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Sono-Solidification in Hypereutectic Al-Si Alloy

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Ultrasonic irradiation during the solidification of molten metals, that is, sono-solidification, is known to achieve grain refinement. The present study is focused on the sono-solidification with acoustic cavitation in hypereutectic and eutectic Al-Si alloys. There generally appears an equilibrium microstructure composed of primary silicon and coupled α-Al/Si eutectic in Al-18mass%Si alloy, however, non-equilibrium α-Al grains develop along with the equilibrium microstructure through the sono-solidification. During the sono-solidification of Al-18mass%Si alloy, non-equilibrium α-Al grains are crystallized in the molten metal close to the ultrasonic radiator just before reaching the eutectic temperature of 577 ^{o}C besides the fine primary silicon particles. The crystallization of α-Al grains is understood through acoustic cavitation: ultrasound in molten Al-Si alloys exhibits two outstanding behaviors of cavitation bubbling and acoustic streaming. When molten Al-12.6mass%Si alloy was rapidly cooled down from just above the eutectic temperature after the ultrasonic irradiation, the microstructure observation exhibits that ultrasonic irradiation above the eutectic temperature causes crystalline α-Al and silicon to nucleate. It is known that the collapse of acoustic cavitation generates extremely high pressure of over 1GPa. At highly pressurized sites, the eutectic temperature rises, and non-equilibrium α-Al nodules, which contain higher amount of silicon compared with those solidified at ambient pressure, can be crystallized before reaching the eutectic temperature in the sono-solidification.

Keywords: *ultrasonic vibration, acoustic cavitation, hypereutectic Al-Si alloy, non-equilibrium α-Al, primary silicon*

1. Introduction

It has been widely accepted that application of ultrasound to molten metal processes is an effective process control tool, especially cast metal grains have been refined by ultrasonic treatment. With ultrasonic irradiation to molten metals, it is known that acoustic streaming and cavitation are generated in the melt [1]. These kinds of fundamental phenomena of ultrasound are closely related to the grain refinement [1-3]. The improvement in wettability by ultrasonic vibration, which is based upon the sono-capillary effect, has applied to brazing process [4], as well as melt infiltration [5] and stirring process [6] for manufacturing metal matrix composites. The liquid adhesion phenomenon at a vibrating end surface was found out recently, it was applied to the novel casting process with extremely high casting efficiency [7].

The sono-solidification, in which ultrasound is irradiated to molten metal during the solidification, is expected to cause improved mechanical properties based upon the grain refinement. However, the mechanism of grain refinement in the sono-solidification is not clearly understood whether the promotion of nucleation is predominant or the breakage of developing crystals by ultrasonic vibration. From the nucleus promotion view-point, for example, the sono-solidification is explained that the acoustic cavitation causes effective nucleation sites due to the adiabatic expansion and compression [1]. The cavitation bubbles generated in liquid, that is, above the liquidus temperature, are remained after stopping the ultrasonic irradiation, and they survive below the liquidus temperature, so that they can work as nucleation sites [8]. Recently the grain refinement in aluminum alloys has been carried out above the liquidus temperature by ultrasonic irradiation [9, 10].

With the sono-solidification of hypereutectic Al-Si alloy, the authors found out the crystallization of non-equilibrium α-Al grains along with the equilibrium microstructure. In the present study, their crystallizing mechanism is discussed via a variety of quenching experiments of ultrasonically treated both hypereutectic and eutectic Al-Si alloys, because the generation and collapse of acoustic cavitation bubbles are expected to play an important role for the crystallization of non-equilibrium α-Al phase.

2. Experimental Procedures

In order to vibrate molten metal in a stainless steel crucible, ultrasonic vibration was transmitted from the crucible bottom via an ultrasonic radiator in the vertical direction, as shown in Fig.1. The specification of vibration conditions was: the output power of 2000 W, the peak to peak amplitude of 20 μm and the resonant frequency of 20 kHz. Two kinds of Al-Si alloys were supplied to the sono-solidification: Al- 18mass%Si and Al-12.6mass%Si alloys. The hypereutectic Al-18mass%Si alloy was heated at 730 ^{o}C and poured at 690 ^{o}C to a stainless steel crucible, and Al-12.6mass%Si alloy heated at the same temperature of 730^{o}C and poured at 640^{o}C. The molten metal in a crucible was vibrated from the beginning of pouring, and the aluminum billet was rapidly quenched into water when it reached a certain temperature. The temperature of molten Al-Si alloys was continuously measured at three points in the billet, that is, 3 mm, 8 mm and 13 mm apart from the bottom in the crucible center line by thermocouples.

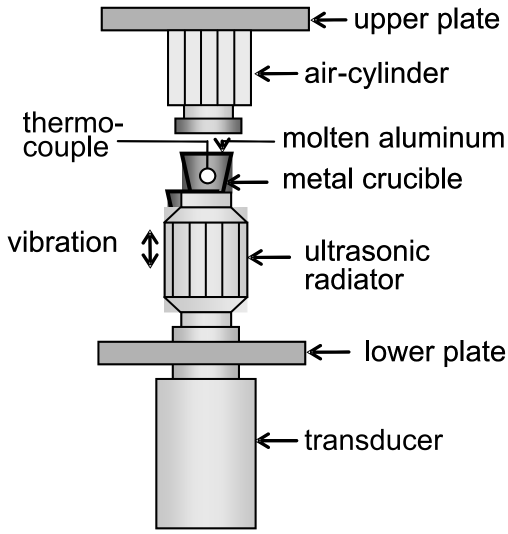

Fig.1 Experimental setup for solidification of molten Al-Si alloy with ultrasonic vibration.

3. Results and Discussion

3.1 Microstructure of hypereutectic Al-Si alloy solidified with ultrasonic irradiation

Typical microstructures of hypereutectic Al-Si alloy quenched right after the full solidification are shown in Fig.2, which is without and with ultrasonic irradiation during the solidification. The white region corresponds to α-Al phase and gray particles do primary silicon. Without ultrasonic irradiation, α-Al phase around big primary silicon particles is recognized along with eutectic silicon plates in Fig.2(a). In contrast, refined α-Al grains, which are non-equilibrium in hypereutectic Al-Si alloys, are crystallized besides refined primary silicon particles and fine

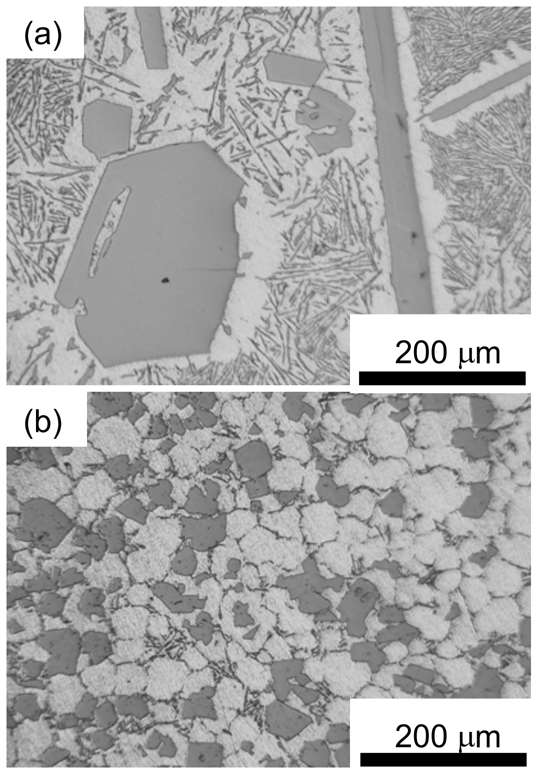

Fig.2 Typical microstructures solidified (a) without and (b) with ultrasonic vibration till their full solidification in Al-18mass%Si.

eutectic silicon particulates. The eutectic region markedly decreases owing to the crystallization of α-Al grains. Ultrasonic irradiation to molten hypereutectic Al-Si alloy during the solidification affects not only the size of primary silicon particles, but the crystallization of non-equilibrium α-Al grains, so that it will be discussed how non-equilibrium α-Al grains are crystallized in the sono-solidification in next sections.

3.2 Crystallization of non-equilibrium α-Al grains

It was examined when non-equilibrium α-Al grains crystallized during the solidification with ultrasonic irradiation. Molten hypereutectic Al-18mass%Si alloy, which was ultrasonically irradiated from the beginning of pouring, was rapidly quenched from a certain temperature during the solidification. Typical microstructures quenched from different temperatures (different solid fractions) are shown in Fig.3. In the case of Fig.3(a) quenched from just above the eutectic temperature of 578°C, there exist α-Al grains grown at the interfaces of refined primary silicon particles, where the area of dark gray exhibit liquid state just before quenching. The microstructure of Fig.3(b) and (c) were taken in the billets quenched at 1 s and 20 s passed after reaching the eutectic temperature. The eutectic solidification continues for 45 s after reaching the eutectic temperature when ultrasound is irradiated on the molten aluminum alloy. Non-equilibrium α-Al grains seem to exist in addition to refined primary silicon particles just before the quenching, that is, just before reaching the eutectic temperature. Comparing Fig.3(b) with (c) of the sono-solidification, it is worth noting that the number (different solid fractions) and area of non-equilibrium α-Al grains increase as the eutectic solidification proceeded.

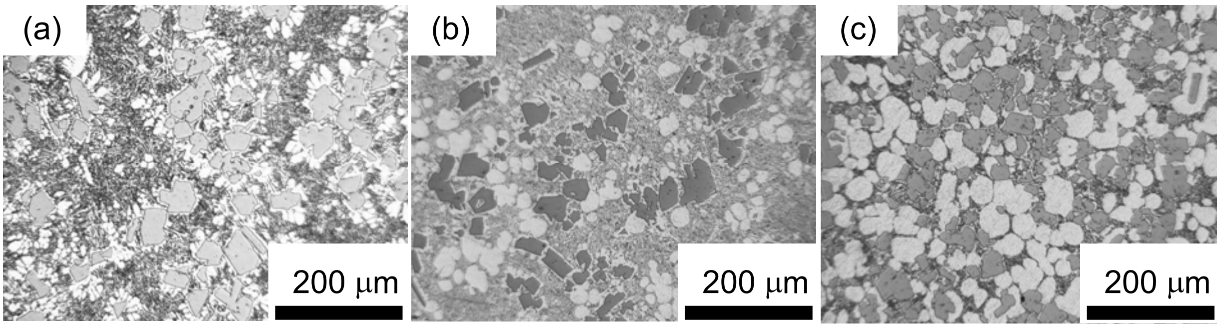

Fig.3 Microstructures water-quenched from (a) 578°C, (b) 577°C after 1 s and (c) 577°C after 20 s passes at the eutectic.

3.3 Ultrasonic irradiation on eutectic Al-Si alloy

Figure 4 shows optical micrographs of two eutectic Al-Si billets solidified (b) without and (c) with ultrasonic irradiation for 10 s at 583°C, and quenched just after ultrasonic irradiation. For comparison of quenching effect on microstructures, the micrograph of the billet solidified slowly

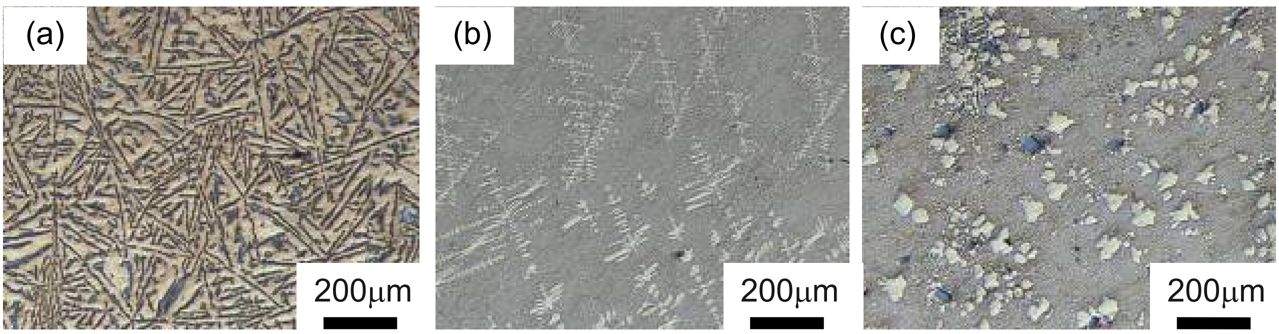

Fig.4 Effect of ultrasonic irradiation and solidification rate on microstructure of Al-12.6mass%Si, (a) solidified slowly without ultrasonic irradiation, (b) quenched from 583°C without ultrasonic irradiation and (c) quenched from 583°C after ultrasonic irradiation for 10 s.

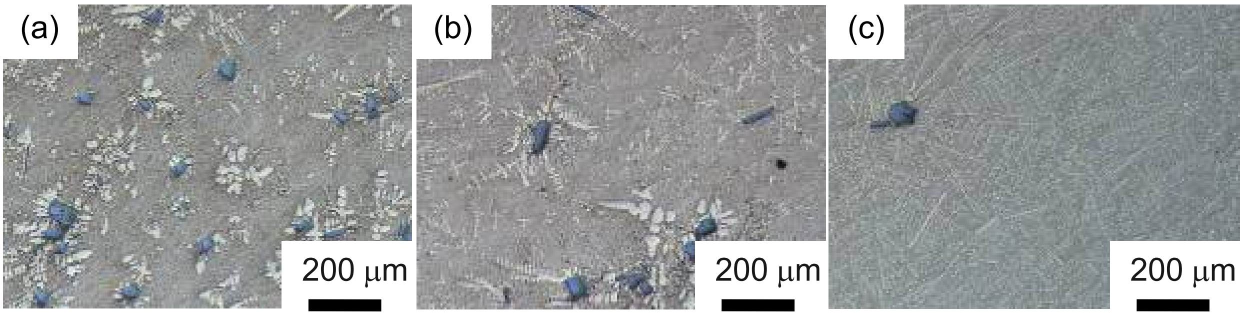

Fig. 5 Effect of melt temperature during ultrasound radiation for 10 s on quenched microstructure, (a) 587°C, (b) 597°C and (c) 601°C.

without ultrasonic irradiation is also shown in Fig.4(a), which consists of only coarse eutectic structure. The quenched billet without ultrasonic irradiation exhibits fine α-Al dendrites, silicon and eutectic structure [Fig.4(b)]. The quenched billet with ultrasonic irradiation exhibits α-Al and silicon grains and fine eutectic structure [Fig.4(c)], so the billet solidified slowly without ultrasonic irradiation consists of only eutectic structure. Thus compared with slowly solidified and quenched billets without ultrasonic irradiation, it can be seen that fine α-Al dendrites in the quenched billet without ultrasonic irradiation was crystallized by quenched effect, a kind of divorced eutectic. Grains of α-Al and silicon in the quenched billet with ultrasonic irradiation are of different shape than the fine α-Al dendrites of rapid solidification. Thus non-equilibrium α-Al and refined silicon grains are definitely crystallized by ultrasonic irradiation.

The average size of silicon grains in billet quenched from 583°C with ultrasonic irradiation is about 30 μm. In the equilibrium, the crystallization of silicon grains is not observed. Thus, if it is believed that silicon grains are crystallized due to the silicon concentration shift to hypereutectic, that is, due to α-Al formation. Crystallization of silicon particles also indicates that α-Al grains nucleate above the eutectic temperature during ultrasonic irradiation. So the amount of silicon grains shows the effect of α-Al nucleation by ultrasonic irradiation.

Figure 5 shows micrographs of billets quenched from different melt temperatures (587, 597, 601°C) after ultrasonic irradiation for 10 s. At lower temperatures (583, 587°C), α-Al grains can be observed, by contrast at higher temperatures (597, 601°C), α-Al dendrites are observed. Figure 5 shows that all billets have primary silicon particles, and the number decreases with increasing the quenching temperature. From the analyses of these microstructures, the average size and number of primary silicon in each billet were measured. The average size of primary silicon does not change with quenching temperature. It can be seen also that the number of primary silicon decreases with increasing quenching temperature.

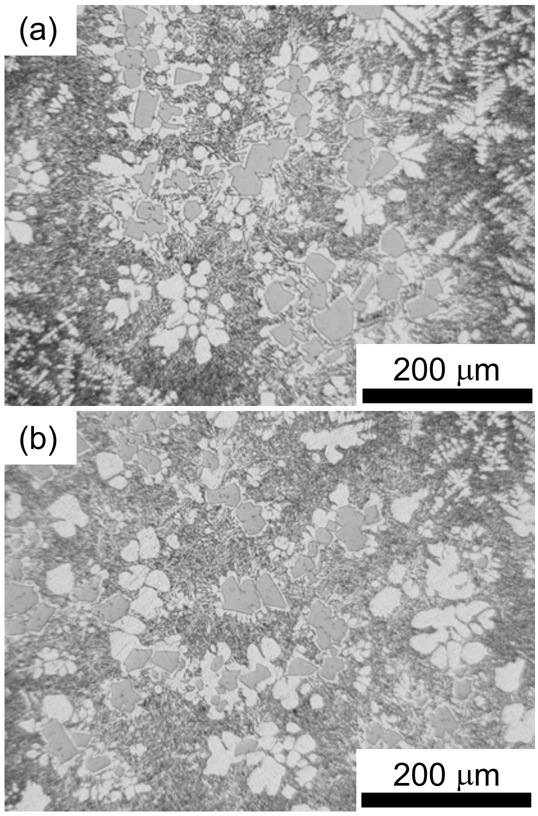

Fig.6 Microstructures at the billet bottom water-quenched from (a) 582°C and (b) 578°C with ultrasonic vibration.

3.4 Crystallization at a bottom part of billet

The microstructure at a billet center (8 mm apart from the bottom), as shown in Fig.3 is different from the one at a bottom (3 mm apart from the bottom). Typical microstructures at a bottom part of the sono-solidified billet are shown in Fig.6 quenched respectively from 582°C and 578°C, which are a little higher than the eutectic temperature. Non-equilibrium α-Al grains are recognized not only at a bottom part of the billet quenched from 578°C, but also the one quenched from 582°C which is 5°C higher than the eutectic temperature of 577°C. It is expected that non-equilibrium α-Al grains definitely exist in the liquid state just before quenching at a bottom part of the sono-solidified billet. The above explanation regarding the microstructure generation becomes clearer compared with that based on Fig.3 observed at the billet center.

In this study, temperatures of the molten Al-18mass%Si alloy were continuously recorded at 3 mm, 8 mm and 13 mm apart from the bottom in the billet center line by CA thermocouples during the sono-solidification. Without ultrasonic irradiation, the molten metal reaches the eutectic temperature in the order of top, bottom and finally center, the time difference was approximately 5 s between those at the top and center. However, there exists no time difference in reaching the eutectic temperature in the sono-solidification, owing to the acoustic streaming with ultrasonic cavitation. Consequently, it is concluded that non-equilibrium α-Al grains exist at a bottom part of the billet along with primary silicon particles before reaching the eutectic temperature. Comparing Fig.6(a) with Fig.6(b), non-equilibrium α-Al grains become more granular and keep on increasing the number as the sono-solidification proceeded. The appearance of non-equilibrium α-Al grains before reaching the eutectic temperature cannot be fully explained from the divorced eutectic due to the acoustic streaming.

Table 1 Physical properties of aluminum and silicon.

items	symbol	aluminum	silicon
melting point (°C)	T_m	660.1	1412
volume change during melting (%)	ΔV_m	6.5	-10
latent heat of fusion (kJ/mol)	L_m	10.47	50.66
atomic weight (g/mol)	m	26.91815	28.0855
density of the liquid (kg/m³)	ρ_{liq}	2385	2530

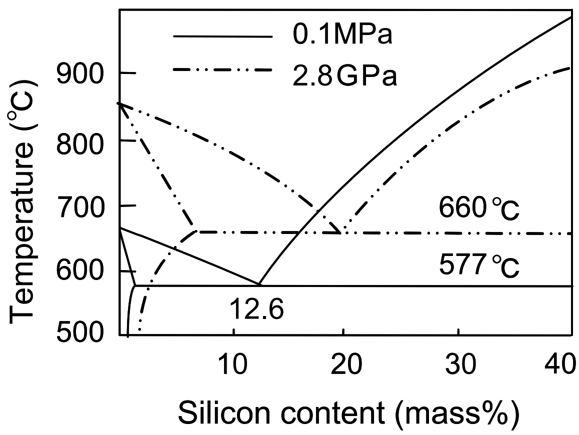

Fig.7 Phase diagram of Al-Si system at ambient pressure and high pressure.

3.5 Role of ultrasonic cavitation on sono-solidification

The model experiments were carried out with distilled water using the same ultrasonic vibration system as the sono-solidification. Acoustic cavitation bubbles violently appear close to the bottom of distilled water in a transparent container with the same size as the stainless steel crucible in the sono-solidification. Nucleation sites for cavitation bubbles are mainly the bottom surface of container due to the fine crevasses [7]. The interface of cavitation bubbles is known to become a nucleation site for the crystallization of molten metals, moreover, cavitation bubble generate extremely high pressure of over 1 GPa when they collapse [12]. A change in the melting point due to high pressure can be estimated from Eq.(1) based on the Clausius- Clapeyron equation:

$$dT/dP=T_m(V_{liq}-V_{sol})/\Delta H_m \quad .....(1)$$

where the symbols in Eq.(1), and the physical values of aluminum and silicon are listed in Table 1 [13]. The density of solid aluminum is higher than that of liquid, and silicon is just opposite, so that the pressure dependence on the melting point is calculated to be 6.2°C/0.1 GPa in aluminum and -4.1°C/0.1 GPa. Since the melting point of aluminum increases at high pressure, α-Al grains can stably exist as a solid state at high pressure, though a liquid state at ambient pressure.

It has been reported many studies on an Al-Si phase diagram at high pressure, as typically shown in Fig.7 [14]. The diagram exhibits that the liquidus temperature of α-Al increases at high pressure, the silicon content at the eutectic point also increases. On the temperature zone crystallized primary silicon in Al-18mass%Si alloy, the silicon content in the corresponding liquid changes from 18mass% to 12.6mass% at ambient pressure. Non-equilibrium α-Al grains are expected to crystallize over the eutectic temperature of 577°C, especially at a bottom part of molten alloy in the crucible, because there exist extremely high pressure sites such as over 1 GPa due to the collapse of cavitation bubbles at a bottom part of the crucible, close to the end surface of ultrasonic radiator. At higher temperature than the eutectic, the crystallized α-Al grains may disappear due to the acoustic streaming. This is the reason why no α-Al grains are clearly observed in a center area of the quenched billet from 578°C as shown in Fig.3(a). However, crystallized α-Al grains can stably exist when molten metal temperature decreases to the eutectic temperature.

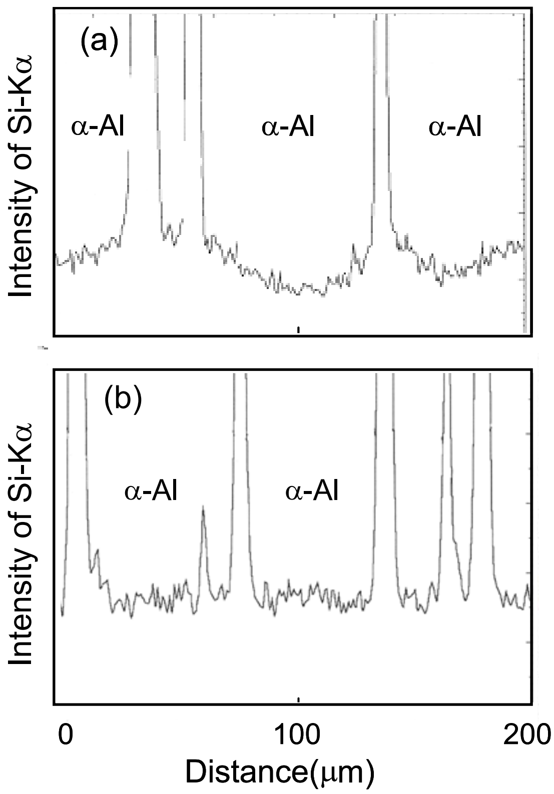

Fig.8 Intensity profiles of Si-Kα on α-Al grain cross-sections of (a)Al-7mass% Si solidified without ultrasonic vibration and (b)Al-18mass% Si with ultrasonic vibration.

Based upon the Al-Si phase diagram of Fig.7, it is expected the silicon content in α-Al grains solidified at high pressure increases in the sono- solidification. The silicon content in α-Al grains of Al-18mass%Si alloy solidified with ultrasonic irradiation was measured by EPMA. The silicon content in α-Al of Al-7mass%Si solidified without ultrasonic irradiation was also measured to compare with that in the sono-solidification, as shown in Fig.8. The profile of silicon content in primary α-Al grains is a concave shape, that is, primary α-Al grains crystallized at higher temperature has the lowest silicon content at the grain center based on the consideration of Fig.7 at ambient pressure. The Fig.8(b) exhibits that the silicon content in non- equilibrium α-Al grains of Al-18mass%Si alloy solidified with ultrasonic irradiation is higher at each grain center. This experimental results support that sono-solidified non-equilibrium α-Al grains have higher silicon content than that solidified at ambient pressure. However, the mechanism based on the de-coupled eutectic theory cannot be fully denied at this moment. Since the particular microstructure of hypereutectic Al-Si alloy arising from the sono-solidification is different from that solidified at ambient pressure, sono-solidified alloys are expected to exhibit new characteristics.

4. Conclusion

Sono-solidification, which is defined as the solidification with ultrasonic irradiation, was carried out using hypereutectic and eutectic Al-Si alloys, and the following conclusions are obtained:

(1) Sono-solidification causes granular non-equilibrium α-Al grains to appear in hypereutectic Al-Si alloy, in addition to fine primary silicon particles and fine eutectic silicon plates.
(2) Non-equilibrium α-Al and fine silicon grains, which are non-equilibrium, are crystallized above the eutectic temperature in the sono-solidification of eutectic Al-Si alloy.
(3) Extreme high pressure generated at collapsed sites of cavitation bubbles causes the liquidus temperature of α-Al phase to increase, so that the non-equilibrium α-Al grains can be nucleated above the eutectic temperature.
(4) Non-equilibrium α-Al grains contain higher silicon content than that in primary α-Al grains of hypoeutectic Al-Si alloy solidified without ultrasonic irradiation. This experimental result supports non-equilibrium α-Al grains crystallized at the collapsed sites of acoustic capitation with extremely high pressure.

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