partially coherent plane between aluminum matrix and (Ti, Al)B_2 particle, that is, $(111)_{Al}//(0001)_{(Al,Ti)B_2}$[16], $[\bar{1}10]_{Al}//[\bar{1}2\bar{1}0]_{(Ti,Al)B_2}$ [16]. ZHANG et al[17] has examined the crystallographic features of nucleating substrates and Al matrix in terms of the edge-to-edge matching model and presented many orientation relationships for TiC, Al_3Ti, TiB_2, AlB_2 substrates and Al matrix. However, some orientation relationships have not been verified by experiments, especially the model can’t actually explain the different nucleating potency of TiC, TiB_2, AlB_2 and Al_3Ti substrates in aluminum melting. This is because that the inter-atomic spacing misfit along most possible matching directions and inter-planar spacing along most possible matching planes between TiC, TiB_2, AlB_2, Al_3Ti substrates and aluminum matrix do not obviously differ from each other, while the actual refining potency of the TiC, TiB_2, AlB_2, Al_3Ti substrates in the aluminum melting varies greatly from each other[8−11].

3.4 Morphology of Al_3Ti, (Ti, Al)B_2 type in aluminum castings

According to former results and discussion, it can be deduced that the Al_3Ti particle is superior to the (Ti,Al)B_2 type particle as a heterogeneous nuclei for the aluminum matrix because the Al_3Ti particle possesses more orientation relationships and the relative less misfit with aluminum matrix than the (Ti, Al)B_2 type particle. This can be ascertained from Fig.1, while the (Ti, Al)B_2 type particle is pushed to grain boundary during the solidification (Figs.6(a, b). However, if there does not exist Al_3Ti particle in the aluminum melting, the (Ti, Al)B_2 type particle can be taken as heterogeneous

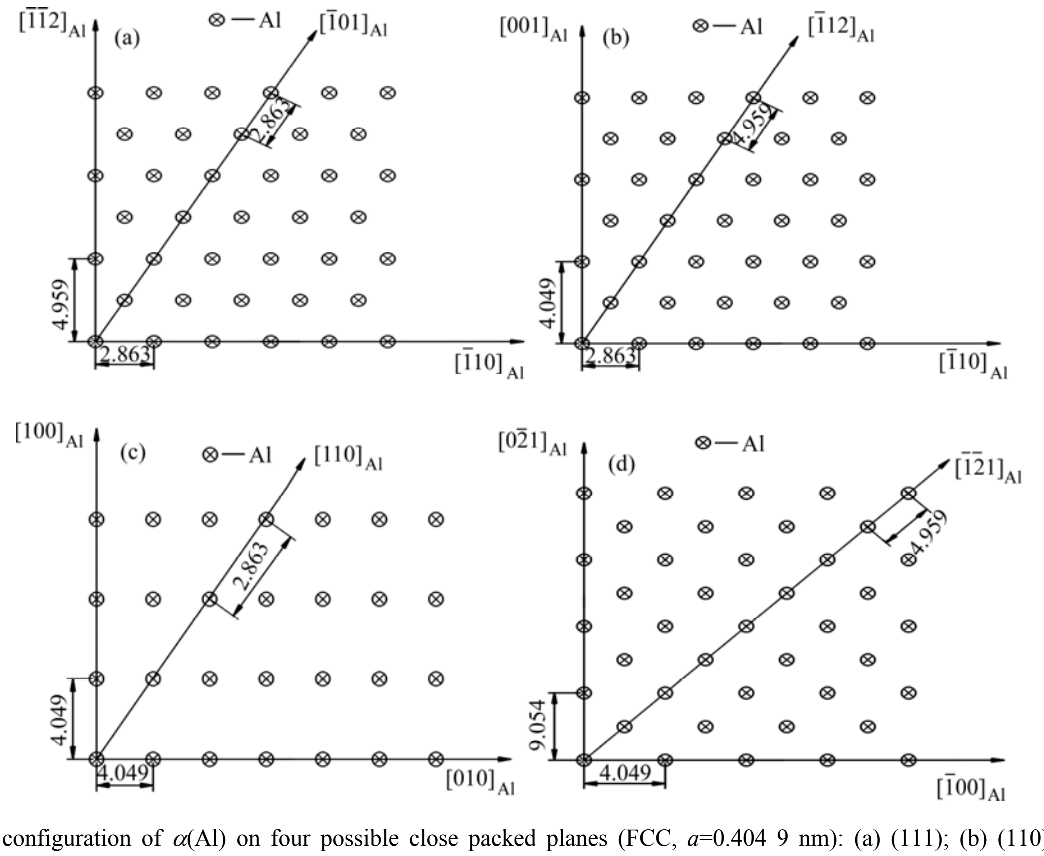

Fig.3 Atom configuration of α(Al) on four possible close packed planes (FCC, a=0.404 9 nm): (a) (111); (b) (110); (c) (001); (d) (012)

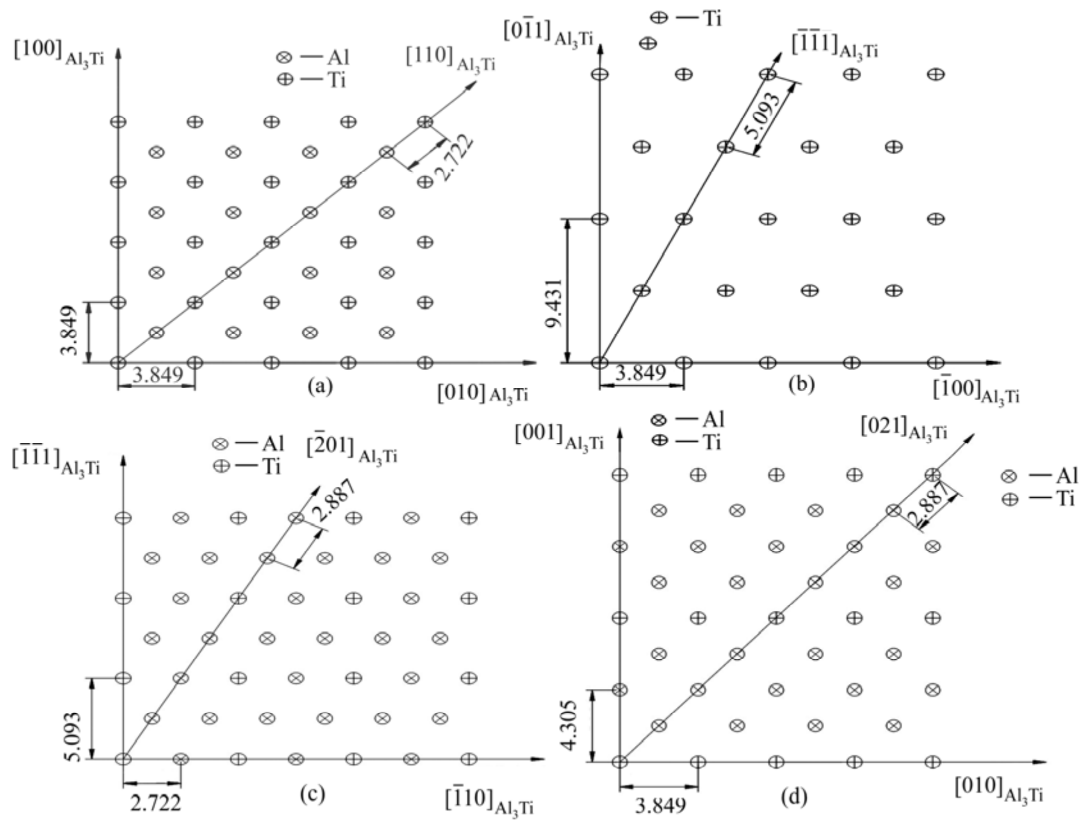

Fig.4 Atom configuration of Al_3Ti on four possible close packed planes (Tetragonal, a=0.384 9 nm, c=861 0 nm): (a) (001); (b) (011); (c) (112); (d) (100)

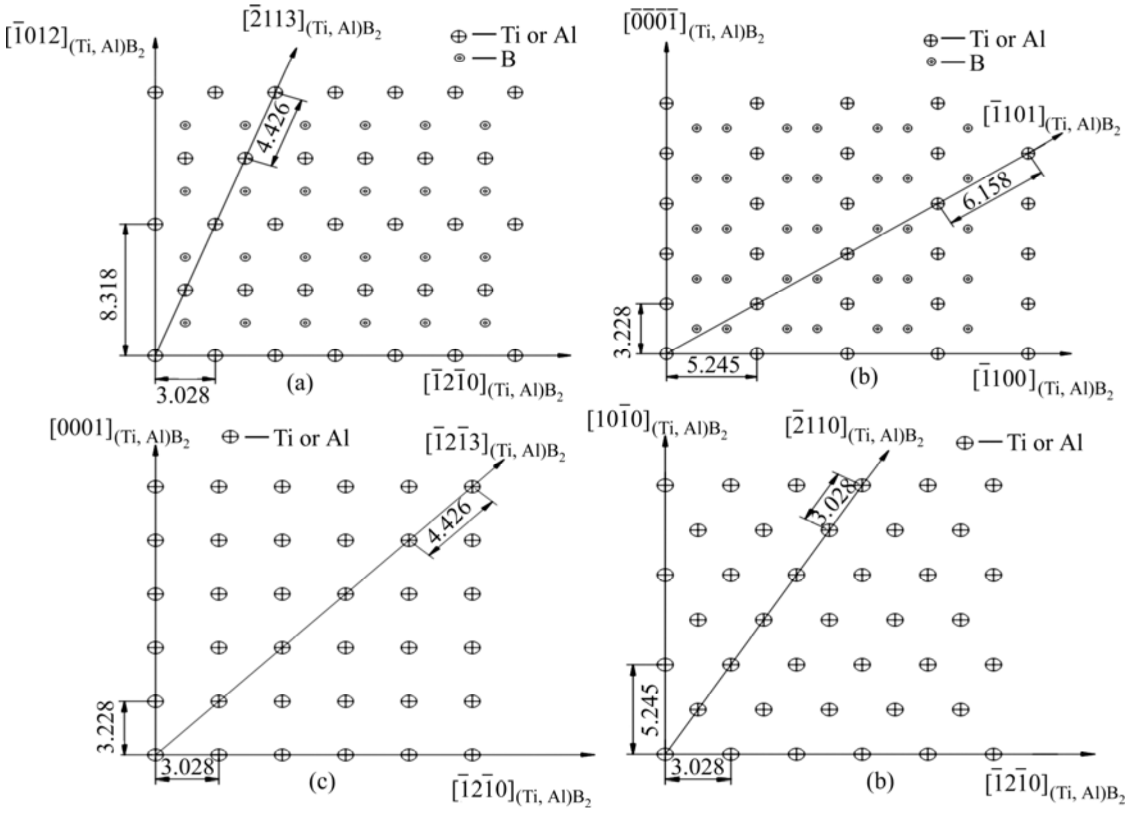

Fig.5 Atom configuration of (Ti, Al) B_2 on four possible close packed planes (Hexagonal, a=0.302 8 nm, c=0.322 8 nm): (a) $(10\bar{1}1)$; (b) $(11\bar{2}0)$; (c) $(10\bar{1}0)$; (d) (0001)

Table 1 Structure parameters of Al, Al_3Ti and (Ti, Al)B_2 phases

Phase	Structure	Space group	Atom position
Al	FCC	*Fm*3*m*	$(0, 0, 0)_{Al}$; $(0.5, 0.5, 0)_{Al}$; $(0, 0.5, 0.5)_{Al}$; $(0.5, 0, 0.5)_{Al}$
Al_3Ti	Tetragonal	*I*4/*mmm*	$(0, 0, 0)_{Ti}$; $(0.5, 0.5, 0.5)_{Ti}$; $(0, 0, 0.5)_{Al}$; $(0, 0.5, 0.25)_{Al}$; $(0.5, 0, 0.25)_{Al}$; $(0.5, 0.5, 1)_{Al}$; $(0.5, 1, 0.75)_{Al}$; $(1, 0.5, 0.75)_{Al}$
(Ti, Al)B_2	Hexagonal	*P*6 *mmm*	$(0, 0, 0)_{Ti\ or\ Al}$; $(1/3, 2/3, 1/2)_B$; $(2/3, 1/3, 1/2)_B$

Table 2 Possible coherent planes between Al and Al_3Ti phases (%)

$(111)_{Al}//(112)_{Al_3Ti}$		$(001)_{Al}//(001)_{Al_3Ti}$		$(012)_{Al}//(011)_{Al_3Ti}$	
$[\bar{1}10]_{Al}//[\bar{1}10]_{Al_3Ti}$	$[\bar{1}\bar{1}2]_{Al}//[\bar{1}\bar{1}1]_{Al_3Ti}$	$[010]_{Al}//[010]_{Al_3Ti}$	$[100]_{Al}//[100]_{Al_3Ti}$	$[\bar{1}00]_{Al}//[\bar{1}00]_{Al_3Ti}$	$[0\bar{2}1]_{Al}//[0\bar{1}1]_{Al_3Ti}$
4.92	2.63	4.94	4.94	4.94	4.00

Table 3 Possible coherent planes between Al and (Ti, Al)B_2 phases (%)

$(111)_{Al}//(0001)_{(Ti,Al)B_2}$	
$[\bar{1}10]_{Al}//[\bar{1}2\bar{1}0]_{(Ti,Al)B_2}$	$[\bar{1}\bar{1}2]_{Al}//[10\bar{1}0]_{(Ti,Al)B_2}$
5.76	5.76

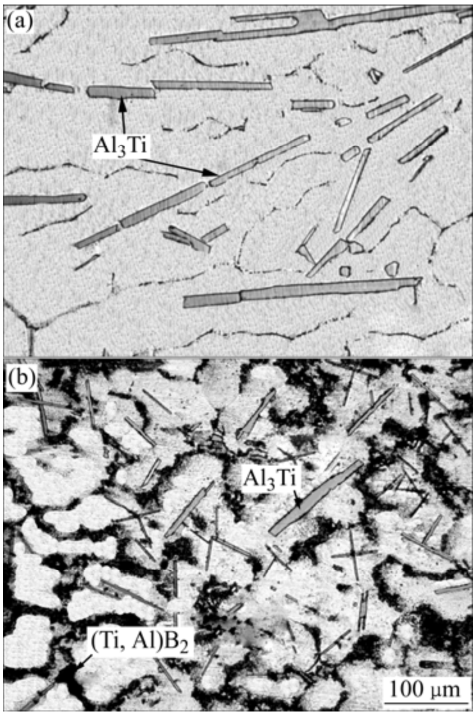

Fig.6 Typical microstructures of Al-4.12Ti-1.24B master alloy (Long bar in Figs.6(a, b) is Al_3Ti particle, and black strip in Fig.6(b) is (Ti, Al)B_2 type particle): (a) Al-4.3%Ti; (b) Al-4.12%Ti-1.24%B

nuclei for the aluminum matrix, and it may require lower temperature or larger under-cooling (see Fig.1).

Fig.7 shows the morphologies of heterogeneous nuclei in α(Al) grain. The compositions (mole fraction, %) of central particle in Fig.7(b) measured by SEM-EDAX is similar to the (Al, Ti)B_2 constitution. The difference of B content between measurement and calculation in (Ti, Al)B_2 constitution is mainly resulted from the limitation of SEM-EDAX. The area surrounding the central (Ti, Al) B_2 particle measured by SEM-EDAX is $TiAl_3$, and the outside is α(Al) grain. This phenomenon can be also found in Refs.[12, 18].

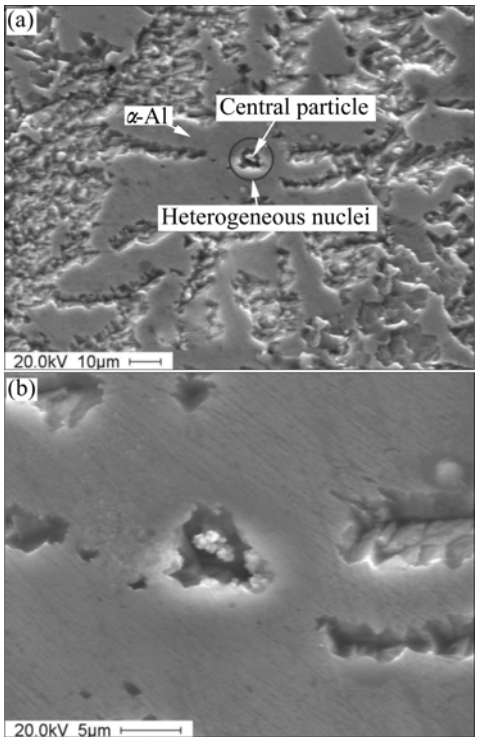

Fig.7 Morphologies of heterogeneous nuclei in pure aluminum refined with salts mixture containing 0.2% Ti+0.009% B

It is clear that the α(Al) nucleates at $TiAl_3$ particle, while $TiAl_3$ nucleates at (Ti, Al)B_2 type particle. So it can be concluded that the (Ti, Al)B_2 can refine $TiAl_3$ particles since its size is much smaller than that of $TiAl_3$ (This can be tested by comparing the size of long bar in Fig.6(a)and Fig.6(b)), and refine the α(Al) grain indirectly. That's why the pure B contained salt has a little or no refining effect on the pure aluminum. However, the salts mixture containing 5Ti1B exhibits better refining effect than the pure Ti contained salt (see Fig.1).

4 Conclusions

1) From crystallographic point of view, although Al_3Ti, TiB_2, AlB_2 and (Ti, Al)B_2 can be taken as effective heterogeneous nuclei, Al_3Ti is the best grain refiner for Al alloys.

2) When both (Al, Ti)B_2 type and Al_3Ti particles exist in the aluminum melting, only the Al_3Ti particle can be taken as effective nucleating site for the aluminum grain, so it can refine the aluminum castings. The (Al, Ti)B_2 type particle may be pushed into grain boundary and has a little or no refining effect, but it can reduce the size of Al_3Ti, since the Al_3Ti nucleates and grows along the (Al, Ti)B_2 type particle. That is to say, B atom also has refining effect on the pure aluminum when it is added simultaneously with Ti atom.

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