Volume Change Effects during Solidification of Alloys

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Doctoral Thesis

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I would like to dedicate this work to:
Maryam,
Alí
Abstract

Volume change during solidification is an important concept in achieving of casting soundness. The solidification shrinkage can cause different defects in the ingot casting as well as the shape casting. The volume change due to phase transformation during solidification is the other concept which has to be studied. In addition, the solidification shrinkage can be affected by the volume change of liquid metals due to the structure change of liquid.

In this work, first, the solidification shrinkage was measured in copper-lead base alloys by a dilatometer which was developed to use for melting and solidification processes. The volume change was measured during primary solidification and monotectic reaction. The macrostructure evaluation of samples was used to explain the volume change results. A shrinkage model was used to explain the volume changes during solidification. In addition, the microsegregation of alloying elements was studied in the alloys.

In the second part, the solidification of brass alloys was investigated in different cooling rates. Microstructure evaluation showed that the peritectic transformation occurred as diffusionless (partitionless) as well as the diffusion-controlled transformation. In addition, the volume change was measured in the peritectic alloys. A theoretical analysis was developed to evaluate the volume change effect on the peritectic reaction.

Hot crack formation was investigated during the solidification of peritectic steels as a volume change concept during the transformation of ferrite to austenite. A series of in situ solidification experiments was performed using a MTS tensile testing machine combined with a mirror furnace to measure the sample temperature and the force change during solidification. It was observed that a rise in tensile force began with the start of solidification and suddenly dropped. The sudden drop of force, which occurred around the peritectic temperature of the alloy, was accompanied by a crack or a refilled crack in the microstructure. Furthermore, the peritectic reaction types were studied theoretically and experimentally to understand their effects on the force change during solidification. The analyses showed that the volume change due to the peritectic transformation is a reason for crack formation. In addition, when the peritectic reaction occurred as a diffusionless manner (partitionless), the crack formation is more probable.

In the last study, the effect of cooling rate and super heat temperature were studied on the precipitation of primary silicon in Al-Si hypereutectic alloys. The liquidus temperature was found to decrease with cooling rate. In addition, the fraction of primary silicon decreased with increasing the cooling rate and the super heat temperature. Furthermore, the morphology of the primary silicon changed as an effect of cooling rate and super heat temperature. It was concluded that the solidification characteristic and silicon morphology relate to the liquid structure.
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Stockholm, 2009
LIST OF PUBLICATIONS

1. On Solidification Shrinkage of Copper-Lead and Copper-Tin-Lead Alloys
   B. Korojy, L. Ekbom, and H. Fredriksson
   In press in:"International journal of cast metals research” (Sep. 2008).

2. Microsegregation and Solidification Shrinkage of Copper-Lead Base Alloys
   B. Korojy, L. Ekbom, and H. Fredriksson
   TRITA –MG 2009:3
   ISRN  KTH/MSE--09/22--SE+CER/AVH

3. On Solidification and Shrinkage of Brass Alloys
   B. Korojy and H. Fredriksson
   In press in:"International journal of cast metals research” (Sep. 2008).

4. Hot Crack Formation during Solidification of Peritectic Steels
   B. Korojy, H. Nassar, and H. Fredriksson
   TRITA –MG 2009:3
   ISRN  KTH/MSE--09/22--SE+CER/AVH

5. A Study of Shell Growth Irregularities in Continuously-Cast 310S Stainless Steel
   H. Nassar, B. Korojy and H. Fredriksson
   Accepted for publication in:" Ironmaking and Steelmaking” (March 2009).

6. On Solidification of Hypereutectic Al-Si Alloys
   B. Korojy and H. Fredriksson
   TRITA –MG 2009:3
   ISRN  KTH/MSE--09/22--SE+CER/AVH
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CHAPTER 1

INTRODUCTION

Volume change during solidification is an important concept in achieving casting soundness. The solidification shrinkage can cause defects in the ingot casting as well as the shape casting, e.g., deformation of the casting, formation of cavities, pipe formation, and shrinkage cracks. In addition, volume change due to phase transformation during solidification is the other concept which has to be studied. Furthermore, the solidification shrinkage can be affected by volume change of liquid metals due to the structure change of liquid. The structural change also influences the solidification process.

In this work, first of all, the solidification shrinkage was measured in copper-lead base alloys by means of a dilatometer which was developed to use for the melting and solidification processes. In the second part, the effect of volume change was studied on the solidification of brass alloy when the alloys have shown a peritectic reaction and transformation during solidification. Then, hot crack formation was investigated during the solidification of peritectic steels as a volume change concept during the transformation of ferrite to austenite. In the last study, the influence of volume change due to the structural change was investigated in the hypereutectic Al-Si alloys. In the following sections the volume change concept will be reviewed in the solidification process of the investigated alloys.

1.1 Solidification shrinkage in copper-lead base alloys

Investigations on copper-lead base alloys show a miscibility gap between copper-rich and lead-rich melts. This creates a monotectic reaction in which a lead-rich liquid is formed. Investigations on the Cu-Pb system shows that the monotectic alloy becomes solid copper (α-phase) and lead-rich melt without any change in volume. In addition,
from the specific volume measurements of monotectic phases, it was predicted that a melt with the monotectic composition would solidify without shrinkage in the Cu-Pb system. In this part of work, the volume change was measured during solidification of the Cu-Pb and the Cu-Sn-Pb systems. To investigate the volume change during solidification, a specific method was developed using a dilatometer (Netzsch DIL 402 C). In addition, differential thermal analysis (DTA) was used to evaluate the precipitation of primary phase and the monotectic temperature. An empirical model was used to explain the volume changes during solidification of copper-lead base alloys.

1.2 Peritectic reaction during solidification of brass alloys

Copper-zinc alloys are produced in a different variety of zinc content. According to the Cu-Zn binary phase diagram, an alloy with zinc content between 32.5 wt.% and 37.5 wt.% solidifies as a single phase followed by a peritectic reaction. In addition, brass alloys are cast in many types of casting processes such as sand, investment, permanent mould, centrifugal, and die-casting. These processes produce castings with different cooling rates, as known as non-equilibrium conditions.

Some studies on copper based alloys show a decrease in the latent heat, the solidus and the liquidus temperatures when the cooling rate increases. However, investigations on some peritectic alloys show that the peritectic temperature increases progressively to above the equilibrium peritectic temperature when the cooling rate increases, but this observation is reversed in some other works.

The effect of cooling rate was studied on the solidification of brass alloys with zinc content between 32.2 and 47.1 wt.% using differential thermal analysis (DTA) and a mirror furnace. The volume change during the solidification of the peritectic alloys was investigated using a dilatometer that was developed for the solidification process. A theoretical analysis was developed to evaluate the volume change effect on the peritectic reaction.

1.3 Hot crack formation during solidification of peritectic steels

It is well known that it is difficult to cast peritectic steels because they are very crack sensitive, for instance continuously-cast peritectic steel contains a large number of surface cracks. As a general practical aspect, hot crack formation in steels is more probable when a transformation takes place from ferrite to austenite. It also claimed that the shrinkage strain induces crack formation at the last stage of solidification in which a liquid film presents. Experimental studies have shown that the peritectic reaction might occur in two different ways. Either by the traditional diffusion controlled process or by a diffusionless transformation process. An assumption is that the later type of reaction gives a much more crack sensitive process. This assumption is based on that the reaction is much faster than the diffusion controlled process and it occurs late in the solidification process, at a temperature where the material is very crack sensitive.

It is difficult to find an experimental method to verify this assumption. In an earlier investigation of peritectic steels, no difference was observed in the stress-strain behavior between steels solidifying primarily austenite and steels solidifying to ferrite. In
the present study, a new experimental method was developed to verify the above given assumption.

**1.4 Solidification of Al-Si hypereutectic alloys**

Primary silicon crystals in Al-Si hypereutectic alloys may display a large range of growth morphologies depending on the solidification condition and the chemical composition, e.g. plate-like primary silicones formed as silicon morphology in the ordinary eutectic structure, octahedral, and star-like morphologies. However, the hopper and dendrite-like crystals are formed at high cooling rate.

X-ray investigations in hypereutectic Al-Si alloys show that the interatomic distance and coordination number of liquid change with super heat temperature. Moreover, it was showed that silicon atoms formed tetrahedral cluster in the melt. Density and fluidity changes were observed in the hypereutectic Al-Si metal during which a minimum in density and a maximum in fluidity occurred in the alloy with 18 wt. % silicon.

Effect of cooling rate and super heat temperature were studied on the solidification of hypereutectic Al-Si alloys. Differential thermal analysis (DTA) was used for a low cooling rate solidification (0.1 Ks\(^{-1}\)). A high cooling rate (50 Ks\(^{-1}\)) was achieved using a mirror furnace. The morphology and fraction of primary silicon were studied in the microstructure of samples.
CHAPTER 2

EXPERIMENTAL METHODS

Different experimental techniques were used in the present work as following:

1. Differential thermal analysis
2. Mirror furnace
3. Dilatometer
4. In situ shrinkage-force measurement
5. Structural characterization

2.1 Differential thermal analysis (DTA)

The DTA equipment, Fig 2.1, consists of a resistance furnace that heats and cools the sample at a controlled rate. A sample of 8 mm diameter and 14 mm height was placed in an alumina crucible which was closed with a lid using a ceramic fastener. The temperature was measured inside the sample using an S-type thermocouple with a shield of alumina. A hallow cylinder of graphite was used as a temperature reference which was placed a few millimeters around the sample. The reference temperature was also measured using an S-type thermocouple. Argon protective gas was flowed through the furnace chamber at slightly higher pressure than the surrounding atmosphere during all experiment. More details of the experimental technique is explained elsewhere. The obtained cooling curves were used to study none-equilibrium solidification processes. In order to study the precipitation of phases during solidification, the sample was quenched to room temperature by letting the crucible fall into a 1 m tall tube filled with water.
2.2 Mirror furnace

Mirror furnace equipment, Fig. 2.2, was used to study solidification behavior at a cooling rate of 7 to 60 Ks\(^{-1}\). Briefly, a typical experiment consisted of holding a sample in a quartz tube inside a mirror furnace with two ellipsoidal mirrors and two halogen lamps and then cooling the sample by blowing argon against the sample. To achieve different cooling rate, some power was put into the lamps during cooling sequence. The temperature was measured inside the sample using a B-type thermocouple shielded with alumina. The details are explained elsewhere\(^{31}\). The samples were protected from oxidation by blowing argon inside quartz tube during the melting process.
2.3 Dilatometer

To investigate volume change during solidification, a specific method was developed using a dilatometer (Netzsch DIL 402 C) which is not ordinarily used for measuring solidification shrinkage. Experiments were done using alumina holder with a cylindrical sample supporter which is made from graphite. Figure 2.3 shows schematic sketch of the sample supporter. In order to evaluate shrinkage during solidification, a molten salt (calcium chloride) was used to avoid sticking between the pistons and the sample. In addition, the molten salt provided permanent contact between the sample and pistons as a lubricant which is necessary for an accurate measurement. The melting point of calcium chloride is around 780°C\textsuperscript{32}. Argon protective gas was passed through the furnace chamber. In order to evaluate the method reliability, the volume change of commercially pure silver (99.5 %) was measured during the solidification and melting process. The measurements were done above the melting point of calcium chloride between 880 and 1020 °C.

![Fig. 2.3: Schematic sketch of the sample supporter.](image)

The experimental result and the tabulated values are presented in Table 2.1. As can be seen, the experimental result agreed reasonably well with the tabulated values. The expansion and contraction of the sample supporter took into account during the calculating of volume change.

<table>
<thead>
<tr>
<th>Cooling and Heating Rate (Ks\textsuperscript{-1})</th>
<th>β Experimental</th>
<th>Tabulated melting volume change\textsuperscript{32}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heating</td>
<td>Cooling</td>
</tr>
<tr>
<td>0.016</td>
<td>3.58±0.14</td>
<td>2.56±0.30</td>
</tr>
</tbody>
</table>

Table 2.1: Experimental and tabulated solidification shrinkage of commercially pure silver, %.
2.4 In situ shrinkage-force measurement

A series of sample was prepared to test using a high temperature tensile testing of in situ solidified samples. The experiments were performed using a MTS tensile testing machine, combined with a mirror furnace, which was used frequently throughout many investigations. The schematic picture of the equipment presents in Fig. 2.4. The mirror furnace consisted of three halogen lamps with ellipsoid, gold-plated reflectors. The lamps were fixed in one focal point, and the sample in the other focal point. The sample had a circular cross section with a diameter of 4 mm (for the Fe-Cu alloy) or 8 mm (for the other alloys). A hole, with a diameter of 1.5 mm, was drilled in the center of each sample to allow a thermocouple to be inserted.

An S-type thermocouple was used to measure the sample temperature and controlled the furnace. Each sample was fixed in the tensile testing machine by water-cooled rods. A quartz tube with argon atmosphere surrounded the specimens to prevent them from oxidation. The machine was set to keep the sample at zero force level until 20 °C below the solidus temperature, and then the tensile testing machine started to measure the force change during melting and solidification processes. The temperature of sample was recorded completely during the process time.
2.5 Structural characterization

The microstructures of the samples were studied by light optical microscopy (LOM) and scanning electron microscopy (SEM). The LOM was a Leica DMRM microscope equipped with Qwin V3 image analyser software for measuring the volume fraction of phases and evaluating the microstructure of samples. The SEM analyses were performed using a scanning electron microscope (JEOL-JSM840) with a LINK (Isis) energy dispersive analysis system (EDS) to evaluate microsegregation of alloying elements during solidification as well as the chemical composition of phases. As a reference pure cobalt was used. In order to chemical analysis mapping, an electron probe micro analysis (EPMA) was used. The samples were prepared for metallography by mounting in bakelite (conductive bakelite for the SEM analyses), grinding, and polishing with 1µm diamond paste and finally etching. According to the composition of the alloys, different etching solutions were used which are given in Table 2.2.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Etching solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper alloy:</td>
<td></td>
</tr>
<tr>
<td>Brass, Cu-Pb, Cu-Pb-Sn, Cu-Pb-Sn-Zn.</td>
<td>FeCl₃ 5gr+HCl 10ml+ H₂O 100ml.</td>
</tr>
<tr>
<td>Low alloy steel:</td>
<td></td>
</tr>
<tr>
<td>Fe-Cu, 4HS64, 22378, 22001.</td>
<td>HNO₃ 2ml+ Ethanol 98ml.</td>
</tr>
<tr>
<td>Stainless steel:</td>
<td></td>
</tr>
<tr>
<td>AISI310S.</td>
<td>HCl 50ml+H₂O 50ml at 80°C.</td>
</tr>
</tbody>
</table>
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Solidification shrinkage in copper-lead base alloys

Experimental alloys were produced in a high frequency induction furnace under an argon atmosphere using a graphite crucible. Pure Cu (99.95%), Sn (99.9%), Pb (99.98%), and Zn (99.9%) were used as starting materials to minimize trace element effects. The alloys were poured into a small cylindrical copper mould. The composition of the alloys is given in Table 3.1.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Zn</th>
<th>P</th>
<th>Sn</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-5Sn-5Pb</td>
<td>-</td>
<td>0.004</td>
<td>5.2</td>
<td>4.7</td>
<td>Bal.</td>
</tr>
<tr>
<td>Cu-5Sn-5Zn-5Pb</td>
<td>4.5</td>
<td>0.006</td>
<td>5.2</td>
<td>4.9</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cu-5Pb</td>
<td>-</td>
<td>&lt;0.004</td>
<td>&lt;0.04</td>
<td>5</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cu-15Pb</td>
<td>-</td>
<td>&lt;0.004</td>
<td>&lt;0.04</td>
<td>15</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

3.1.1 Results

The volume fraction of primary phase was determined in the quenched samples. Figure 3.1 shows the experimental results and theoretical calculations concerning the lever rule for the Cu-Pb system and Scheil’s equation for the Cu-Sn-Pb system. The experimental results showed a higher solid fraction than the calculated solid fraction. Furthermore, the quenched samples were inspected to evaluate the relative fraction of pores that were precipitating during solidification.
Figure 3.1: Experimental and calculated values of solid fraction in Cu-5Pb and Cu-5Pb-5Sn alloys.

Figure 3.2 presents the micrograph and the composition profile of a quenched sample of the Cu-5Sn-5Pb alloy. It shows that the initially-solidified $\alpha$-phase had the lowest tin concentration (1.6 wt. %), and it increased to 3 wt. % during the final part of the primary solidification. The measurements of the composition of lead inclusions showed that tin was not solved in the lead inclusions, which, according to the isothermal ternary phase diagram at 170°C\textsuperscript{35} was expected. The copper content of the lead inclusions varied between 2.5 to 3.5 wt. %.

Fig. 3.2: Composition profile and micrograph of a dendrite cross-section in Cu-5Sn-5Pb alloy quenched from the monotectic temperature.
The chemical composition analysis of the Cu-5Sn-5Zn-5Pb alloy, as is presented in Fig. 3.3, shows an inverse segregation for zinc.

The copper-tin-lead and the copper-tin-zinc-lead alloys were homogenized at approximately 15 degrees above the monotectic reaction temperature for 24 hours and then quenched in water. Table 3.2 gives the chemical composition of different areas on the homogenized samples. This shows that the so-called the partition coefficient of zinc is larger than one, which is the reason for the inverse segregation of zinc during the solidification process.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sn</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-5Sn-5Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary phase</td>
<td>3.25±0.08</td>
<td>-</td>
<td>-</td>
<td>Bal.</td>
</tr>
<tr>
<td>Quenched area</td>
<td>12.39±0.56</td>
<td>-</td>
<td>18.63±2.38</td>
<td>Bal.</td>
</tr>
<tr>
<td>Cu-5Sn-5Zn-5Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary phase</td>
<td>2.77±0.11</td>
<td>4.35±0.14</td>
<td>-</td>
<td>Bal.</td>
</tr>
<tr>
<td>Quenched area</td>
<td>11.98±0.59</td>
<td>2.30±0.12</td>
<td>18.87±2.51</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

The volume change during solidification and melting of the Cu-Pb alloy between the liquidus and the monotectic temperatures was evaluated. The results are given in Table 3.3. It can be revealed that the volume change decreased when the cooling rate increased. In addition, in each run, the volume change during melting of the Cu-Pb alloy was larger than the volume change of solidification. Furthermore, the contraction of the alloy was linear below the monotectic reaction, as is the case for a solid phase. The expansion coefficient measurement showed that increasing the cooling rate decreased the liquid expansion coefficient, whereas the expansion coefficient of the sample below the monotectic temperature increased.
Table 3.3: Volume change and thermal expansion coefficient of the Cu-Pb alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cooling &amp; Heating Rate (Ks⁻¹)</th>
<th>Cooling Melting Solidification Heating Cooling</th>
<th>( \alpha ) Below Monotectic Temperature (K⁻¹) ( \times 10^6 )</th>
<th>Volume Change Between Monotectic and Liquidus Temperature (%)</th>
<th>( \alpha ) (K⁻¹) ( \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-5Pb</td>
<td>0.016</td>
<td>16.23±0.60</td>
<td>3.89±0.04</td>
<td>3.77±0.11</td>
<td>23.05±0.81 23.40±0.94</td>
</tr>
<tr>
<td></td>
<td>0.167</td>
<td>21.26±0.35</td>
<td>3.27±0.33</td>
<td>3.24±0.06</td>
<td>21.46±0.69 19.13±1.05</td>
</tr>
<tr>
<td>Cu-15Pb</td>
<td>0.016</td>
<td>-</td>
<td>3.26±0.01</td>
<td>3.00±0.03</td>
<td>23.03±0.57 19.11±1.77</td>
</tr>
</tbody>
</table>

Table 3.4 gives the volume change of the Cu-5Sn-5Pb alloy during melting and solidification at a rate of 0.016 Ks⁻¹. In the solidification sequence, an expansion was observed below 930°C. The major part of the expansion occurred as the same time as the monotectic reaction, during which a lead-rich liquid is formed.

Table 3.4: Volume change of the Cu-5Sn-5Pb alloy during melting and solidification at a cooling rate of 0.016 Ks⁻¹, %.

<table>
<thead>
<tr>
<th>Melting</th>
<th>Solidifying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Monotectic</td>
<td>After Monotectic</td>
</tr>
<tr>
<td>-1.28±0.09</td>
<td>3.57±0.13</td>
</tr>
</tbody>
</table>

3.1.2 Microsegregation calculation

For the Cu-Sn-Pb system, the volume fraction of the primary \( \alpha \)-phase and the lead content of the monotectic melt can be calculated according to Fredriksson 36. During the primary precipitation of the \( \alpha \)-phase, the concentrations of the alloying elements \( C_{Sn}^L \) and \( C_{Pb}^L \) in the melt are described as:

\[
C_{Sn}^L = C_{Sn}^0 \left( 1 - f_\alpha \right)^{-1 - K_{Sn}^l} \tag{3.1}
\]

\[
C_{Pb}^L = C_{Pb}^0 \left( 1 - f_\alpha \right)^{-1 - K_{Pb}^l} \tag{3.2}
\]

where the initial concentrations of tin and lead are \( C_{Sn}^0 = 5.24 \) wt. % and \( C_{Pb}^0 = 4.76 \) wt. %. To calculate the liquid composition, the partition coefficients \( K_{Sn}^l = 0.368 \) and \( K_{Pb}^l = 0 \) are driven from the binary phase diagrams 37. The results at 900°C are \( f_\alpha = 0.758 \), \( C_{Sn}^L =12.85 \), and \( C_{Pb}^L = 19.67 \). These results are in good agreement with the EDS measurements on the homogenized sample (Table 3.2).

The calculation for the Cu-Sn-Zn-Pb system showed a considerable difference with the experimental values. In fact, when zinc was added to the Cu-Sn-Pb system, the solidification process and microsegregation changed to inverse zinc segregation during the solidification of the primary \( \alpha \)-phase. Therefore, the model, which is based on the behavior of binary system, could not be applied to the Cu-Sn-Zn-Pb system.
3.1.3 Shrinkage calculation

The solidification shrinkage can be described as the sum of four parts. The first part is the shrinkage due to the thermal contraction of liquid to the solid state. The second and third parts are, respectively, the volume change in the solid and the liquid phases. The last part is the volume change due to the change in the liquid composition. The differential Eq. (3.3) expresses the temperature derivative of the total volume:

\[
\frac{dV_{\text{total}}}{dT} = 3\alpha_S V^S_0 (T_0 - T) \frac{df_s}{dT} + 3\alpha_L V^L_0 (T_0 - T) \frac{df_L}{dT} + \beta V^L_0 \frac{df_L}{dT} + \beta^{\text{Comp}} (C_0 - C_L) V^L_0 \frac{df_L}{dT}
\]  

(3.3)

where \( V \) represents the volume and \( \alpha_S \) and \( \alpha_L \) are the thermal expansion coefficients of solid and liquid, respectively. The solid and liquid fractions are \( f_s \) and \( f_L \), respectively. The volumetric expansion coefficient is represented by \( \beta \). \( C_0 \) is the initial composition and \( C_L \) is the liquidus composition, which can be extracted from the Cu-Pb phase diagram\(^{38} \). \( T_0 \) is the liquidus temperature, and \( \beta^{\text{Comp}} \) is defined as a volumetric expansion coefficient that is due to the composition change. \( \beta^{\text{Comp}} \) is calculated using Eq. (3.4):

\[
\beta^{\text{Comp}} = \frac{1}{V^L_0} \frac{\partial V^L}{\partial C}
\]  

(3.4)

Literature data\(^{37} \) give an analytical relation between the specific volume of the melt and its lead content. That is used to calculate \( \beta^{\text{Comp}}_{\text{Cu-Pb}} \) given by Eq. (3.5):

\[
\beta^{\text{Comp}}_{\text{Cu-Pb}} = \frac{1}{V^L_0} \left( 4.34 \times 10^{-6} C^\text{Pb}_L - 4.605 \times 10^{-4} \right)
\]  

(3.5)

The \( \beta \) value is defined using Eq. (3.6):

\[
\beta = \frac{V_L - V_S}{V_L}
\]  

(3.6)

where \( V_L \) and \( V_S \) are defined by Eq. (3.7) and Eq. (3.8) separately:

\[
V_L = V^L_0 \left[ 1 - 3\alpha^L_L (T - T_0) + \beta^{\text{Comp}}_{\text{Cu-Pb}} (C_L - C_0) \right]
\]  

(3.7)

\[
V_S = V^S_0 \left[ 1 - 3\alpha^S_S (T - T_0) \right]
\]  

(3.8)

According to Eqs. (3.5), (3.7), (3.8), the literature data\(^{9,39} \) and the Cu-Pb phase diagram\(^{38} \), the \( \beta \) value can be calculated as a function of temperature, as given by Eq. (3.9):

\[
\beta_{\text{Cu-Pb}} = 8.8 \times 10^{-4} T - 0.8902
\]  

(3.9)

The total volume change of Cu-5Pb alloy was calculated from liquidus to the monotectic temperature by integrating of Eq. (3.3). The experimental values and the calculated volume change of the Cu-5Pb alloy is plotted in Fig. 3.4 as a function of the temperature using data from other studies (as given in Appendix). The difference between the
experimental and calculated values is partly due to the pore formation (e.g., 0.35 Vol.% at 1022 °C) and the difference in the actual and experimental liquidus temperature.

As it mentioned above, the contraction of the alloy was linear below the monotectic reaction. To evaluate the contraction of the alloy below the monotectic temperature, the following relation defined:

$$
dV = f_{L}^{Mono} (V_{L}^{Mono} - f_{S}^{Cu-Mono} V_{S}^{Cu-Mono} - f_{L-Mono}^{Cu-Pb} V_{L-Mono}^{Cu-Pb})
$$

where $f_{L}^{Mono}$ is the fraction of liquid that is contributed in the monotectic reaction. $f_{S}^{Cu-Mono}$ and $f_{L-Mono}^{Cu-Pb}$ are the fraction of the monotectic products that are evaluated from the phase diagram. $V_{L}^{Mono}$ is the specific volume of the melt before the monotectic reaction. $V_{S}^{Cu-Mono}$ and $V_{L-Mono}^{Cu-Pb}$ are the specific volumes of the phases that are produced during the monotectic reaction. The volume change can be calculated using the literature data (Appendix), e.g., the volume change is zero for the monotectic composition in the Cu-Pb system.

Eq. (3.11) gives the total thermal expansion coefficient of the Cu-5Pb alloy below the monotectic temperature:

$$
\alpha_{Total}^{Cu5Pb} = f_{S}^{primary} \alpha_{S}^{Cu} + f_{Mono}^{Mono} \alpha_{Mono}
$$

The thermal expansion coefficient of the monotectic phases, $\alpha_{Mono}$, is given by Eq. (3.12):
\[ 3 \alpha_{\text{Mono}} V_{\text{Mono}} = 3 \alpha_S^C V_S^C \int_{s}^{C} + 3 \alpha_L^C V_L^C \int_{L-Mono}^{C} + \beta^{L-Mono} V_{L-Mono} \frac{df_L}{dT} \]

\[ + \beta_{\text{Cu-Pb}} \left( C_0 - C_{\text{Mono}} \right) V_{L-Mono} \frac{df_L}{dT} \]  

(3.12)

where,

\[ V_{\text{Mono}} = f_{\text{Cu-Mono}} V_0^C \left( 1 - 3 \alpha_S^C \left( T_M - T_{\text{Mono}} \right) \right) + f_{L-Mono} V_{L-Mono} \]

(3.13)

\[ V_{S-Mono} = V_0^C \left( 1 - 3 \alpha_S^C \left( T_M - T_{\text{Mono}} \right) \right) \]

(3.14)

The last term of Eq. (3.12) is the volume change of the liquid after the monotectic reaction, which is calculated from literature data. The total thermal expansion coefficient of the Cu-5Pb alloy is \( 15.9 \times 10^{-6} \) K\(^{-1}\). The calculated \( \alpha_{\text{Cu5Pb}} \) value is lower than the experimental values given in Table 3.3, which are evaluated from non-equilibrium solidification processes, and the difference becomes larger when the cooling rate increases. In order to apply the shrinkage model to the ternary and quaternary alloys, the compositional volume change has to be evaluated for the both systems. The literature data show that the specific volume varies with composition in parallel with the copper-lead alloy when tin and zinc are added to a copper-lead alloy. Thus, \( \beta_{\text{Comp}} \) of the alloys can be calculated by adding the effect of tin and zinc content on the specific volume of the Cu-Pb alloy. Therefore, Eq. (3.3) can now be written as:

\[ \frac{dV_{\text{Total}}}{dT} = 3 \alpha_S V_0^S \left( T_0 - T \right) \frac{df_S}{dT} + 3 \alpha_L^S V_0^L \left( T_0 - T \right) \frac{df_L}{dT} + \frac{df}{dT} \]

\[ + \beta_{\text{Pb}} \left( C_{\text{Pb}} - C_{\text{Mono}} \right) V_0^L \frac{df}{dT} + \beta_{\text{Sn}} \left( C_{\text{Sn}} - C_{\text{Mono}} \right) V_0^L \frac{df}{dT} + \beta_{\text{Zn}} \left( C_{\text{Zn}} - C_{\text{Mono}} \right) V_0^L \frac{df}{dT} \]

(3.15)

where,

\[ \beta_{\text{Pb}} = \frac{1}{V_0^L} \frac{\partial V_L}{\partial C_{\text{Pb}}} \]  

(3.16)

\[ \beta_{\text{Sn}} = \frac{1}{V_0^L} \frac{\partial V_L}{\partial C_{\text{Sn}}} \]  

(3.17)

\[ \beta_{\text{Zn}} = \frac{1}{V_0^L} \frac{\partial V_L}{\partial C_{\text{Zn}}} \]  

(3.18)

Figure 3.5 shows the experimental and theoretical volume change of the Cu-5Pb-5Sn alloy as a function of temperature. Scheil’s equation was used to calculate the solid fraction and
the composition of the liquid. Eq. (3.6) calculates the $\beta$ value of the Cu-5Pb-5Sn alloy when $\nu_L$ is defined by Eq. (3.19):

$$V_L = V_0^L \left[ 1 - 3\alpha^L (T - T_0) + \beta_{Pb}^\text{Comp} (C_{L}^{Pb} - C_0^{Pb}) + \beta_{Sn}^\text{Comp} (C_{L}^{Sn} - C_0^{Sn}) \right]$$

(3.19)

Fig. 3.5: Experimental and modelling results of the solidification shrinkage in Cu-5Pb-5Sn alloy.

### 3.1.4 Discussion

An evaluation of the microstructure of the Cu-5Pb alloy shows that the fraction of solid is larger than the value calculated using the lever rule. The same behavior is observed in the Cu-5Sn-5Pb alloy when Scheil’s equation was use to calculate the fraction of solid. These observations indicate that the solidification process occurred faster than the equilibrium prediction.

A comparison between the calculated and measured values of shrinkage shows that the measured shrinkage during solidification is smaller than the calculated one. As is mentioned above, the solid fraction measured by the quench experiment presented in Fig. 3.1 shows that the volume fraction of the solid during the solidification process is larger than the obtained via equilibrium calculation. This deviation should increase the shrinkage because the solid has a larger density than the liquid. The explanation can be that the solid phase gets a larger volume than the equilibrium one during the solidification process due to the formation of lattice defects. This is also supported by the observation that the thermal contraction is larger than the equilibrium one at temperatures below the monotectic temperature. At these temperatures, it can be expected that the lattice defects condense and give a larger shrinkage. The condensation will contribute partly to shrinkage and partly to the formation of small pores.

The volume change of the Cu-5Sn-5Pb alloy appeared as an expansion when the temperature decreased to the monotectic temperature, because of precipitating a lower-density solid from a higher-density liquid. Therefore, the alloy expands in which the primary solidification shrinkage in the alloy will be partly compensated.
3.2 Peritectic reaction during solidification of brass alloys

In this investigation, brass alloys with zinc content between 32.2 and 47.1 wt.%, were produced in a high frequency induction furnace under an argon atmosphere. Starting materials were pure Cu (99.95%) and Cu 50 wt. % Zn to minimize trace element effects. The alloys were poured into a small cylindrical copper mould. The zinc content of the alloys is given in Table 3.5.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>47.1</td>
</tr>
<tr>
<td>B2</td>
<td>38.9</td>
</tr>
<tr>
<td>B3</td>
<td>36.3</td>
</tr>
<tr>
<td>B4</td>
<td>34.2</td>
</tr>
<tr>
<td>B5</td>
<td>32.5</td>
</tr>
</tbody>
</table>

3.2.1 Results

The solidification parameters evaluated from DTA experiments are given in Table 3.6. As can be seen, the maximum under cooling occurred on alloy B3, which is close to peritectic composition.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>T_L (K)</th>
<th>Liquidus undercooling (K)</th>
<th>T_P (K)</th>
<th>Experimental α-phase (%)</th>
<th>Equilibrium α-phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>1150-51</td>
<td>4-5</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B2</td>
<td>1163-66</td>
<td>7-10</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B3</td>
<td>1174-76</td>
<td>10-12</td>
<td>1164-66</td>
<td>18.8±0.6</td>
<td>11.6</td>
</tr>
<tr>
<td>B4</td>
<td>1188-95</td>
<td>3-10</td>
<td>1154-63</td>
<td>72.6±0.7</td>
<td>60.4</td>
</tr>
<tr>
<td>B5</td>
<td>1202-03</td>
<td>2-3</td>
<td>1163</td>
<td>81.3±0.6</td>
<td>100</td>
</tr>
</tbody>
</table>

In Fig. 3.6, the peritectic temperature is plotted as a function of the cooling rate of the liquid. The maximum under cooling of the peritectic reaction occurred at the cooling rate around 10 Ks⁻¹, and then the peritectic temperature increased to near the equilibrium peritectic temperature at a cooling rate around 50 Ks⁻¹. However, in alloy B5, the solidification progressed without any peritectic reaction at a cooling rate of 46 Ks⁻¹.
The microstructure evaluation of DTA samples showed that the α-phase and the β-phase were observed in B5 alloy which is expected to solidify as a single α-phase according to equilibrium phase diagram. It shows that the composition of the peritectic line was changed to the lower zinc content. In addition, the peritectic reaction started from at least 10 degrees below the equilibrium peritectic temperature when the alloy solidified at a cooling rate of 0.16 Ks⁻¹. Figure 3.7 shows the microstructure and the microprobe mapping result of alloy B4 that was quenched from peritectic temperature during the solidification at a cooling rate of 0.16 Ks⁻¹. As can be seen, the β-phase formed as a partitionless peritectic reaction accompany with a diffusional reaction. The partition less type was not observed in B3 alloy at different cooling rates. In the higher cooling rate, alloys B4 and B5 had shown both the partitionless and the diffusional peritectic reactions, Fig. 3.8. The amount of partitionless reaction decreased in B4 and B5 alloys when the cooling rate was increased to 20 Ks⁻¹. However, the partitionless reaction increased when the cooling rate reached to the highest value (51 Ks⁻¹) in the alloy B4.
Fig. 3.8: Microstructures of B5 sample solidified at a cooling rate of 20 Ks\(^{-1}\).

Figure 3.9 presents the volume change of alloys B3 and B4 during solidification. The alloy B4 showed an expansion around 0.4 vol. % after a contraction.

### 3.2.2 Discussion

According to the experimental data, the peritectic reaction took place with a volume change due to the density difference between the \(\alpha\)-phase and the \(\beta\)-phase. The volume change can create an elastic strain due to the mismatch \(\Delta\) at the interface given by:

\[
\Delta = \varepsilon_{\alpha} = \frac{|\rho_{\beta} - \rho_{\alpha}|}{\rho_{\alpha}} = \beta
\]

(3.20)

The elastic strain at the interface introduces molar strain energy:
where \( E \) is the elastic modulus and \( V_m \) is the molar volume of the interface. The following equation (3.22) gives the total driving force when the strain energy dissipates in the \( \beta \)-phase:

\[
-\Delta G_{\text{strain}}^{a \rightarrow L \rightarrow \beta} = -\Delta G_{\text{strain-free}}^{a \rightarrow L \rightarrow \beta} + E e_{el}^2 V_m^\beta
\]  

(3.22)

Gibbs free energy of a transformation in a non-ideal system, e.g. the Cu-Zn system, given by\(^{40}\):

\[
\Delta G_i^{a \rightarrow \beta} = G_i^{\beta} - G_i^{a} = -RT \ln \frac{a_i^{\beta/a}}{a_i^{\alpha/a}} = -RT \ln \frac{x_i^{\beta/a}}{x_i^{\alpha/a}}
\]  

(3.23)

where \( G_i^{\beta} \) and \( G_i^{a} \) are the Gibbs free energy of \( i \) component at the \( \alpha \)-phase and \( \beta \)-phase respectively. \( x_i \) is the concentration of \( i \) component in the alloy. \( a_i \) is the activity of \( i \) component. \( \gamma_i \) is the activity coefficient which is assumed to be constant.

The molar strain energy at the interface \( W_{el} \) can be added to Gibbs free energy of each phases which are co-existence in the interface. If the strain energy was added only to the Gibbs free energy of the \( \beta \)-phase, the following equations express the difference in Gibbs free energy of Cu and Zn between the melt and the \( \beta \)-phase:

\[
G_i^{\beta} - G_i^{L} = -RT \ln \frac{x_i^{\beta/L}}{x_i^{\alpha/L}} + W_{el}^{\beta}
\]  

(3.24)

\[
G_i^{\beta} - G_i^{L} = -RT \ln \frac{x_i^{\beta/L}}{x_i^{\alpha/L}} + W_{el}^{\beta}
\]  

(3.25)

In order to calculate the molar strain energy \( W_{el}^{\beta} \) the elastic modulus was estimate using the literature data\(^{41}\) during which the elastic modulus was determined by fitting a line on the existing data and then extrapolating the line to the equilibrium peritectice temperature. The estimated value in the direction \(<111>\) is 146 GPa. The molar strain energy of the \( \beta \)-phase is approximately 17 J/mol\(^{1}\).

Figure 3.10 shows the equilibrium and the strain-modified phase diagrams (dashed lines). As can be seen, the peritectic temperature was decreased around 12 degrees when the strain energy only stored in the \( \beta \)-phase (Fig. 3.10a). A similar observation can be seen when the strain energy was added into the both phases (Fig. 3.10b). This observation is reversed when the strain energy was dissipated in the \( \alpha \)-phase (Fig. 3.10c). Therefore, the elastic strain can change the peritectic temperature. The peritectic temperature deviation depends on the distributing of the strain energy between the \( \alpha \)-phase and \( \beta \)-phase.
Fig. 3.10: Equilibrium and strain-modified phase diagrams.
3.3 Hot crack formation during solidification of peritectic steels

In this study, different iron-based alloys were used. Iron-copper binary alloys, rock tool steel 4HS64 produced at Sandvik, low-alloy steels 22378 and 22001 produced at SSAB Oxelösund, and stainless steel AISI310S produced at Outokumpu. The composition and solidification characteristics of the alloys are presented in supplement 4. The shrinkage force and temperature of sample were measured during solidification.

3.3.1 Results

Rock tool steel 4HS64

Table 3.7 presents the measured drop in force, the temperature at which the drop occurred and the temperature difference between the start and end of the drop for some selected samples. The largest drops in force was observed in samples HS3 and HS8, which exhibited also the lowest change in temperature.

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Cooling Rate (Ks⁻¹)</th>
<th>Supper Heat Temp. (°C)</th>
<th>Holding Time (sec)</th>
<th>Force Drop during Solidification</th>
<th>Force Temp. (°C)</th>
<th>TStart-TEnd (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS3</td>
<td>2.5</td>
<td>1495</td>
<td>60</td>
<td>15</td>
<td>1453.7</td>
<td>0.3</td>
</tr>
<tr>
<td>HS5</td>
<td>Air cooled</td>
<td>1492</td>
<td>180</td>
<td>6</td>
<td>1463.3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1440.2</td>
<td>6</td>
</tr>
<tr>
<td>HS6</td>
<td>Air cooled</td>
<td>1502</td>
<td>420</td>
<td>7</td>
<td>1454.2</td>
<td>2</td>
</tr>
<tr>
<td>HS8</td>
<td>Air cooled</td>
<td>1497</td>
<td>240</td>
<td>17</td>
<td>1466.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Figure 3.11 shows the temperature and force variations during the solidification of samples HS3 and HS5. As can be seen, the rise in tensile force began with the start of solidification, and followed by sudden drops in force. The drops in force occurred at a temperatures close to the peritectic point. Figure 3.12 shows micrographs of the solidified regions of samples HS3 and HS5. Cracks can be seen clearly in the samples HS3 and HS8, whereas a light-colored region, believed to be a crack refilled with melt is seen in the micrograph of sample HS5.
Fig. 3.11: Temperature and force changes during the solidification of samples HS3 and HS5.

Fig. 3.12: Micrograph of samples HS3 and HS5.

The compositions of Si, Mn, Cr, and Ni were mapped along the surfaces of samples HS6 and HS8. Table 3.8 presents the micro segregation evaluation of samples HS6 and HS8 from the mapping results, where $X_{\text{min}}$, $X_{\text{max}}$, and $X_{\text{Ave}}$ represent the minimum, maximum and average compositions in the mapped area. The results showed that in sample HS8 the variations of Cr and Si from the average values were larger than HS6 sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>$X_{\text{max}}$</th>
<th>$X_{\text{min}}$</th>
<th>$X_{\text{Ave}}$</th>
<th>$X_{\text{max}}/X_{\text{min}}$</th>
<th>$X_{\text{min}}/X_{\text{Ave}}$</th>
<th>$X_{\text{max}}/X_{\text{Ave}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS8</td>
<td>Si</td>
<td>0.224</td>
<td>0.041</td>
<td>0.094</td>
<td>5.46</td>
<td>0.44</td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>0.742</td>
<td>0.237</td>
<td>0.33</td>
<td>3.13</td>
<td>0.72</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>2.752</td>
<td>1.066</td>
<td>1.19</td>
<td>2.58</td>
<td>0.89</td>
<td>2.31</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>4.274</td>
<td>2.341</td>
<td>2.96</td>
<td>1.83</td>
<td>0.79</td>
<td>1.44</td>
</tr>
<tr>
<td>HS6</td>
<td>Si</td>
<td>0.392</td>
<td>0.105</td>
<td>0.18</td>
<td>3.73</td>
<td>0.58</td>
<td>2.18</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>0.751</td>
<td>0.386</td>
<td>0.54</td>
<td>1.94</td>
<td>0.71</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>1.891</td>
<td>1.136</td>
<td>1.28</td>
<td>1.66</td>
<td>0.89</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>3.921</td>
<td>2.323</td>
<td>3.10</td>
<td>1.68</td>
<td>0.75</td>
<td>1.26</td>
</tr>
</tbody>
</table>
**Low-alloy steels 22378 and 22001**

In two experiments conducted on samples of low-alloy steel 22378, labeled HA2 and HA4, the melt was rapidly solidified in air. The variation in temperature and tensile force in the two experiments are shown in Fig. 3.13. In the sample HA2, a pre-peak of force was observed at a temperature around 1460°C, close to the peritectic temperature of the alloy (Table 2 in supplement 4), followed by a sudden drop. Whereas, a smaller rise in force was observed at a higher temperature in sample HA4. As can be seen from the micrographs of the two samples, Fig. 3.14, the crack observed in the sample HA2 is larger than in the sample HA4.

![Fig. 3.13: Temperature and force changes during solidification of alloy 22378 samples.](image1)

In alloy 22001, sample labeled HB6, the drop of force was observed at 1380°C close to the peritectic reaction temperature for this alloy. Figure 3.15 shows the solidified microstructures and force change of the sample HB6 and cracking is clearly seen in the sample.

![Fig. 3.14: Micrograph of alloy 22378 samples.](image2)
**Fe-Cu Alloys**

The Fe3Cu samples solidified without any crack formation. It seems the early solidified part was strong enough to resist shrinkage stress. In the Fe7Cu alloy, cracks were observed in the samples which were cooled at 0.16 and 2 Ks⁻¹. The samples ruptured when the cooling rate increased to 16.6 Ks⁻¹ and air cooling condition. The Fe15Cu samples were failed due to rupture during cooling.

**AISI310S Alloy**

According to previous DTA results ⁴², (Table 2 in supplement 4), the alloy AISI 310S solidified as a single primary phase (γ) or through primary precipitation of metastable δ followed by a peritectic reaction and transformation to γ depending on the cooling rate and composition. Figure 3.16 shows temperature and force variations with time during solidification of alloy 310S sample. It can be seen, some small pre-peaks took place during solidification. Figure 3.17 present the microstructure and microprobe analysis of SS3 sample in which the microsegregation pattern of Cr along line 2 is more even than line 1 (Fig.3.17).

![Fig. 3.15: Microstructure and force change during solidification of alloy 22001 sample.](image)

![Fig. 3.16: Temperature and force changes during solidification of alloy 310S sample.](image)
3.3.2 Discussion

3.3.2.1 Theoretical analysis explanation

The shrinkage force measurements show that the force started to increase below liquidus temperature when the fraction of solid part was strong enough to resist shrinkage. In the elastic region, the force amount relates to the elongation according to Hooke’s law. The elongation is due to the shrinkage caused by thermal contraction and volume change during the phase transformation. The following equation expresses the relation between force increasing rate and the cooling rate:

\[
\frac{dF}{dt} = EA(\alpha^T \frac{dT}{dt} + \alpha^{\delta \rightarrow \gamma} \frac{df}{dt})
\]

(3.26)

where, \(F\) is the shrinkage force, \(E\) is the elastic modulus, \(A\) is the cross-section area of solidifying sample, \(\alpha^T\) is the thermal expansion coefficient. \(\alpha^{\delta \rightarrow \gamma}\) the contraction
coefficient due to the phase transformation, \( \frac{dT}{dt} \) is the cooling rate, and \( \frac{df_{\gamma}}{dt} \) is the fraction rate of peritectic transformation.

In order to evaluate the peritectic transformation rate from Eq. (3.26), the literature data was used for \( E = 42 \) GPa \(^{43} \) and \( \alpha^{T} = 14.6 \times 10^{-6} \) K\(^{-1} \). \(^{32} \) \( \alpha^{\delta \rightarrow \gamma} \) was calculated in accordance with the alloys composition \(^{44} \). The cross-section area of solidifying part was set to be 40\( \text{mm}^{2} \). Table 3.9 presents the cooling rate, the force change rates in different samples that were calculated from the force-time curves. It can be revealed that the solidified sample cracked when the force change rate is high enough to overcome the material strength.

The microprobe analysis on the alloy 4HS64 samples (Table 3.8) indicates that the peritectic transformation took place as diffusionless transformation as well as the diffusion controlled one. When the solidification of sample finishes with diffusionless transformation, the sample contraction is fast due to rapidly transformation of \( \delta \) to \( \gamma \) \(^{20} \) in which the sample is very sensitive to the crack formation.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sample</th>
<th>( \frac{dT}{dt} ) (Ks(^{-1}))</th>
<th>( \frac{dF}{dt} ) (Ns(^{-1}))</th>
<th>( \frac{df_{\gamma}}{dt} ) (s(^{-1}))</th>
<th>( \alpha^{\delta \rightarrow \gamma} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4HS64</td>
<td>HS3</td>
<td>3.43</td>
<td>2.03</td>
<td>0.0024</td>
<td>Cracked</td>
</tr>
<tr>
<td></td>
<td>HS4</td>
<td>3.88</td>
<td>3.6</td>
<td>0.0027</td>
<td>Cracked</td>
</tr>
<tr>
<td></td>
<td>HS5</td>
<td>7.53</td>
<td>4.9</td>
<td>0.0053</td>
<td>Cracked</td>
</tr>
<tr>
<td></td>
<td>HS6</td>
<td>2.92</td>
<td>1</td>
<td>0.0021</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>HS8</td>
<td>4.05</td>
<td>2.50</td>
<td>0.0028</td>
<td>Cracked</td>
</tr>
<tr>
<td>22001</td>
<td>HB1</td>
<td>3.75</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>HB5</td>
<td>12.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>HB6</td>
<td>36</td>
<td>3.55</td>
<td>0.028</td>
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</tr>
<tr>
<td>22378</td>
<td>HA1</td>
<td>14.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>HA2</td>
<td>10.56</td>
<td>7</td>
<td>0.0067</td>
<td>Cracked</td>
</tr>
<tr>
<td></td>
<td>HA4</td>
<td>7.8</td>
<td>3.08</td>
<td>0.0050</td>
<td>Cracked</td>
</tr>
</tbody>
</table>

### 3.3.2.2 Theory of fraction rate

Peritectic reaction starts with the precipitation of secondary phase and grows as a shell around the primary phase. When the secondary phase covered the primary phase, the growth of secondary phase continues as a transformation from the primary phase to the secondary phase during which the diffusion of alloying elements through the secondary phase controls the transformation rate.

As it already mentioned, peritectic reaction occurs in a traditional diffusion controlled way \(^{18} \) or by a diffusionless (short-range diffusion) transformation process \(^{19, 20} \). Therefore, to evaluate the diffusionless transformation rate, it seems that the evaluation of peritectic transformation rate could be useful.

Fredriksson et al. \(^{18, 45} \) studied the growth of secondary phase (\( \gamma \)) during the peritectic transformation. They suggested that the total growth rate of \( \gamma \) layer is equal to the sum of
growth towards liquid and into the primary phase (δ). The total growth rate for Iron-m binary system was given by:

$$\frac{\partial d_\gamma}{\partial t} = \frac{\partial d_{\gamma/\delta}}{\partial t} + \frac{\partial d_{\gamma/L}}{\partial t} = \frac{D_m^\gamma}{d_\gamma} \cdot \frac{x_m^{\gamma/L}}{V^\gamma} \left[ \frac{V^\delta}{x_m^{\gamma/\delta} - x_m^{\delta/\gamma}} + \frac{V^L}{x_m^{L/\gamma} - x_m^{\gamma/L}} \right]$$

where $d_\gamma$ is the $\gamma$ layer thickness, $\frac{\partial d_{\gamma/\delta}}{\partial t}$ and $\frac{\partial d_{\gamma/L}}{\partial t}$ are the growth rate of $\gamma$ phase at the $\gamma/\delta$ and the $\gamma/L$ interfaces, respectively, $D_m^\gamma$ is the diffusion coefficient of alloying element $m$ in $\gamma$, $x_m$ is the solute concentration, and $V^\gamma$, $V^\delta$, and $V^L$ are the molar volumes of $\gamma$, $\delta$, and the melt respectively. In order to calculate the fraction of $\gamma$, $\frac{\partial d_\gamma}{\partial t}$ has to be divided by half of the secondary arm spacing, which can be estimated from the cooling rate according to the literature data, and then integrated over time. The growth rate, the fraction rate and the fraction of precipitated $\gamma$ were calculated numerically using Eq. (3.27) for the Fe-C and Fe-Ni systems. According to the experimental observation, the growth rate was calculated from 5 K below the peritectic temperature for the Fe-C system and 10 K below the peritectic temperature for the Fe-Ni system. Figures 3.18 and 3.19 present the calculation results for the Fe-C and the Fe-Ni systems, respectively. As can be seen, the fraction rate of $\gamma$ at the beginning of the transformation is much higher than the end of transformation. The calculations show that the transformation occurs faster when the cooling rate is increased.

The fraction rate of the transformation was calculated as a function of alloy composition in the Fe-C and the Fe-Ni systems. First, the solid fraction was calculated by the lever rule at different compositions using the Fe-C and the Fe-Ni phase diagrams. Second, the solid fraction was used to find the concerning fraction rate from Figs. 3.18 and 3.19 for each cooling rate. Finally, the fraction rate was calculated by multiplication the fraction rate by its solid fraction. The results are shown in Fig. 3.20. The fraction rate decreases when the solute content is increased. It can also be seen, the fraction rate in the Fe-Ni system is much smaller than the Fe-C system due to the difference between the diffusion coefficient of C and Ni in austenite. Furthermore, the fraction rate increases when the cooling rate was increased which means the higher cooling rate corresponds to the higher fraction rate at which the crack formation is more probable.

The fraction rate calculations (Fig. 3.20) indicate that the fraction of primary solidification is the major factor with contributes from the peritectic transformation. When the peritectic transformation occurs in an alloy with around 90 percentage primary solidification, the crack formation due to the shrinkage is more probable than an alloy with small amount of primary phase where any formed crack will be refilled by remaining melt. The difference between the Fe-C system and Fe-Ni system where Ni atoms dissolved substitutionally and C atoms dissolved interstitially, leads us to use Scheil’s equation for calculating the fraction rate. Therefore, the following equation was used based on Scheil’s equation multiplied by cooling rate:
where \( \frac{dT}{dt} \) is the cooling rate, \( T_P \) is the peritectic temperature, \( K \) is the partition coefficient of alloying element between \( \delta \) and \( \gamma \) phases which is equal to 0.91 \(^{48}\), \( f \) is the fraction of peritectic transformation which can be calculated from the migration of austenite towards ferrite given as:

\[
f = \frac{d_{\gamma/\delta}}{f_\delta \lambda_{\text{den}}}
\]

(3.29)

where \( \lambda_{\text{den}} \) is half of the secondary arm spacing according to the cooling rate\(^{46}\), \( f_\delta \) is the fraction of primary precipitation calculated by the lever rule. \( d_{\gamma/\delta} \) is the thickness of austenite immigrated towards ferrite which can be calculated as function of time by integrating Eq. (3.27). The results are presented in Fig. 3.21 where the fraction rate was calculated when the fraction of primary phase (\( \delta \)) was equal to 0.9.

A comparison between the calculated fraction rate from the theoretical analysis and experimental values shows that the experimental values are much smaller than the theoretical values. This could be because of volume creep which is very rapid at high temperature\(^{12}\). In addition, the force change rate and the microstructure of 4HS64 and 22378 samples indicate that there is a correlation between the shape of crack and the force change rate. When the force change rate was lower, a narrow crack formed. Furthermore, the results of microsegregation mapping in 4HS64 samples (Table 3.8) indicate that the peritectic transformation occurred as a diffusionless transformation in the HS8 sample during which Cr and Si segregated into the melt, whereas the sample HS6 showed a diffusion-controlled transformation in which Cr and Si diffused back wards into the ferrite and decreased the segregation ratio. The types of peritectic transformation can change the fraction rate as well as the force change rate.

Recent studies on the solidification of alloy AISI310S showed that the alloy could solidify direct to austenite or to primary metastable ferrite followed by a peritectic reaction to austenite depending on the cooling rate and the composition variations\(^{42}\). Microprobe analysis of alloy AISI310S sample (Fig. 3.17) showed different segregation patterns due to the different solidification behavior in which the primary ferrite precipitated with a rather uniform chromium distribution because of the high diffusivity of Cr in ferrite. The primary ferrite transformed to austenite and was accompanied by shrinkage which could cause a force change in the force-time curves (Fig. 3.16).
Fig. 3.18: Fraction rate and fraction of $\gamma$ during peritectic transformation as a function of time and cooling rates in Fe-C system at 5K under cooling.
Fig. 3.19: Fraction rate and fraction of $\gamma$ during peritectic transformation as a function of time and cooling rates in Fe-Ni system at 10K under cooling.

Fig. 3.20: Fraction rate as a function of composition at the solidified fraction of 0.9.
Fig. 3.21: Fraction rate as a function of time for 0.9 fraction of primary phase in Fe-Ni system according to Scheil’s equation.
3.4 Solidification of Al-Si hypereutectic alloys

Al-Si alloys with composition of 15, 18, and 25 wt. % Si were produced in a high frequency induction furnace and an arc melting machine under an argon atmosphere. The starting materials were pure Al (99.999%), Si (99.999%) to minimize trace element effects. The alloys were cast into a small cylindrical copper mould. The solidification process of the alloys at different cooling rate were studied using DTA (cooling rate of 0.1 Ks⁻¹), and a mirror furnace (cooling rate of 50 Ks⁻¹). In order to evaluate the morphology of primary silicon during solidification, some of the DTA samples were quenched at different temperatures below the liquidus temperature. The effect of super heat temperature was investigated on the primary precipitation of silicon and its morphology. Three different melting temperatures were selected: 50 degrees above the liquidus temperature, 850°C, and 1050°C.

3.4.1 Results

Microstructure

In the Al15Si and Al18Si samples, which were processed at a cooling rate of 0.1Ks⁻¹, most of primary silicon particles nucleated on the lateral surface. The microstructure of Al15Si alloys at different super heat temperatures are shown in Fig. 3.22. As can be seen, the primary silicon morphology changed from the hopper-like to the plate-like crystal when the supper heat temperature was increased to above 850°C. At the super heat of 1050°C, a complex regular structure was formed which is called fishbone structure (Fig. 3.22c). The fishbone silicon morphology has been classified as a pseudo primary phase.

![Fig. 3.22: Microstructure of Al15Si alloys solidified at a cooling rate of 0.1 Ks⁻¹ from the super heat temperatures of: a) 670°C, b) 850°C, and c) 1050°C.](image-url)
The octahedral primary silicon particles were observed in the Al15Si samples which were processed at a cooling rate of 50 Ks\(^{-1}\). In the sample with the highest super heat temperature, the primary silicon particles grew as a fishbone structure. A few octahedral silicon particles were observed which nucleated on the lateral surface.

Silicon dendrite and equiaxed plate-like primary silicon were observed in the Al18Si samples solidified at a cooling rate of 0.1 Ks\(^{-1}\). The octahedral primary silicon particles were found in the Al18Si samples which were processed at a cooling rate of 50 Ks\(^{-1}\). In the sample solidified from the highest super heat temperature, the primary silicon particles grew as fishbone and stare-like morphologies.

In the Al25Si samples solidified at a cooling rate of 0.1 Ks\(^{-1}\) and quenched during solidification, the primary silicon particles were observed as two different morphologies, as shown in Fig. 3.23. The primary silicone particles started to grow in the form of platelike morphology. As can be seen, the primary silicon particles grew as equiaxed plate like in the quenched area. The equiaxed plate-like morphology was found also in the samples which were solidified at a cooling rate of 50 Ks\(^{-1}\).

Figure 3.24 shows the volume fraction of primary silicon versus the super heat temperature in DTA and mirror furnace samples. As can be seen, the fraction of primary silicon decreases with increasing super heat temperature. In the Al18Si alloy, the reduction was more than the other alloys. The fraction of primary decreased when the cooling rate increased. A considerable change did not observe in the primary silicon amount of the Al25Si alloy.

Fig. 3.23: Microstructure of Al25Si alloy quenched from the beginning of primary silicon precipitation.

Fig. 3.24: Primary silicon fraction versus super heat temperature in DTA and mirror furnace samples.
**Under cooling**

The temperature of primary silicon precipitation was evaluated from the cooling curves for the investigated alloys at the low cooling rate. The results are shown in Fig. 3.25. It is observed that the under cooling of primary silicon precipitation increased when super heat temperature increased.

The evaluation of primary silicon precipitation was very hard for Al15Si and Al18Si alloys which were solidified in the mirror furnace at a cooling rate of 50 Ks⁻¹. No nucleation of primary Si could be observed from the cooling curves of these alloys. However, evaluation of the cooling curves showed that the primary solidification started at a temperature between 680°C and 690°C in Al25Si alloy.

![Fig. 3.25: Liquidus temperature versus super heat temperature in DTA samples.](image)

**3.4.2 Discussion**

The morphology of primary silicon in hypereutectic Al-Si alloy was affected by composition, cooling rate, and super heat temperature. The primary silicon particles were nucleated on the lateral surface of sample in the Al15Si and the Al18Si alloys. No correlation was observed between nucleation place and cooling rate as well as super heat temperature, but the morphology of primary silicon changed when cooling rate and super heat temperature were increased. The volume fraction of primary silicon and liquidus temperature decreased with increasing super heat temperature. It indicates that the nucleation of primary Si became more difficult in these alloys as a result of tetrahedral Si-cluster formation in the liquid due to the super heat temperature. Furthermore, the nucleation difficulty of primary silicon leads to grow a large plate-like morphology when the super heat temperature was increased. It is revealed that a few number of silicon nuclei could lead to grow large plate of silicon particles. The precipitation of primary silicones became even more difficult when cooling rate increased to 50 Ks⁻¹ in the Al15Si and Al18Si alloys. In the Al25Si alloy, no correlation was observed between the super heat temperature and volume fraction of primary silicon. However, increasing cooling rate changed primary silicon morphology from a large plat-like to small equiaxed plate-like particle.
CHAPTER 4

CONCLUSION

Volume change measurements in Cu-Pb alloy showed that the solidification shrinkage decreased when the cooling rate was increased. On the other hand, below the monotectic temperature, the thermal contraction of the alloy increased with the cooling rate. The theoretical analysis of shrinkage showed that the measured shrinkage during solidification was smaller than the calculated one. The volume change measurements suggested that the difference between the calculated and the measured values was a result of non-equilibrium solidification.

Thermodynamic analysis of the effect of the elastic strain on the peritectic reaction during solidification of Cu-Zn alloy showed that the peritectic temperature changed when the strain energy was dissipated into the peritectic phases. In addition, the contribution of diffusionless and diffusion controlled peritectic transformation during solidification explained the effect of cooling rate on the peritectic reaction temperature.

Microsegregation studies on peritectic steels indicate that the peritectic transformation could occur as a diffusion-controlled or diffusionless (partitionless) transformation, in which the rate of volume change is higher in the diffusionless than the diffusion-controlled transformation. That leads to higher shrinkage force, which can increase crack formation sensitivity. Furthermore, theoretical calculations of the rate of peritectic transformation for the Fe-C and Fe-Ni systems showed that higher cooling rates resulted to higher rates of peritectic transformation that increased the probability
of crack formation. In addition, the calculations showed that an alloy with a higher ratio of primary precipitated ferrite exhibited a higher transformation rate.

The investigation of the cooling rate and super heat temperature on the solidification of hypereutectic Al-Si alloys showed that the temperature of primary-Si precipitation decreased drastically when the cooling rate and the super heat temperature were increased. In addition, the microstructure evaluation showed that the volume fraction of primary silicon decreased when the cooling rate was increased in the alloys with 15 and 18 wt. % silicon content. It was suggested that the primary silicon precipitation could be affected by the melt structure change due to the super heat temperature.
APPENDIX

Cu-5Pb Alloy

<table>
<thead>
<tr>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{L_{Mono}} = 0.1092 , (cm^3 g^{-1})$</td>
<td>6</td>
</tr>
<tr>
<td>$V_{L_{Cu-Pb}} = 0.099 , (cm^3 g^{-1})$</td>
<td>6</td>
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<tr>
<td>$V_{S_{Cu-Mono}} = 0.1183 , (cm^3 g^{-1})$</td>
<td>9</td>
</tr>
<tr>
<td>$V_{S_{L}} = 0.123 , (cm^3 g^{-1})$</td>
<td>6</td>
</tr>
<tr>
<td>$V_{0_{Cu}} = V_{0_{S}} = 0.119 , (cm^3 g^{-1})$</td>
<td>9</td>
</tr>
<tr>
<td>$\alpha_{L_{Cu-Pb}} = 36.14 \times 10^{-6} , (K^{-1})$</td>
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<tr>
<td>$\alpha_{S_{Cu-Pb}} = \alpha_{S_{Cu}} = 20.3 \times 10^{-6} , (K^{-1})$</td>
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<tr>
<td>$\beta_{Mono} = 0.187$</td>
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<tr>
<td>$C_{L} = -0.287T + 312.4 , (wt.%)$</td>
<td>38</td>
</tr>
<tr>
<td>$C_{Mono} = -0.133T + 213 , (wt.%)$</td>
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<tr>
<td>$V_{L_{Cu-Pb}} = 2.17 \times 10^{-4} C_{oo} - 4.605 \times 10^{-4} C_{oo} + 0.1253 , (cm^3 g^{-1})$</td>
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<tr>
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<tr>
<td>$T_{M} = 1084.87 , (^oC)$</td>
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<tr>
<td>$T_{o} = 1067 , (^oC)$</td>
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<tr>
<td>$C_{o} = 5 , (wt.%)$</td>
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Cu-5Sn-5Pb Alloy

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<td>Exp.</td>
</tr>
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</tr>
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<td>$C_{Sn} = 5.2 \left( wt.% \right)$</td>
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<td>$C_{Pb} = 4.7 \left( wt.% \right)$</td>
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<td>$T_M = 1357.87 \left( K \right)$</td>
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<tr>
<td>$T_\alpha = 1293 \left( K \right)$</td>
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<td>$\beta_{Cu-Sn-Pb} = 2.45 \times 10^{-4} T - 0.2042$</td>
<td>Cal.</td>
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<td>$V_{Cu-Pb-Sn}^L = 2.17 \times 10^{-6} C_S^2 - 4.605 \times 10^{-4} C_S + 1.1810 \times 10^{-4} C_{Sn} + 0.1253 \left( cm^3 g^{-1} \right)$</td>
<td>6</td>
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References


