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## Density Changes during Solidification of Hypoeutectic Al-Si Alloys

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### Abstract

It is necessary to know the density changes during the liquid-solid transformation in order to prevent macrosegregation and to secure the soundness in conventional castings. In this study the density changes of hypoeutectic Al-Si alloys were measured in liquid and solid states. By using the obtained values, the following relationships, between density and liquidus temperatures, and between the density and solidus temperatures, are established:

$$\rho_L = 1.862 + 2.46 \times 10^{-3} \times T_L - 2.59 \times 10^{-6} \times T_L^2 \quad (2)$$

$$\rho_S = 3.383 - 0.227 \times 10^{-2} \times T_S + 0.155 \times 10^{-5} \times T_S^2 \quad (6)$$

where  $\rho_L$  and  $\rho_S$  are liquid density at the liquidus temperature  $T_L$  and solid density at the solidus temperature  $T_S$ , respectively.

Furthermore a method is formulated to calculate the changes in density during liquid-solid transformation of a binary alloy by using the fraction solid, fraction liquid and the corresponding densities of the liquid and solid phases.

### 1. Introduction

Solidification of alloys is accompanied with changes in density. This results in solidification shrinkage, gravity segregation, pore formation etc. Thus it is necessary to know the density changes during the liquid-solid transformation in order to prevent macrosegregation and to secure the soundness in conventional castings.

In this paper, the density changes of hypoeutectic Al-Si alloys were measured in liquid and solid states. By using the obtained values, relationships, between density and liquidus temperatures, and between the density and solidus temperatures, are established and a method is formulated to calculate the changes in density during liquid-solid transformation of a binary alloy. Al-Si alloys are studied as they have good castability and are simple eutectic alloys with a wide range of liquid-solid transformation zone, which makes them suitable for the study of solidification

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processes.

It is possible to calculate the density of an alloy, at a certain temperature in the solidification zone, by knowing the solute concentration in the solidifying liquid and solid coexisting phases, and by knowing the corresponding densities of the liquid and solid phases. The former values can be determined from the binary phase diagram and the latter can be obtained by knowing the liquid density at the liquidus temperatures and solid density at the solidus temperatures.

The liquid density data at the liquidus temperature and solid density data at the solidus temperature for Al-Si alloys were reported by J. D. Edwards<sup>(1)</sup> in 1925, and by T. Takase<sup>(2)</sup> in 1931. Aluminum used for measurements by T. Takase, in the latter study, was only 99.74% pure, and had an iron content of 0.19%. Furthermore, in both of the studies, solid density of pure aluminum at the melting point and solid density of Al-1.65%Si alloy at the eutectic were measured, but solid density changes along the solidus were not established.

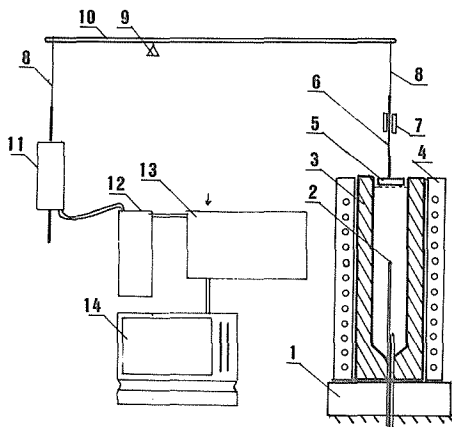
## 2. Experimental methods

### 2.1 Liquid density in relation to fall in temperature

The liquid density measurements for the selected alloys were carried out by continuously measuring the density changes with the fall in temperature, in the range from 700°C to the liquidus temperature of the alloy, by measuring the fall in the metal level in a cylindrical mold. The density of the corresponding alloy at 700°C was taken as the reference point for converting the fall in the metal level into density.

The change in liquid density along the liquidus line, for Al-Si alloys, was then established by joining the measured values of liquid density at the liquidus temperature, for six hypoeutectic alloys, of which the liquid density was determined.

The experimental apparatus shown in Figure 1 consisted of a graphite mold of 20 mm inner diameter and 36 mm outer diameter, having a height of 110 mm. Two thermocouples were inserted from the bottom of the graphite mold, to monitor and control the temperature of the metal bath. The mold was then placed in a cylindrical electric furnace that had a 38 mm inner diameter.



**Fig. 1** Experimental apparatus for liquid density measurements.

- 1; isolite base, 2; thermocouples, 3; graphite mold, 4; electrical furnace, 5; graphite float, 6; silica glass rod, 7; guide pipe, 8; thread, 9; pivot, 10; balance rod, 11; differential transformer, 12; mv converter, 13; data logger, 14; computer.

Liquid metal was poured in the preheated mold at 700°C. The upper level was fixed by inserting, from the top, a preheated graphite crucible as shown in Figure 2. After fixing the top level of the melt, a graphite float, connected to a differential transformer, was placed over the melt surface. The float was connected to a silica glass rod which passed through a guide pipe, so that the rod would stay in one direction. This arrangement kept the graphite float from deviating from the vertical axis and also from touching the wall of the graphite mold. The silica glass rod was connected to a balance rod through a cotton thread. The differential transformer was fixed on the other side of the balance rod with the aid of a cotton thread. The thermocouples and the differential transformer were connected to

the data logger and the computer, to record the required data. During the fixing of the float after pouring, the temperature was maintained at 700°C. Then the current to the electrical furnace was cut off, allowing the temperature to fall, and the data recorders were switched on.

The weight of the melt in the mold was established by subtracting the weight of the solidified ingot cooled to room temperature from the previously measured weight of the inserted thermocouples. Initial liquid volume of the alloy at 700°C was calculated by dividing the weight of the melt by the density of the alloy at that temperature. The density of the alloy at 700°C,  $\rho$ , was determined by using the following equation<sup>(3)</sup>:

$$\rho = 2.347 + 3.9 \times 10^{-3} \times C_{Si} \quad (1)$$

where  $C_{Si}$  is the silicon content in the alloy.

As the diameter of the mold was known, the fall in the molten metal level was converted to volume change, which in turn was used to calculate the density, knowing the weight of the ingot.

In calculating the initial volume the liquid volume was automatically adjusted to that of the mold at the beginning of the experiment (at 700°C), including the volumetric expansion of the mold. Any further effect of the mold contraction, due to the thermal contraction of graphite, was neglected as maximum density deviation due to it could only be of in the order of 0.001 g/cm<sup>3</sup>.

To calculate the volumetric contraction, it was necessary to know the diameter of

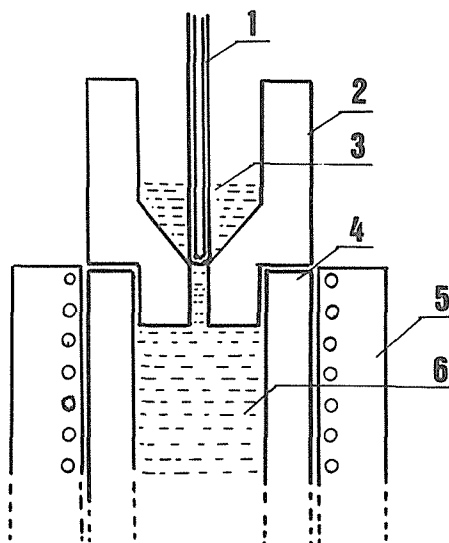


Fig. 2 The process of removal of extra liquid from the mold.

1; silica glass pipe, 2; graphite crucible, 3; scooped off liquid, 4; top of graphite mold, 5; electrical furnace, 6; liquid metal.

the mold at the time of the reading. Due to the small linear expansion coefficient of graphite, and also due to a narrow temperature range between 700°C and the liquidus temperature of the alloy, (the maximum range was 123°C in case of Al-11 wt%Si alloy), the diameter of the mold was taken as that at the average temperature and was calculated using the linear expansion coefficient for non-crystalline graphite, used for making the mold.

## 2. 2 Solid density in relation to rise in temperature

The solid state density measurements were carried out by measuring the linear expansion of the specimen and then calculating the continuous density changes for the respective specimen, with the rise in temperature, by using the room temperature density of the specimen as a base value.

The change in density, along the solidus line, for Al-Si alloys, was then established by using solid density values at the solidus for all the alloys.

Experiments were conducted for pure aluminum, Al-1 wt%Si, Al-1.5 wt%Si and Al-3 wt%Si alloys.

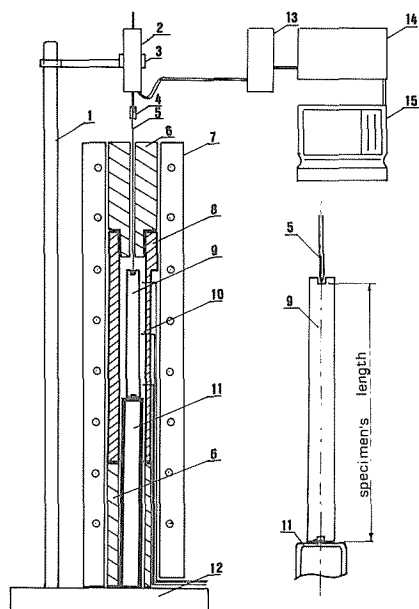


Fig. 3 Experimental apparatus for solid density measurements.

1; steel stand, 2; differential transformer, 3; clamps, 4; rubber joint, 5; silica glass rod, 6; graphite block, 7; electrical furnace, 8; copper block, 9; specimen, 10; thermocouples, 11, silica glass stand, 12; isolite base, 13; mv converter, 14; data logger, 15; computer.

Ingots were cast in a copper mold having 60 mm outer diameter and 20 mm inner diameter. The length of the cast ingots was about 150 mm. All the cast ingots were heat treated, at 500°C for 24 hours and cooled slowly in the furnace, to remove any internal stresses and homogenize the solute content. Then specimens were prepared from these cast cylindrical ingots, which had a diameter of 10 mm and length of 100 mm to 102 mm. Each specimen had a hole of 2 mm in depth and of 2 mm diameter, at the top and bottom surfaces. The one at the bottom served as the centering point for the specimen. The top one, as the center, for connecting the specimen to a differential transformer.

The experimental apparatus is schematically illustrated in Figure 3. The specimen was mounted on a silica glass stand. The effective length of the specimen, for measuring the thermal expansion, ranged from 98 mm to 100 mm, from the base of specimen to the point where the silica glass rod end touched the specimen. This is also illustrated in figure 3.

The silica glass stand was placed on a

isolite brick. A cylindrical graphite block, of 40 mm outer diameter and 22 mm inner diameter and 100 mm in height, was placed around the silica glass stand. A copper block, of 40 mm outer diameter and 20 mm inner diameter and having a length of 200 mm, was then mounted on the graphite block. It covered 50 mm of the silica glass stand, enclosed the specimen and extended 50 mm above the specimen. The purpose of this block was to homogenize the thermal distribution during the rise of temperature. Three thermocouples were inserted through the holes in the side of the copper block. The tips of the thermocouples were located at about 1 mm from the specimen at 10 mm from the top and bottom of the specimen and around the center of the specimen. A glass rod was then fixed in the hole at the top of the specimen. The lower end of the glass rod was sharpened in such a manner as to touch the center of the specimen, alone without touching the walls of the hole. A graphite block was placed at the top of the copper block. The glass rod, connected to the top of the specimen, passed through a 5 mm diameter hole in the center of the graphite block. An electrical furnace was placed around the apparatus. The furnace had an inner diameter of 42 mm and was 400 mm in height. The specimen was attached to the core of the differential transformer through a silica glass rod.

The differential transformer and all the thermocouples were connected to the computer, through a data logger and the furnace was controlled by an automatic temperature regulator, for constant heating of the specimen.

The furnace was heated at a rate of about 4°C/min. The temperature was raised to 640°C for pure aluminum specimens, which is 20°C below its melting point, and up to 555°C for Al-1, 1.5, and 3 wt%Si alloy specimens, which is 22°C below the eutectic temperature of the Al-Si alloys. Expansion and temperature, were automatically recorded at 10 seconds intervals.

With the rise in temperature there was also an expansion of the silica glass stand, and of the silica glass rod. To eliminate the influence of these expansions, a blank test of the apparatus was also carried out.

### 3. Results

#### 3.1 Liquid density

The actual composition of the alloy was determined from the temperature at the start of solidification with slow cooling of the respective alloy.

Calculations of density in liquid state were carried out by knowing the weight and the volume of the melt at a given time. The volume at that time was established by subtracting the contracted volume up to that time, from the initial volume. Density changes corresponding to changes in temperature were established by plotting, at a certain time, the density against the average of the temperatures at the center and the bottom of the melt.

The results are presented in Figure 4. The bottom curve is for Al-1 wt%Si alloy,

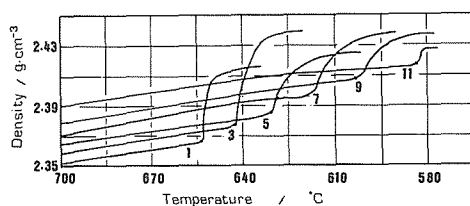


Fig. 4 Liquid densities of Al- 1, 3, 5, 7, 9 and 11 wt%Si alloys, obtained by continuous measurements.

Tabl 1. Liquid density of Al-Si alloys at liquidus temperature.

Composition wt%Si	Liquidus temperature $T_L$ , °C	Density at liquidus $\rho_L$ , g/cm <sup>3</sup>
1.00	654.1	2.366
2.81	642.4	2.378
4.39	631.2	2.385
6.16	618.8	2.397
8.20	604.0	2.408
10.91	583.7	2.418

and moving upwards for Al-3, 5, 7, 9 and 11 wt%Si alloys. Density increases with decreasing temperature, during the liquid state for all of the hypoeutectic Al-Si alloys, and all of the alloys had almost the same density gradient. The density of the alloy changes abruptly after crossing the respective liquidus temperature. The density data after crossing the liquidus, cannot be considered correct, since it does not take into account the pores formed or the solid contraction of the ingot.

Liquid densities at the liquidus temperature of the respective alloys can be obtained from figure 4. These values are given in Table 1. The first column shows the Si composition of the Al-Si alloys, the second column shows their respective liquidus temperatures and the third column shows the density at liquidus temperatures for the respective alloys.

The relationship between the liquid density,  $\rho_L$ , at corresponding liquidus temperature,  $T_L$ , representing the composition of the respective alloys, was established as follows:

$$\rho_L = 1.862 + 2.46 \times 10^{-3} \times T_L - 2.59 \times 10^{-6} \times T_L^2 \quad (2)$$

By using the same contraction data, it was also possible to calculate the volumetric contraction coefficient,  $\beta$ , as defined in equation (3) below:

$$\beta = (V_T - V_L) / [V_L \times (T - T_L)] \quad (3)$$

where,

$T$ ; temperature above the liquidus  $V_T$ ; volume at temperature  $T$

$V_L$ ; volume at liquidus temperature

The value of  $\beta$  for all the alloys was approximately equal to  $1.24 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ .

The approximate density,  $\rho$ , of an alloy at a certain temperature  $T$  above the liquidus, can also be established by using the following relationship, knowing the liquid density at the liquidus,  $\rho_L^*$ , liquidus temperature and the volumetric expansion coefficient  $\beta$ , of the alloy:

$$\rho = \rho_L^* / [1 + (T - T_L) \times \beta] \quad (4)$$

### 3. 2 Solid density

Solid densities at room temperature (20°C), were measured for three samples each, for the specimens of pure Al and Al-Si alloys having silicon concentration of 1, 1.5

and 3 wt%. The samples were forged to eliminate any microporosity. Densities of these samples were determined by using the Archimedes method and then the density at room temperature of the respective specimens was determined by taking the average value of the three samples for each silicon concentration. The values for the respective alloys, are given in Table 2. The first column shows the silicon composition of the alloys, the second—the number of the specimens and the third—density at room temperature. The average density, is given in the fourth column for the respective alloys. The maximum deviation from the average density, for each alloy, is in the range of  $\pm 0.001 \text{ g/cm}^3$ . The density of pure aluminum is equal to the reported values<sup>(4)</sup>.

**Table 2.** Density of Al-Si alloys at room temperature.

Si wt%	No.	Density $\rho$ , $\text{g/cm}^3$	Average Density $\rho$ , $\text{g/cm}^3$
0	1	2.701	2.700
	2	2.699	
	3	2.699	
1.0	1	2.697	2.697
	2	2.697	
	3	2.696	
1.5	1	2.695	2.694
	2	2.694	
	3	2.693	
3.0	1	2.688	2.688
	2	2.688	
	3	2.689	

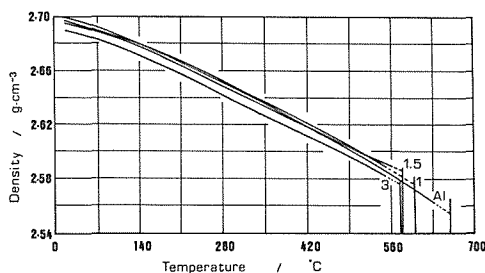
By knowing the linear thermal expansion of the specimen and by using the density at room temperature,  $\rho_r$ , of the specimen as the base point, it was possible to determine the density,  $\rho$ , at a certain temperature, T, by using the following equation:

$$\rho = \rho_r / [1 + (L_T - L_r) / L_r]^3 \quad (5)$$

where  $L_T$  and  $L_r$  are specimen length at temperature T and room temperature, respectively.

The experiments for measuring the expansions of the specimens were carried out up to  $640^\circ\text{C}$  for the aluminum specimen and up to  $555^\circ\text{C}$  for all other specimens. Therefore the density change could only be calculated up to the measured limits and the density curves were extrapolated to the respective solidus temperature of the alloy, in such a way as to determine the solid density of the alloy at the solidus.

The density changes with the rise in temperature for 99.99% Al and Al-Si alloys containing 1, 1.5 and 3 wt% Si, are given in Figure 5. The dashed lines represent



**Fig. 5** Solid density curves determined from the linear expansion data for Al, Al-1 wt%Si, Al-1.5 wt%Si and Al-3 wt%Si alloy specimens.

**Table 3.** Solid density of Al-Si alloys at solidus temperature.

Composition wt%Si	Solidus temperature $T_s$ , $^\circ\text{C}$	Density at solidus $\rho_s$ , $\text{g/cm}^3$
0	660.0	2.558
1.0	600.0	2.577
1.5	580.0	2.587
3.0	577.0	2.578

the extrapolated data, extended to the vertical lines, marking the solidus temperature of the respective alloys. The established values are given in Table 3. The first column shows the composition of the alloy, the second shows the solidus or eutectic temperature for the respective alloys and the third indicates the corresponding density at that temperature.

By utilizing the solid density values at the solidus of 99.99% Al, Al-1 wt%Si and Al-1.5 wt%Si alloys the following quadratic equation was established for the change in solid density, along the solidus line,  $\rho_s$ , in relation to the solidus temperature,  $T_s$  :

$$\rho_s = 3.383 - 0.227 \times 10^{-2} \times T_s + 0.155 \times 10^{-5} \times T_s^2 \quad (6)$$

The expansion data for the specimens can also be used for calculating the linear expansion coefficient of the specimen as defined by the following equation :

$$\alpha = (L_T - L_r) / [L_r \times (T - 20)] \quad (7)$$

where  $\alpha$  is the linear expansion coefficient from room temperature to temperature T.

Thus, knowing the linear expansion coefficient and the solidus temperature  $T_s$ , and the solidus density,  $\rho_s^*$ , of an alloy, the solid density,  $\rho$ , at any temperature T below the solidus temperature, can also be expressed by the following equation :

$$\rho = \rho_s^* \times \{1 + (T_s - 20) \times \alpha^*\} / \{1 + (T - 20) \times \alpha\}^3 \quad (8)$$

$\alpha$ ,  $\alpha^*$  ; linear expansion coefficients from room temperature to a given temperature T and to the solidus temperature of the alloy  $T_s$ , respectively.

#### 4. Comparison between the present and reported densities

The liquid and solid densities at liquidus and solidus temperatures, respectively for Al-Si alloys, were previously reported by J. D. Edwards<sup>(1)</sup> and by T. Takase<sup>(2)</sup>. J. D. Edwards measured the density in liquid state and extrapolated the data to establish the densities at liquidus and solidus temperatures. T. Takase measured the densities in liquid state, as close as one degree below the liquidus temperature, by holding the liquid metal in a fixed volume and then measuring the weight of the ingot and the volume of the mold. In solid state he measured the density by Archimedes method by

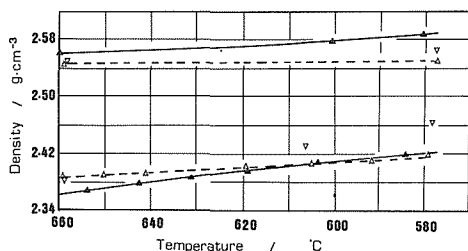


Fig. 6 Comparison between present experimental data and previous data for densities at liquidus and solidus lines of Al-Si binary alloy.

▲-present work    △-T. Takase  
 ▽-J. D. Edwards

measuring the weight of the specimen in a salt bath, of known density, at high temperatures. He measured only the beginning of the solidus i.e. for pure aluminum and for Al-1.65 wt%Si alloy, which is the maximum solubility limit.

The density values obtained by the present study and those obtained by T. Takase and J. D. Edwards are presented in Figure 6 for comparison.

The liquid densities in high solute concentrations obtained in this study are

close to the values reported by T. Takase. In the range of low concentration, his values are higher than that of the present study by  $0.02 \text{ g/cm}^3$ . The deviation may be due to the impurities in aluminum used by T. Takase. Density values presented by J. D. Edwards cannot be considered accurate as he obtained the values by extrapolation of only two specimens.

The values for solid density in the present study are higher than those obtained by either J. D. Edwards or T. Takase. This difference can be attributed to the fact that both of them may have used cast samples having inherent microporosity. Furthermore, in the present study, three points for solid density are established on the solidus line, which makes it possible to predict, more accurately, the density changes during the liquid-solid transformation of the alloys.

### 5. Density changes during solidification

An outline was worked out to express the change in density for any binary alloy. The density of the alloy in the liquid state can be given by the equation (4) and the density of the alloy in the solid state can be calculated from the equation (8).

The density changes in the solid-liquid coexisting zone can be considered as follows:

When solidification occurs, the fraction solid,  $f_s$ , and fraction liquid,  $f_L$ , at any temperature,  $T$ , are known. On the other hand, enrichment of solute occurs with the advance of the solidification front and fall of temperature. The liquid and solid concentrations can be established by the liquidus and solidus lines respectively. If we know the liquid density at the liquidus and the solid density at the solidus, then it is possible to determine the density of the alloy, at a certain temperature  $T$ , in the freezing zone, as expressed in the following equation:

$$\rho = f_s \times \rho_s + f_L \times \rho_L \quad (9)$$

Here the fraction solid,  $f_s$ , can be calculated using Pfann's equation<sup>(5)</sup>, and fraction liquid  $f_L$  as  $f_L = 1 - f_s$ .

Figure 7 shows the density changes of Al-3 wt%Si alloy from the complete liquid state to the complete solid state, passing through the solidification zone, which was calculated by using the equations (4), (8) and (9). The density in the solidification zone increases with decreasing temperature. This tendency is in agreement with that for other aluminum alloys<sup>(1,6)</sup>. The jump in the density at  $577^\circ\text{C}$  marks the change in density due to the transition from the solidification of primary crystals to eutectic solidification.

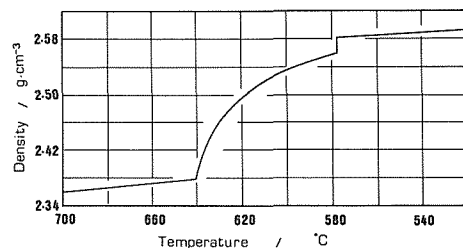


Fig. 7 Density changes for solidifying Al-3 wt%Si alloy.

## 6. Conclusions

Liquid and solid densities for Al-Si alloys were determined by using volumetric and linear expansion methods respectively. The obtained values are considered to be more reliable than the previous reported values<sup>(1,2)</sup> because of the accuracy of measurements by the present methods.

The following quadratic relationships between density and temperature were established for the density values of hypoeutectic Al-Si binary alloy system along the liquidus and solidus lines :

$$\rho_L = 1.862 + 2.46 \times 10^{-3} \times T_L - 2.59 \times 10^{-6} \times T_L^2 \quad (2)$$

$$\rho_S = 3.383 - 0.227 \times 10^{-2} \times T_S + 0.155 \times 10^{-5} \times T_S^2 \quad (6)$$

where  $\rho_L$  and  $\rho_S$  are the liquid density at the liquidus temperature  $T_L$  and solid density at the solidus temperature  $T_S$ , respectively.

An outline is established for calculating the density changes in a binary alloy during solidification. Density changes for Al-3 wt%Si alloy were calculated by using the established outline.

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