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# Zone-melted unidirectional solidification of particulate dispersed composites

SHUSEN WU
*College of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China*
*E-mail: wushusen@public.wh.hb.cn*

H. NAKAE
*Department of Materials Science and Engineering, Waseda University, Tokyo 169, Japan*

T. KANNO, Y. YOU
*Kimura Foundry Co., Ltd., Shizuoka 411, Japan*

In order to solve the problem of particles settling and agglomeration in front of solidifying interface in unidirectional solidification (UDS) experiments, a zone-melted process has been utilized in this study. The experimental results show that, the melting zone could be kept in 30–40 mm width and the zone melted UDS experiments are realized with $Al_2O_3$ particle reinforced aluminum-matrix composites. But particle settling still occurs in the liquid, and becomes severe as the particle volume fraction decreases. However, when the volume fraction of the particles is more than 20–22 vol.%, no further settling occurs under a solidification rate of 8–16 mm/h. Investigation on the interaction of particles and solid/liquid interface reveals that the $Al_2O_3$ particles are rejected into liquid and pushed by the growing solid phase in $Al_2O_{3(P)}$/Al and $Al_2O_{3(P)}$/Al-0.23wt.%Ce composites. Some particles are mechanically entrapped between cells, and distributed along the crystal grain boundaries.

## 1. Introduction

As the particulate dispersed metal matrix composites (MMCs) are superior in strength and wear resistance, the applications of the composites have been advanced in many aspects, such as in automobile parts and sports articles [1]. However, for the massive production of the composites, the liquid metal processes, including the casting process, are necessary. There exists an important problem of how to make the particles distribute uniformly in the solidified solid. As we know, most of the ceramic particles are pushed by the solidifying front, and segregate at grain boundaries [2]. It is very difficult to obtain an uniform distribution of particles under the condition of gravity casting. The distribution state of particles is governed by the interaction result of particles and solid/liquid (S/L) interface. Therefore it is important to understand the behavior of ceramic particles at solidifying front.

The unidirectional solidification (UDS) method is an important means to determine the behavior of foreign particles at S/L interface during solidification. However, the UDS studies of particulate dispersed metal-matrix composites are very scarce [3]. There exists a problem in the conventional UDS method: most of the particles will settle to the bottom or float to the top due to specific gravity difference between the liquid and the particles, such as $Al_2O_{3(P)}$/Al, $SiC_{(P)}$/Al and $Gr_{(P)}$/Al, as the solidification is carried out after the melting of the whole specimen in the furnace. This phenomenon leads to difficulty in the precise observation of the particle movement at the S/L interface. In order to overcome the settling, it is desirable to increase volume fraction of particles. But this will lead to particle accumulation before the solidifying front and mechanical entrapment of particles into the solid. Under these circumstances, a steady state solidification cannot occur.

The purpose of this paper is the substitution of zone melting for conventional integrate melting to obtain steady-state solidification for MMCs, as well as to understand the interaction between the particles and S/L interface for aluminum-matrix composites.

## 2. Experimental procedure

The zone-melting UDS equipment is schematically shown in Fig. 1. The specimen is partly melting/solidifying in this process in order to avoid particle settling and accumulation. The crucible with specimen is stationary while the directional solidification is conducted by moving an electric furnace mounted on a table and driven with an electric motor. Any vibration to the specimen from the driving system is avoided. The moving speed, namely the solidification rate, varies in the range of 0.5–24 mm/h. The temperature distribution in the furnace is shown in Fig. 2. The temperature gradients are 4.7 K/mm at the melting position and 4.4 K/mm

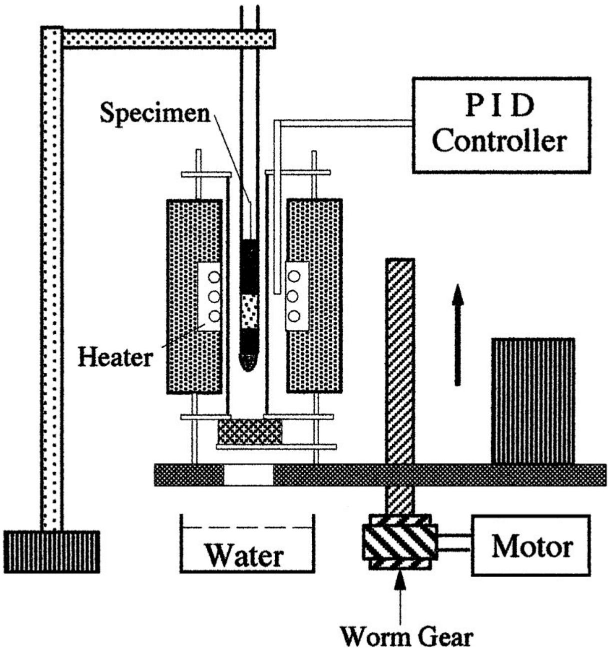

*Figure 1* Schematic representation of the zone UDS apparatus.

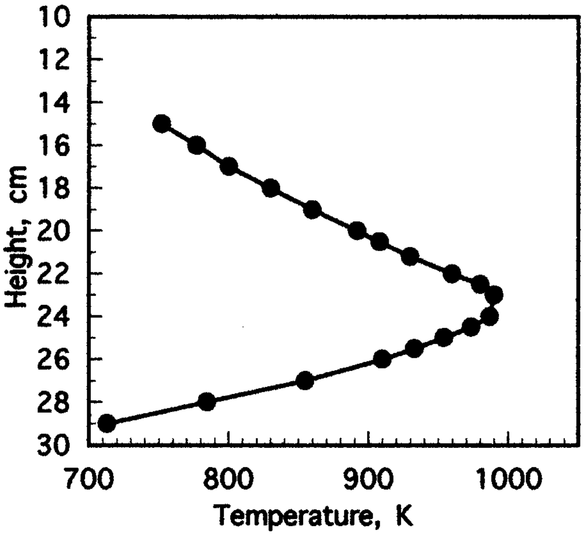

*Figure 2* Temperature profile of the zone melting furnace.

at the freezing position. The width of the melting zone is about 30–40 mm.

Two kinds of composites were used in this study, the $Al_2O_3$/Al composites and the $Al_2O_3$/Al-0.23wt.%Ce composites. These composites were prepared from the DURALCAN W6A20A (6061 aluminum alloy reinforced with 20 vol.% $Al_2O_3$ particles with a 30 $\mu$m average particle diameter). In order to convert the composite into the target composites, the composite was melted and diluted with pure aluminum, in a siliconit furnace under argon atmosphere. After holding the melt for the settling of particles, the upper part of the melt was poured out. By adding pure aluminum metal in the residual melt, the dilution was carried out and repeated three times for the purification of the matrix. The purified composite was $Al_2O_3$/Al composite with very small amount of impurities. By adding pure Ce(99.7wt.% Ce) it was obtained the $Al_2O_3$/Al-0.23wt.%Ce composites. The matrix chemical compositions of these composites are shown in Table I. The volume fractions of the particles were 2–20 vol.%. In order to avoid the chemical reaction of the melt with the crucible, high purity alumina tubes (99.9wt.% $Al_2O_3$, with a 6 mm diameter) were used as the crucible material in the following UDS experiments. The samples were quenched in chilled water during the experiments, and then analyzed by an optical microscope, scanning electron microscope (SEM) and electron probe microanalyser (EPMA).

## 3. Results and discussion

### 3.1. Particle's settling behavior in composite melt

The materials used in the experiment of particle's settling behavior were $Al_2O_{3(P)}$/Al composites. The macro-distribution of $Al_2O_3$ particles in the whole sample after UDS is shown in Fig. 3. The $V_f$ of $Al_2O_3$ particles in the master specimen was 10 vol.%, and solidification rate was $R = 16$ mm/h. The presentation of the whole sample is almost impossible as the sample is very long, and only the upper and lower parts of it are shown in Fig. 3.

During the melting and solidification process, the particles in the melting zone still settled due to specific gravity difference between $Al_2O_3$ particles and aluminum melt. There is no particles in a part of the sample in the upper part in Fig. 3(b). Excepting this part, particles are comparatively macro-uniformly distributed in the sample.

The relation of settling height with particle content is shown in Fig. 4. Here $H$ represents the height of the sample, and $h$ is the height of the part with no particles in the upper. Therefore, the height of particles existed is expressed as particles height $(H - h)$. The $H$ for the data in Fig. 4 was 120 mm. It is known from Fig. 4 that, the settling of particles is very small when $V_f$ is 15–20 vol.%, and the particles height is about 110 mm, the volume fraction after solidification becomes 17–22 vol.%.

The settling of particles becomes severe with the decrease of $V_f$ in the master specimen. The particles height is about 90 mm when $V_f = 10$ vol.%; about 83 mm

TABLE I Chemical composition of matrix metal

| Composites | Elements (wt. %) Si | Fe | Cu | Mn | Mg | Cr | Ce | Ti | $V_f$ vol% |
|---|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$/Al | 0.10 | 0.05 | 0.03 | <0.01 | 0.11 | 0.01 | <0.001 | <0.01 | 5 ~ 20 |
| $Al_2O_3$/Al-Ce | 0.08 | 0.06 | 0.03 | <0.01 | <0.01 | 0.01 | 0.23 | <0.01 | 2 ~ 10 |

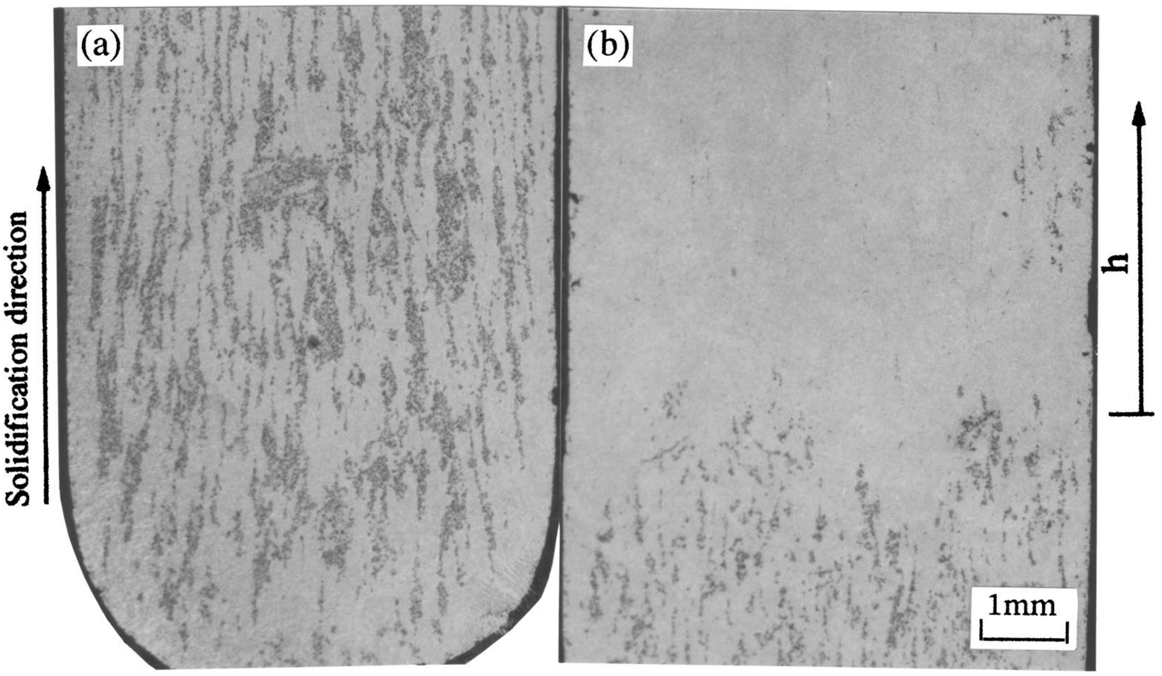

*Figure 3* Representative macro-distribution of particles after freezing of the whole sample. ($V_f = 10$ vol.%, $R = 16$ mm/h). (a) Lower part; (b) Upper part.

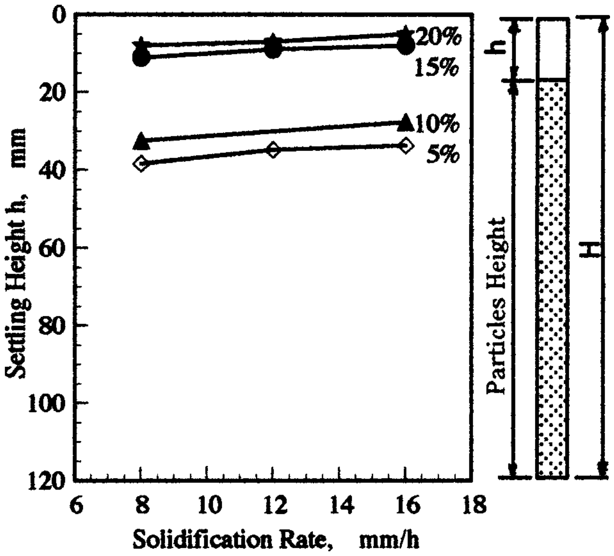

*Figure 4* Relation of settling height with solidification rate and particles content.

when $V_f = 5$ vol.%. The $h$ is decreased in a very small amount with the increase of solidification rate in the range of 8–16 mm/h. Therefore it is obvious that $h$ is mainly determined by volume fraction $V_f$ of particles in the specimen.

The maximum value of $h$ can be considered as the width of melting zone. It is about 40 mm from Fig. 4. Samples with particles height over 80 mm can be obtained. Analyses of the samples reveal that the melting zone could be kept in 30–40 mm width and the zone melted UDS experiments with particle dispersed composites are realized successfully.

The terminal velocity $V$ of a particle's settling can be calculated from the Stokes equation [4]:

$$V = d^2 g(\rho_S - \rho_L)/18\eta_C \quad \text{m/s} \tag{1}$$

where $d$ is the particle diameter, $g$ is gravity acceleration, $\rho_S$ and $\rho_L$ are densities of the particle and the liquid respectively. The viscosity, $\eta_C$, of the composite melt is related with the volume fraction $V_f$ of particles in the melt [5]:

$$\eta_C = \eta_m\left(1 + 2.5V_f + 10.25V_f^2\right) \tag{2}$$

where $\eta_m$ is the viscosity of the matrix alloy, $\eta_m = 2.0 \times 10^{-3}$ N·s/m$^2$ for pure aluminum melt [6].

With the increase of volume fraction of particles in the melt, the settling velocity decreases. This is largely due to the upward velocity of the fluid displaced during settling increasing with concentration. Richardson and Zaki [7] proposed a relationship between Stokes terminal settling velocity at infinite dilution (Equation 1) and $V_h$ the settling velocity of a suspension (referred to as hindered settling):

$$V_h = V(1 - V_f)^n \tag{3}$$

$$n = 4.65 + 19.5d/D \qquad \text{for} \quad Re < 0.2 \tag{4}$$

where $D$ is the diameter of the container and $Re$ is Reynolds number.

Calculations in the given conditions show that the settling velocity $V_h$ is about 260 mm/h for $V_f = 20$ vol.% of particles with grain size of 30 $\mu$m, and $V_h$ is about 960 mm/h for $V_f = 5$ vol.% [9]. This high settling velocity is far away from the maximum solidification rate of 24 mm/h in this study. Namely, the $Al_2O_3$ particles in the melting zone could still settle to the bottom of the melt and accumulate. However, the excessive accumulation of particles is avoided because of the short melting zone kept in the experiments. Moreover, the settling velocity $V_h$ also greatly depends on particle diameter $d$ (Equation 1). Although the average diameter is 30 $\mu$m in this study, particles with a diameter of 10 $\mu$m are also existed. Their settling should be very slowly. For example, when $V_f = 20$ vol.%, the settling velocities are:

$$d = 20\ \mu\text{m}, \quad V_h = 115\ \text{mm/h}$$
$$d = 10\ \mu\text{m}, \quad V_h = 28.7\ \text{mm/h}$$

Therefore, the settling velocity of small particles with a diameter of 10 $\mu$m is in the same order of solidification rate. The variation of settling height $h$ can be explained.

### 3.2. Interaction of particles and solid/liquid interface

In order to observe the S/L interface, samples were quenched into chilled water during solidification when they solidified about 20–40 mm. The S/L interfacial morphology and particle distributions of an $Al_2O_3$/Al-Ce composite are shown in Fig. 5. The $Al_2O_3$ particles are being pushed by S/L interface, and there is no particles in the solid. There are only a few particles before the solid front while there is about 2 vol.% $Al_2O_3$ particles in master specimen. It is well known that it is favorable for the observation and examination of interactions between particles and S/L interface if there are only a few particles in front of S/L interface. This does has the advantage of the zone melted UDS.

The situation with more particles present in the liquid for $Al_2O_3$/Al-Ce composite is shown in Fig. 6. The $Al_2O_3$ particles are still pushed by the solid front under a solidification rate of 2 mm/h. In this case some rejected particles would be pushed into the cell grooves and mechanically entrapped into the cell boundaries (Fig. 6). Of course, the particles could not be uniformly distributed in the solid in this situation.

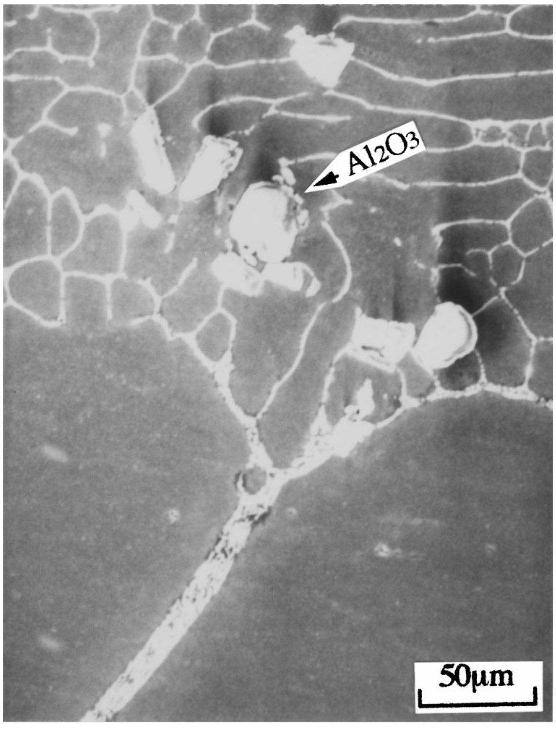

*Figure 5* Interfacial morphology and Particle distributions for $Al_2O_3$/Al-Ce composites. (SEM; upward freezing. $V_f = 2$ vol.%, $R = 2$ mm/h).

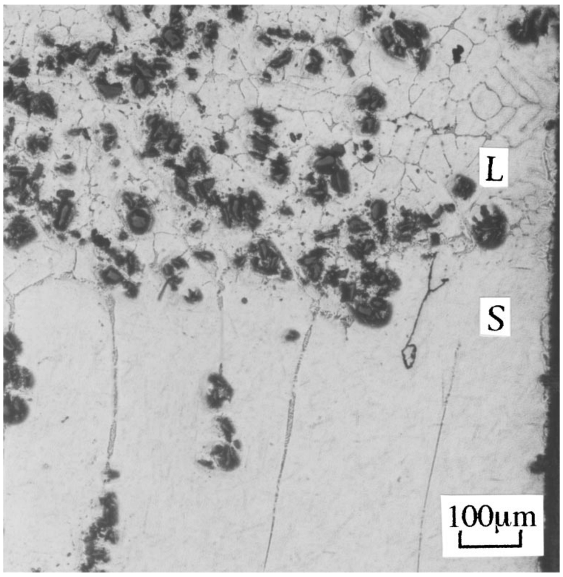

*Figure 6* Particle distributions at S/L interface for $Al_2O_3$/Al-Ce composites. (Upward freezing. $V_f = 5$ vol.%, $R = 2$ mm/h).

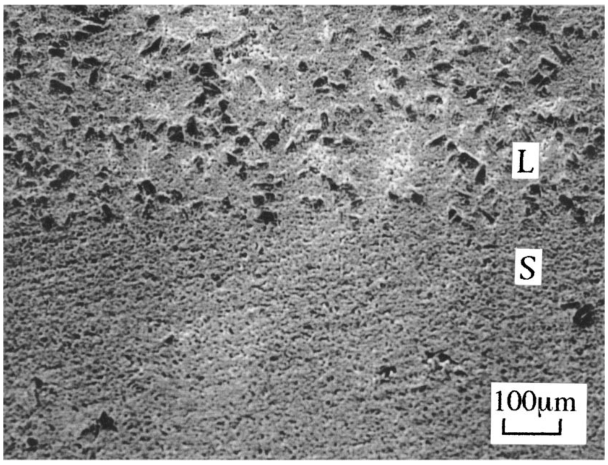

*Figure 7* Particle distributions at S/L interface for a more purified $Al_2O_3$/Al composites. (SEM; upward freezing. $V_f = 7$ vol.%, $R = 2$ mm/h).

From Fig. 3 it could also be observed that the particles are distributed nearly directionally along solidification direction. This is because the $Al_2O_3$/Al composite in Table I is not very pure. It contains a very small amount of Si and Mg. The S/L interface of it during solidification would be not very flat. The solidification morphology is greatly affected by the impurities and alloy elements [8]. By using a more purified $Al_2O_3$/Al composite than that in Table I, the interfacial morphology and particle distribution are shown in Fig. 7. The S/L interface is flat. A large number of $Al_2O_3$ particles are rejected and pushed by the solid front, and accumulate in the liquid before the interface. There are almost no particles in the solid. If the pushed particles are too numerously accumulated in the front to be movable by the growing solid phase, the particles would be mechanically entrapped to form band structure in the solid, as the bridging effect of the accumulated particles prevents the movement of particles [9].

The $Al_2O_3$/Al composite in Fig. 7 has flat S/L interface because of the high purity of the aluminum

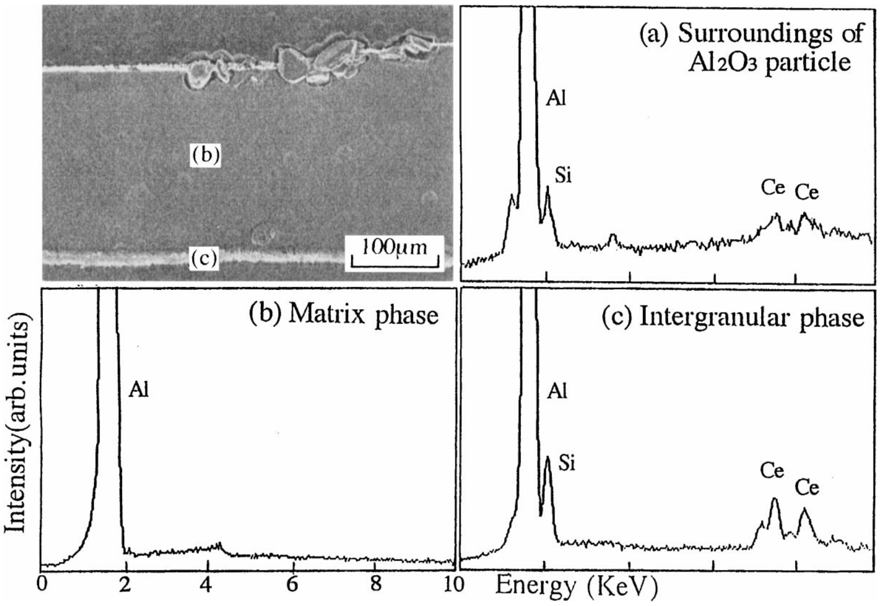

*Figure 8* SEM and EDX analysis for $Al_2O_3$/Al-Ce composites.

liquid. But the cellular growth will replace flat growth in $Al_2O_3$/Al-0.23wt.%Ce composite (Fig. 5). The Ce solute redistribution leads to the formation of cellular growth. The EPMA analysis for $Al_2O_3$/Al-Ce composites shows that Ce is mainly distributed in grain boundaries and around $Al_2O_3$ particles (Fig. 8). Although it has been reported that Ce additive could improve the wettability of $Al_2O_3$ particles with Al alloy melts [10], the result of this study shows that the adhesion of $Al_2O_3$ particles with the solid matrix could not be improved by Ce addition. Therefore, the $Al_2O_3$ particles are still rejected and pushed by the growing solid phase (Figs 5 and 6). The particles are also pushed even at the highest solidification rate of 24 mm/h in this study.

For the particles engulfment or pushing, several models have been proposed, which deal with a critical freezing velocity [11]. If the solidification speed is greater than a particle's movable speed, the pushed particle would be engulfed by the solid phase. However, almost none of these models could forecast actual critical velocity [11]. Moreover, if particles are pushed in Al-matrix composite melt, the critical velocity is as high as up to several millimeters per second [12]. This solidification speed is too high to be reached in conventional casting processes. According to authors' view point [13, 14], for such high interfacial energy systems of metals and ceramics, the behavior of ceramic particles in front of S/L interface is mainly determined by the relationship of interfacial energies between the particle/solid/liquid phases. If the interfacial energy of particle/solid is smaller than that of particle/liquid, and the contact angle between solid and particle is less than 90°, the particle could be engulfed into the solid even at very low solidification rate. In this case particles would be distributed uniformly in the solid [14]. The Ce addition to Al melt could decrease the interfacial energy of $Al_2O_3$ particle and the melt [10], i.e., improving the wettability, but not decrease the particle/solid interfacial energy. As a result, the $Al_2O_3$ particles are not engulfed, but still pushed, segregating in the finally freezing regions or mechanically entrapped into grain boundaries.

## 4. Conclusions

The zone-melted UDS method has been used for the investigation of solidification of particulate dispersed composites to solve the problem involving particle settling. A short melting zone in a width of 30–40 mm is maintained and the excessive accumulation of particles in front of solid/liquid interface is avoided. This process is favorable for the observation of interactions of particles and solidifying front. The results show that $Al_2O_3$ particles are rejected and pushed by the freezing front in both the $Al_2O_{3(P)}$/Al and the $Al_2O_{3(P)}$/Al-Ce composites.

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