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EFFECTS OF HOLDING CONDITIONS ON MICROSTRUCTURE OF Al-5Ti-1B AND ITS REFINING EFFICIENCY ON Al-Cu ALLOY

A series of Al-5Ti-1B master alloys were obtained via fluoride salt process by holding them between 780°C and 880°C for 10-90 min. The influence of holding temperature and time during preparation on the microstructure and its refining performance were investigated by X-ray diffractometer, optical microscopy and scanning electron microscopy equipped with energy dispersive X-ray spectroscopy. The results indicated both the morphology and the distribution of TiB_2 and Al_3Ti were seriously affected by holding conditions. Inadequate TiB_2 particles were generated when holding time was short. However, Fe-containing impurity particles that aggregated along the matrix grain boundaries were found after the prolonged holding time. The refining and microhardness test results revealed that Al-5Ti-1B, the one held at 820°C for 30 min showed the optimum refining efficiency on Al-Cu alloy.

Keywords: Al-5Ti-1B; Holding condition; Microstructure; Refining efficiency.

1. Introduction

As a conventional grain refiner, Al-Ti-B master alloy is widely used in aluminium casting processing owing to its grain refinement efficiency [1,2]. The microstructure and mechanical performance of aluminum and its alloys can be enhanced significantly by the grain refinement which is achieved though adding the master alloy into the melt during casting process [3-6]. The Ti/ B ratios (mole ratio) of Al-Ti-B are generally kept in 3 and 5, while it is Al-5Ti-1B that is considered by the majority of researchers as the more efficient grain refiner [7]. Typically, Al_3Ti and TiB_2 particles that dispersed in Al matrix in various morphologies constitute the microstructure of Al-5Ti-1B, and act as the heterogeneous nucleation sites during solidification of aluminium. The morphology, size and distribution of the particles were thought to have strong effects on the grain refining characteristics of the master alloy [4,8-11]. Commonly, compared with other methods, fluoride salt process is preferentially accepted to manufacture commercial Al-5Ti-1B master alloy owing to its multitudinous advantages, such as low costing, better composition control and high cleanliness of molten alloy, et al [12].

It is worthwhile to note that there are some shortcomings in practice that have not been completely solved yet, for instance, insufficient reaction between the salts and Al melt, agglomeration of second-phase particles in a large range [13]. These problems are thought to be caused by processing conditions, which have a great impact on the morphology, size and dispersion of both Al_3Ti and TiB_2 and the refining performance of Al-5Ti-1B [14]. The sequence and rate of fluoride adding, stirring condition during holding and the grain refining performances of Al-Ti-B on aluminium alloy have been discussed in some previous investigations [8,15-18]. However, there is no unified view on the optimum holding condition (especially the temperature) to prepare Al-5Ti-1B when using the conventional halide salt route [19,20].

In this work, the preparation method was based on the series of reaction between halide salts and molten aluminum [12]. The effects of reaction temperature and holding time on the microstructure of Al-5Ti-1B were investigated in detail. Al-4.4 wt.% Cu alloy was chosen to act as the inoculation sample to illustrate grain refining efficiency of the master alloy. Meanwhile, the optimum processing parameters for the preparation of Al-5Ti-1B master alloy were discussed.

2. Experimental

The preparations of Al-5Ti-1B master alloy were performed in the laboratory on a 2000 g batch scale. The raw materials were fluoride salts (KBF_4 and K_2TiF_6) in commercial purity and electrolytic aluminum (99.8 wt.%). The details of experimental procedures are as follows: Firstly, the aluminium ingot was melted in a medium-frequency induction furnace which was

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precisely gauged by a digital thermocouple. Secondly, the two preheated salts that had been mixed in proportion with a Ti to B ratio of 5: 1, were added into the furnace immediately once the setting temperature was reached, and then the temperature was remained constant. Thirdly, residual salts were drawn out the molten surface by shutting off the electric power when holding time came to an end. Then, not until the spent salt was ladled out thoroughly did the molten alloy was poured into a stainless steel mould (Φ70 mm×100 mm) at 700°C and air-cooled to room temperature. Thus Al-5Ti-1B master alloys which were held between 780°C and 880°C for 10 to 90 min were obtained. Similar to what does in industrial practice, the electromagnetic stirring was employed during in the whole holding processes. In order to avoid the interference caused by multiple process parameters, only one of which was varied in each set of experiment at a time. The specifications of production parameters were showed in Table 1.

TABLE 1

Al-5Ti-1B master alloys prepared in different holding conditions

Alloy no.	1	2	3	4	5	6	7	8	9
Reaction temperature (°C)	780	800	820	840	860	880	820	820	820
Holding time (min)	30	30	30	30	30	30	10	60	90

The grain refining campaigns were implemented to evaluate the grain refining efficiencies of these experimental Al-5Ti-1B master alloys. 1000 g Al-Cu alloy was melted in induction furnace and the temperature was maintained at 700°C. Al-5Ti-1B with the weight percent of 0.3% was added into the furnace. The molten alloy was held for 60 s after inoculation, and then was solidified. The uninoculated sample was also prepared in order to identify the original grain size and morphology of Al-Cu alloy.

The microstructure of experimental Al-5Ti-1B was characterized by a FEI Quanta-200 scanning electron microscope (SEM) equipped with energy disperse X-ray spectroscopy (EDX), Rigaku D/ Max 2500 X-ray diffractometer (XRD) was employed to identify the phase constituents in Al-5Ti-1B system. Specimen preparation for SEM analysis involved fine mechanical polishing for the identification and characterization of the morphology and distribution of the secondary phases, whereas the grain and solidification structures of Al-Cu samples were photographed for visual assessment by Olympus DSX 500 optical microscope (OM) in polarization mode after electrolytic etching of the specimens using Barker's reagent. Five different locations in the center of each inoculated sample were measured by using OLYCIA m3 metallographic image analysis software, and the average grain size was measured. Furthermore, microhardness of Al-Cu sample was measured on a Vickers hardness tester to assist in explain the effect of grain refinement of the experimental Al-5Ti-1B. The testing load and the holding time were 0.98 N and 10 s, respectively, and the hardness value of each sample was the average result of 10 test points.

3. Results and discussion

3.1. The microstructure of Al-5Ti-1B

The XRD results are illustrated in Fig. 1, which indicated that experimental alloy 1-9 were consisted of phases such as α-Al, Al_3Ti and TiB_2. There is no clear difference between these patterns excepting for the more obvious peaks of Al_3Ti in alloy 3-6, this might be attributed to the more sufficient reaction between fluoride salt and melt metals in higher superheating temperature condition. It is interesting to note that alloy 8 and 9 prepared after a longer holding time exhibit weaker diffraction peaks of both Al_3Ti and TiB_2 compared with other alloys.

The SEM microstructural features of experimental alloys labeled as 1-9 are illustrated in (Figs. 1,2), in which the Al_3Ti and TiB_2 particles were marked by arrows. It can be observed that Al_3Ti particles in alloy 1 and 2 were block-like, whereas TiB_2 phases were in the morphology of aggregating along Al grain boundaries (Fig. 2a,b).

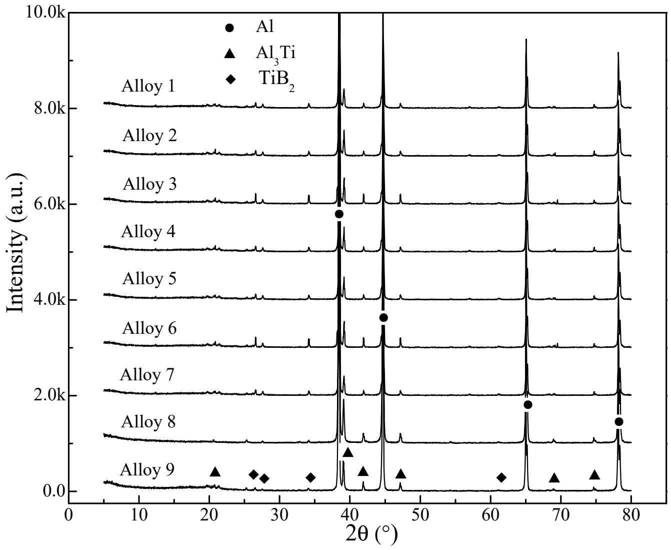

Fig. 1. XRD patterns of experimental Al-5Ti-1B alloys

Al_3Ti particles that exhibited roughly blocky morphology in alloys 3 and 4 (Fig. 2c,d) were dispersed more homogeneous, and the size of which presented a tendency of increasing. The TiB_2 particles, on the other hand, evolved from the state of aggregating at matrix grain boundaries to the uniform and balanced dispersion gradually. It can be noticed that though the two kinds of particles were dispersed uniformly when the temperature reached up to 860°C, the Al_3Ti particles with morphology of short rod were found (Fig. 2e). When the holding temperature increased to 880°C, some stick-like Al_3Ti particles that exhibited the state of parallel distribution along a particular direction were observed in Fig. 2f.

There were significant conversions of agglomerate TiB_2 particles to uniform dispersion when superheating temperature reached up to 800°C. It is the long-range diffusion of B atoms in Al matrix that was considered to play a vital role in distribution

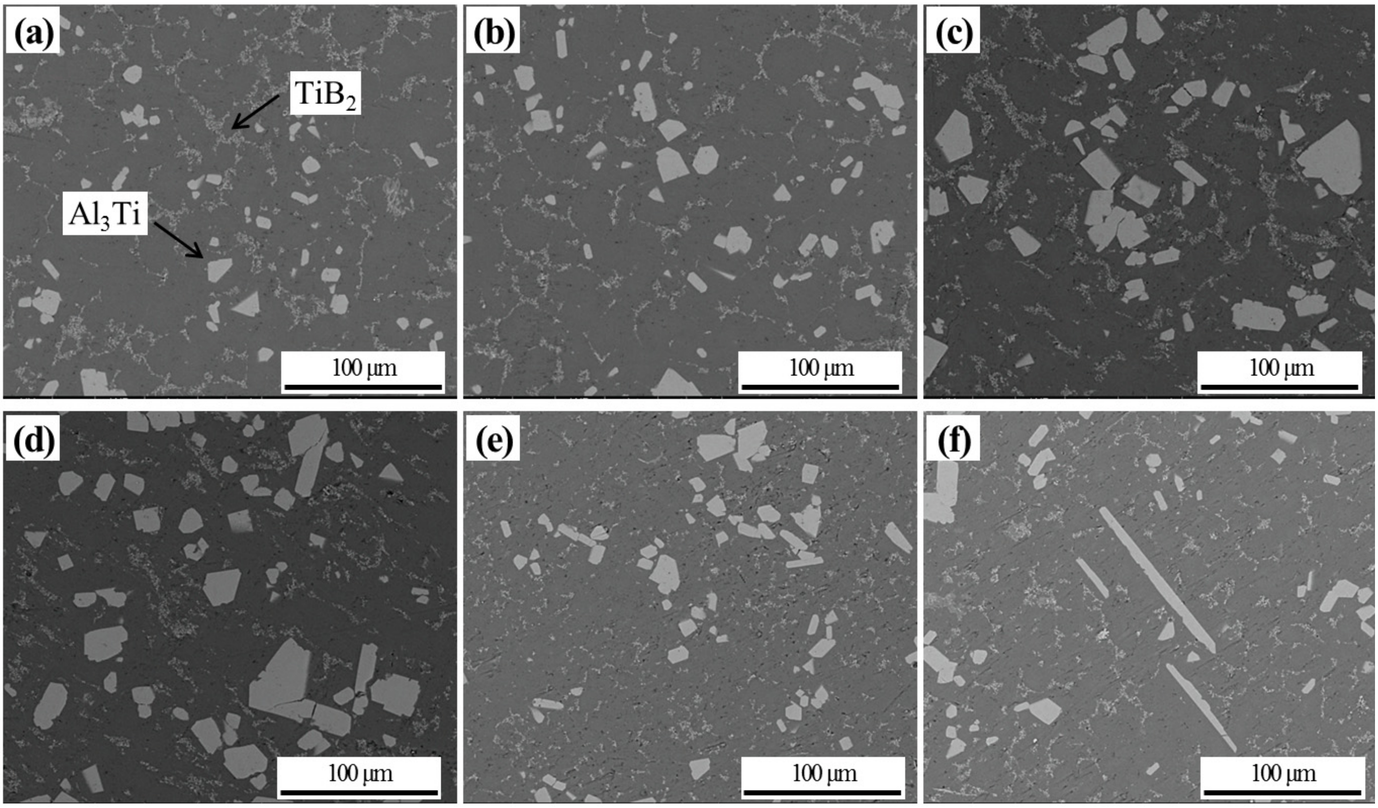

Fig. 2. SEM microstructural features of the experimental Al-5Ti-1B alloys: (a) alloy 1, (b) alloy 2, (c) alloy 3, (d) alloy 4, (e) alloy 5, (f) alloy 6

of TiB_2 particles [21]. The fine TiB_2 particles that possessed with large surface area/ volume ratio and high surface activity revealed a tendency of agglomeration to reduce the surface energy. While with increase of melt temperature, the aggregation along Al grain boundaries was weaken obviously, which was not only because of the influence of B atoms diffusion on boride particles dispersion had been weaken, but also owing to the decrease of melt viscosity [22].

One of the responses of reactions between the salts and Al melt was generating Al_3Ti particles. On the other hand, the large particles of Al_3Ti was inclined to dissolve, which was affected greatly by melt temperature [12,20]. Namely, disintegration of the large particles would be accelerated due to the increasing temperature, and tiny Al_3Ti might combine together to come into being stick-like even dendritic particle. There are some studies [4,23] suggested that the refining process would be significantly accelerated when Al_3Ti particles exhibited blocky morphology, which could be attributed to the multiple contact surface between the particles and molten Al. On the contrary, Al-Ti-B master alloy in which Al_3Ti particles were stick-like or dendritic, produced poor refining performance [12]. It is thought that blocky Al_3Ti particles and TiB_2 that exhibit uniform dispersion are optimal microstructure of Al-5Ti-1B master alloy, and the results in present work illustrated that 820°C and 840°C were the appropriate reaction temperature to prepare Al-5Ti-1B.

Alloy 7-9 in which the second phase particles, especially the TiB_2, were fewer than that in the rest of other alloys. This also could be demonstrated by the weak diffraction peaks in the XRD patterns (Fig. 1). In addition, residual fluoride salt that entrapped in alloy 7 was found (Fig. 3a). What cannot be ignored is that some kind of unknown particle aggregated along the matrix grain boundaries was emerged in alloy 8 and 9 (Fig. 3b,c). The XRD patterns have failed to reveal the diffraction peaks of the particle, maybe the content of this phase was too low and its weak diffraction peaks were covered by the strong peaks of other particles. Whereas the results of EDX (point analysis) showed that there was mainly contented Al, B and Fe in the phase, and the Fe level was increased with the prolonged holding time. Supposedly, the particle not only cannot be heterogeneous nuclei, but also bring harmful elements, for instance Fe, into Al melt during solidification.

Short holding time would result in the reactions between salts and molten Al were insufficient, which not only could lead to inadequate second phase particles, but also might result in residual fluoride salt contaminate the molten alloy. However, if the time was too long, Al_3Ti particles were too fine to exist in molten alloy stably, besides, once the cleanliness of molten system was controlled poorly, a long reaction time was likely to cause complex reactions between fluorides, impurities and the melt, which would conduce to generate Fe-containing impurity particles. Furthermore, longer holding time is regarded to result in excess oxidization of the melt and higher costs of the production.

3.2. Refining and microhardness test

Fig. 4 shows the microstructures of a series of Al-Cu samples that inoculated with experimental Al-5Ti-1B master alloys.

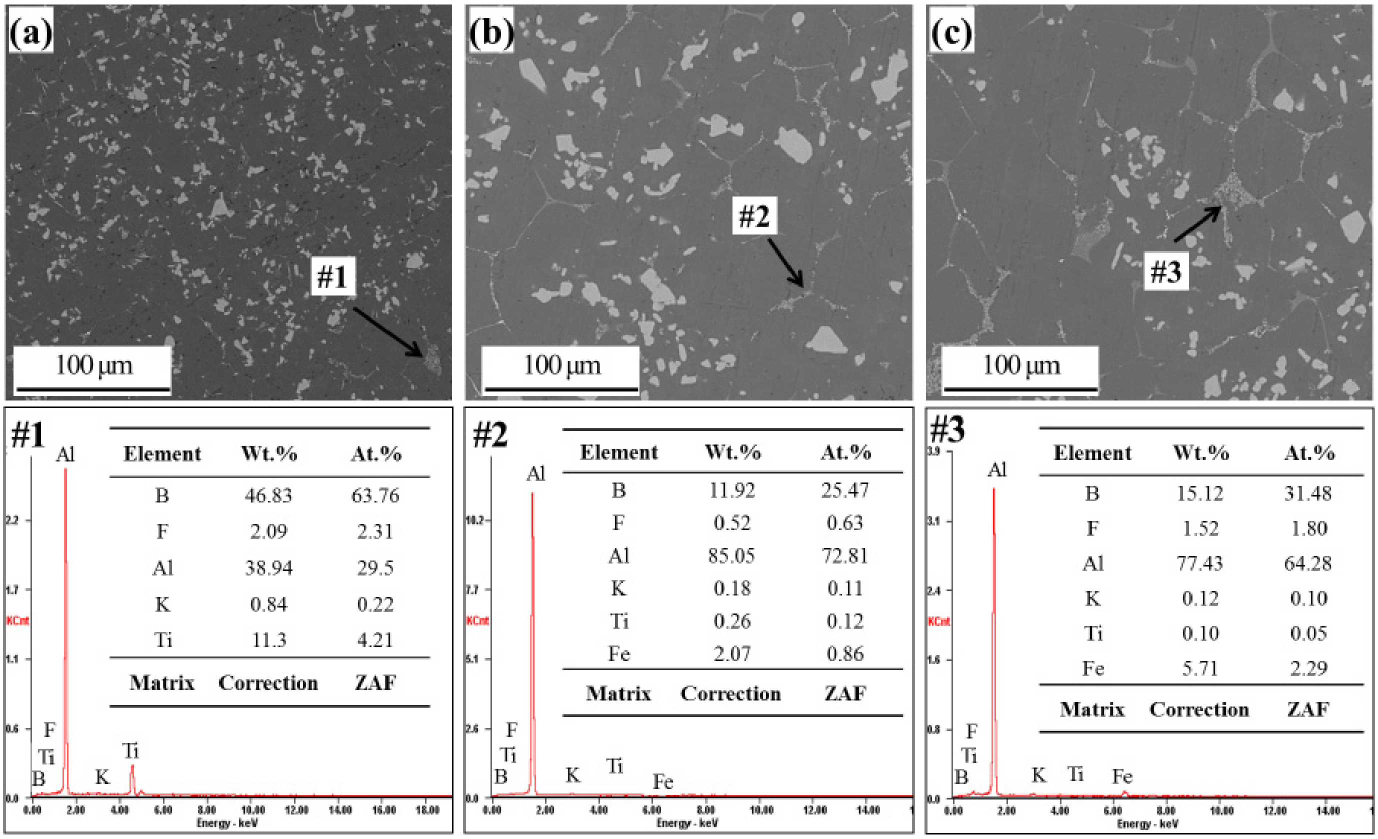

Fig. 3. The microstructure and EDX results of Al-5Ti-1B held at 820°C: (a) alloy 7, (b) alloy 8, (c) alloy 9

Fig. 4a shows a much coarser microstructure in the original Al-Cu sample. The inoculated samples labeled as 1-6 (which inoculated with experimental Al-5Ti-1B alloys 1-6, respectively.), on the other hand, were revealed the dendritic grain refinement with structural transformation from coarse morphology to the thin and small one (Fig. 4b-g). Fig. 5 summarizes the average grain size and the microhardness value of each Al-Cu specimen. It can be seen that the hardness value was negatively correlated with the grain size, approximatively. The original grain size and hardness value were about 227 μm and 28.5 HV, respectively. Compared to the rest of master alloys, alloy 3 and 4 could be appraised as optimal grain refiner for which have produced at least 25% discount on grain size of Al-Cu sample. There was no obvious decrease on the average grain size of sample 1 and 2 which still equipped with analogous coarse dendritic microstructure. Although sample 5 and 6 revealed micron dendrite grains with the average size of about 197 μm and 200 μm, respectively, both of them did not show the decrease of average grain size as much as sample 3 and 4.

Fig. 5 also shows that the microhardness of the inoculated samples was increased with different degrees, especially for samples 3, of which the hardness was larger than that of the rest samples. It could be surmised that alloy 3 had the greatest enhancement on the microhardness of Al-Cu sample, and the its refining efficiency was optimal.

From the refining results of experimental Al-5Ti-1B on the average grain size and microhardness of Al-Cu specimens, it can be seen that the grain refining efficiency of Al-5Ti-1B master alloys prepared at higher holding temperature (above 800°C) were much better than the ones held at low temperature. While, it should be noticed that when the holding temperature was above 840°C, the refining performances of the master alloy were degraded. The theories on the mechanism of grain refinement such as particle theory and heterogeneous nucleation theory [24] assume that Al_3Ti and TiB_2 are potent nuclei for the primary phase during in solidification. Therefore, the different refining results mentioned above, which can be contributed to the amount, morphology and distribution of Al_3Ti and TiB_2 particles presented in the Al-5Ti-1B system [4]. Alloy 3 revealed best refining efficiency on Al-Cu sample, in which Al_3Ti exhibited blocky morphology with an average size of about 30 μm and a uniform dispersion of TiB_2 particles. As for alloy 4, both microstructure and refining performance were similar to that of the former.

Some researchers [19] suggested that 800°C was the optimum holding temperature to produce Al-5Ti-1B (the experiment temperature interval was 50°C). According to their study of Al-Ti-B, when the holding temperature was above 800°C, not only the Ti level in the master alloy was tended to a decrease, but also the refining performance was deteriorated. The authors, however, believe that temperature interval was too wide to establishing the optimum reaction temperature convincingly. Moreover, the grain refining performance cannot be merely accounted by the Ti recovery. The present experimental results show that the superheat of melt was still insufficient under the holding condition of 800°C, which would result in the nonuniform distribution of TiB_2 particles. It was the Al-5Ti-1B held at 820°C and 840°C

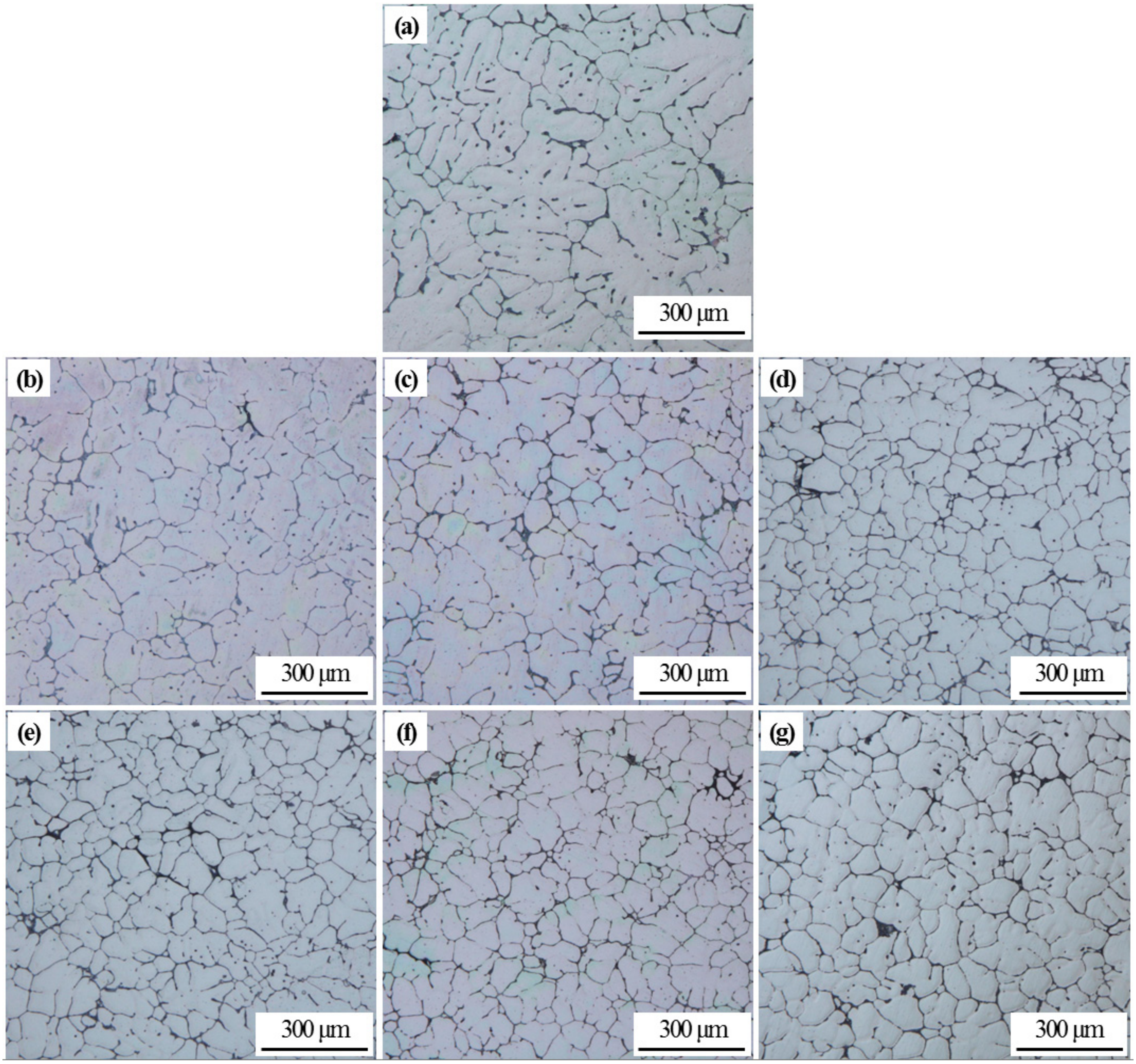

Fig. 4. Micro photographs of Al-4.4 wt.% Cu samples

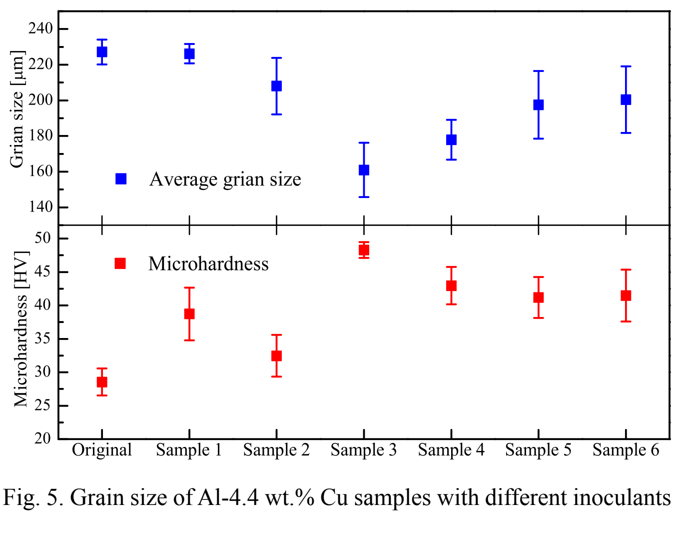

Fig. 5. Grain size of Al-4.4 wt.% Cu samples with different inoculants

that possess the desired microstructure with TiB_2 particles a fine dispersion and the optimal refining efficiency on the Al-Cu alloy. Considering the excess oxidization of the melt might be caused by higher superheating temperature, there comes to the viewpoint that the 820°C was the optimum reaction temperature for preparing Al-5Ti-1B master alloy.

4. Conclusions

The microstructure of a series of Al-5Ti-1B prepared in different holding conditions and the refining efficiencies of the master alloys on Al-4.4 wt.% Cu samples were investigated experimentally. On the basis of the results of this study, we concluded the following:

With holding temperature increasing, TiB_2 particles were converted from the state of aggregation to uniform dispersion in the matrix gradually, and blocky Al_3Ti particles were changed to stick-like morphology when the holding temperature was above 860°C.

Holding time was too short to obtain adequate TiB_2 particles and resulted in residue fluoride salt entrapped in the melt. More than 30 minutes of holding time, however, resulted in Fe-containing impurity particles aggregated along the matrix grain boundaries.

All of the experimental alloys that received in this work produced grain refinement on Al-4.4 wt.% Cu sample. In particular, the Al-5Ti-1B which was held at 820°C for 30 min, refined Al-Cu sample with the decrease of average grain size from 227 μm to 160 μm.

The 820°C was appropriate holding temperature for the production of Al-5Ti-1B employing fluoride salt process, at which Al-5Ti-1B reveled the desired microstructure and optimum refining efficiency.

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