Rapid solidification behaviour of Fe and Al based alloys

Sathees Ranganathan

Doctoral Thesis

Materials Processing
Department of Materials Science and Engineering
School of Industrial Engineering and Management
KTH – Royal Institute of Technology
Stockholm, Sweden
Sathees Ranganathan, Rapid solidification behaviour of Fe and Al based alloys

Materials Processing
Department of Materials Science and Engineering
School of Industrial Engineering and Management
Royal Institute of Technology, KTH
SE-100 44 Stockholm, Sweden.

TRITA-MG 2009:04
ISSN-1104-7127
ISRN-KTH/MSE--09/58--SE+CER/AVH

© Sathees Ranganathan, November 2009
Rapid solidification behaviour of Fe and Al based alloys

Sathees Ranganathan
Materials Processing, Materials Science and Engineering
Royal Institute of Technology KTH
SE-100 44 Stockholm, Sweden

Abstract

Rapid solidification experiment on Fe-Cr-Mo-Mn-Si-C alloy was performed to investigate metastable phases formed during the solidification. A wide range of cooling rate was used to analyse the sample from melt spinning technique (~10^7 K/s) to water quenching method (~10^2 K/s). A single phase featureless structure was obtained initially in the melt spinning experiment for 77Fe-8Cr-6Mn-5Si-4C alloy. Reduction of C and addition of Mo led to form a complete featureless structure for 2.85 mm rod for 72.8Fe-8Cr-5Mo-6Mn-5Si-3.2C. Subsequent investigation of influence of Mo, Cr and Mn on the single phase featureless structure concludes that 7.5 mm thick complete featureless phase could be formed at 63.8Fe-15Cr-7Mo-6Mn-5Si-3.2C alloy composition. In a separate attempt, powder samples of 40 μm dia. size complete featureless powders were produced for three slightly different compositions for the same alloy system.

Characterisation of the featureless phases reveals that it could be a single phase metastable structure of ε phase or austenitic solid solution with high amount of alloying element dissolved in it. Subsequent heat treatment of this featureless phase of the rod and the powder at different temperatures formed bainitic ferrite with fine carbides dispersed in the austenitic matrix. Hardness values measured on featureless phase found to have influenced by the alloying element specially Mo, Cr and Mn.

In an attempt to improve clean melting condition to extend the featureless phase and to form amorphous, an elliptic short arc lamp vacuum furnace was designed with 10 kW lamp power. Around 30 g of iron based alloy system was melted and cast as a 7 mm rod sample in a copper mould. Design details of new mirror and the lamp furnace are presented.

In a separate study, influence of the melt temperature on Al-Y and Al-Si alloys were investigated by levitaion casting in a silver mould at around 2000 K/s cooling rate. Plate like structure of Al₈Y₃ primary phase was observed at low melt temperature with small percentage of peritectic transformation of Al₈Y₃ and liquid melt into Al₉Y₂. A pre-dendritic star like crystal of Al₁₃Y was observed in a fine eutectic matrix at very high melt temperature. Amount and number of primary Si crystals formed in a unit area during the solidification increases as the melt temperature increases.

Keywords: Rapid solidification, Melt spinning, Metastable phases, Fe based alloys, Al based alloy, Bainite, M₇C₃, Al₈Y₃, Al₉Y₂, Al₁₃Y.
"Risk more than others think is safe. Care more than others think is wise. Dream more than others think is practical. Expect more than others think is possible."

Cadet Maxim
To my mother Sellachchí.....
This doctoral Thesis is based on the following supplements:

Supplement 1
Rapid solidification behavior of Fe-Cr-Mn-Mo-Si-C alloys.
S.Ranganathan, A.Makaya, H.Fredriksson and S.J. Savage

Supplement 2
Influence of Mo in the structure of rapidly solidified Fe-Mo-Cr-Mn-Si-C alloy.
S.Ranganathan, A.Makaya and H.Fredriksson.

Supplement 3
Influence of Cr and Mn on rapidly solidified Fe-Cr-Mo-Mn-Si-C alloy system.
S.Ranganathan and H.Fredriksson.
ISRN KTH/MSE--09/59--SE+CER/ART.

Supplement 4
Investigation of microstructures of a rapidly cooled Fe-Cr-Mn-Si-Mo-C alloy after different heat treatments.
S.Ranganathan and H.Fredriksson.
*Proceedings of the 5th Decennial International Conference on Solidification processing*, UK, July 2007, P 723-726

Supplement 5
Influence of Melt temperature on Rapid solidification of Al-Y and Al-Si alloy system.
S.Ranganathan and H.Fredriksson.
ISRN KTH/MSE--09/60--SE+CER/ART

Supplement 6
Designing of Ellipsoidal high energy Short Arc Lamp Furnace.
S.Ranganathan and H.Fredriksson.
ISRN KTH/MSE--09/61--SE+CER/ART
# Table of Contents

Abstract .................................................................................................................................................. iii  
List of Related Publications ................................................................................................................. ix  

Chapter 1  
1. Introduction ...................................................................................................................................... 1  
1.1 Fe based alloy ............................................................................................................................... 1  
1.2 Al based alloys ............................................................................................................................. 3  

Chapter 2  
2. Experimental Methods ..................................................................................................................... 5  
2.1 Alloy preparation .......................................................................................................................... 5  
2.2 Experimental technique .............................................................................................................. 6  
2.3 Characterisation of samples ........................................................................................................ 8  

Chapter 3  
3. Results and Discussions ................................................................................................................ 9  
3.1 Rapid solidification of Fe based alloys ....................................................................................... 9  
3.1.1 Characterization of featureless phase .................................................................................... 14  
3.1.2 Heat treatment of featureless phase ....................................................................................... 15  
3.2 Rapid solidification of Al based alloys ....................................................................................... 18  
3.2.1 Al-Y alloys ............................................................................................................................ 18  
3.2.2 Al-Si alloys ........................................................................................................................... 20  

Chapter 4  
4. Conclusions .................................................................................................................................... 23  

Chapter 5  
5. Elliptical Lamp Furnace .................................................................................................................. 25  
5.1 Introduction .................................................................................................................................. 25  
5.2 Experimental setup ...................................................................................................................... 26  
5.3 Results and discussions ............................................................................................................... 27  
5.4 Conclusions .................................................................................................................................. 27  

Acknowledgements ............................................................................................................................. 29  
References .......................................................................................................................................... 31
Rapid solidification process (RSP) and formation of metastable phases is said to be started around 1960 after Pol Duwez et al. investigation in which a melt droplet was injected at high speed on a copper target to obtain high rate of heat transfer and to make very thin film of casting [1]. Pol Duwez experiment opened a new area of investigation which created several new methods of RSP techniques to obtain metastable phases [1-5], quasicrystalline [6-7] and amorphous [8-10] materials. There are several techniques used ever since to achieve high cooling rate ranging from $\sim 10^7$ K/s to $\sim 10^3$ K/s by melt spinning [1-6] to metal mould casting [9-11] respectively.

Rapid solidification process enables alloys to be designed largely differ from the equilibrium constitution as expressed by T.S. Srivatsan et al. [12].

- Enhanced compositional flexibility
- Significant extension of solid solubility
- Formation of nonequilibrium or metastable crystalline phases and metallic glasses
- Retention of disordered crystalline structures in normally ordered materials and intermetallic compounds.

However the production and application of the materials are limited to small sizes due to the cooling rates required except for some non ferrous materials where Pd and Zr based bulk amorphous metals have been produced in size of several centimeters [13-14].
1.1 Fe based alloys

Rapid solidification process of Fe based alloys have been given more important due to the nature of application and the properties of this materials. It is reported that Fe based amorphous (metastable) alloys have superior mechanical properties compared to crystalline and non ferrous amorphous alloys as shown in the Fig 1.2 [15].

Fig 1.2: Relationship of Tensile strength or Vickers hardness and Young modulus for various bulk amorphous alloys [15].

Production of Fe based amorphous alloys requires high critical cooling rate compare to the non ferrous based amorphous alloys [15]. It is also reported that other metastable phases also require high cooling rate in the Fe based alloys as reported earlier [4, 5]. Since the required cooling rate is high to form metastable phases, achievable thickness is also very much limited.

Extension of the solubility is reported in rapid quenching experiment for Fe based alloy system. Austenitic phase and ε HCP (hexagonal close pack) phase have been reported to contain maximum of 2.3 wt% C and 4.8 wt% C respectively [3-5]. This kind of compositional flexibility and the extension of solubility help one to design materials with superior properties compare to conventional casting material.

Present work is to design materials with extensive solid solubility to obtain better mechanical and physical properties. Investigation was started on the Fe-Cr-Mn-Si-C alloy system after having observed a small amount of featureless structure in a water quenching experiment [16]. Extensive modification was performed by changing the existing composition and adding new elements into the alloy system in order to optimize the composition to form fully featureless structure.
1.2 Al based alloys

1.2.1 Al-Y alloy

Al based alloys have received much attention due to their good combination of high tensile strength with low density. It has been extensively used in the automotive and aerospace industries. Recent discovery of Al based metallic glasses by RSP methods drew more attention towards this alloy [17-21]. Compared with conventional crystalline aluminum alloys, metallic glasses reported to have higher specific strength with good bend ductility, hardness and corrosion resistance [19, 21].

Al-Y binary amorphous alloy was reported by Inoue et.al for a range of 9-13at% Y in single roller melt spinning experiment for 0.02mm thick ribbon [20]. It is reported that a very high cooling rate, which could be achieved normally by melt spinning technique, is necessary to form the Al-Y binary amorphous alloy [20-21]. Q.Li et.al investigated the formation of the amorphous phase for different super heat temperature for Al-Y system in a melt spinning experiment. They concluded from the xray diffraction analyses (XRD) results that as the super heat increased, atomic distance of the clusters (compounds) formed in the melt decreased by expelling some Al atoms from the cluster and some of these compounds were retained in the solid state due to the high cooling effect [22]. This present work analyses structure formation of Al-Y system for different super heat temperature at around 2000 K/s cooling rate which was achieved by levitation casting in a silver mould.

1.2.2 Al-Si alloy

Al-Si eutectic alloy is widely used for producing various commercial products in foundries because of its cast ability. Generally less than 20% Si is used for automobile and aerospace industry applications [23, 24]. Modification of the Al-Si microstructure has been done by changing liquid structure by adding external elements such as Na in to the melt [25, 26]. Effect of casting parameters or the solidification condition something that discussed very little for Al-Si alloy. W.Wang et.al reported a study of influence of super heat on Al-16Si alloy at a 1000 K/s cooling rate. Although a pre-peak, which indicated cluster formation of Si atoms, was observed in the XRD of Al-16Si melt, it was not found in the solid state at this cooling rate [26].This present work studies about the influence of the super heat on the rapidly solidified structure of Al-18Si and Al-25Si at a cooling rate of around 2000 K/s.
CHAPTER 2

EXPERIMENTAL METHODS

2.1 Alloy preparation

2.1.1 Fe based alloy
Initially master alloy ingots were made in an alumina crucible by high frequency induction melting under argon atmosphere. Relatively high purity of alloying elements were used for the ingot making as follows; Fe (99.6 wt% from Höganäs, Sweden), Cr (99.2 wt% from Alfa Aesar, Germany), Mn (99.9 wt% from Alfa Aesar, Germany), Mo (99.9 wt% Kebo Ab, Sweden), B (99.9%), Si crystals and graphite. Depending on the experimental method different amount of sample were taken from the ingot and used.

2.1.2 Al based alloy
Master alloy of Al-Y and Al-Si alloy system were produced in a vacuum arc melting furnace and high frequency induction furnace respectively. Purity of the starting materials was Al (99.99%), Y (99.99%) and Si crystal. Al-Si system was remelted by arc melting under argon atmosphere and casted as rod samples in a copper mould in castmatic machine before further experiments.
2.2 Experimental Technique

2.2.1 Melt spinning

High frequency induction coil was used for the induction melting as shown in the Fig 2.1. Around 4 g of already prepared alloy was melt inside the quartz tube under argon atmosphere and then forced through a 1mm dia. nozzle by argon pressure on to the rotating copper wheel. Depending on the speed of the wheel, different thickness of the melt spun ribbon was achieved. A copper pipe, which was filled with argon gas, was used to collect the ribbons as shown in the diagram.

![Fig 2.1: Schematic diagram of melt spinning experimental set up](image)

2.2.2 Levitation Technique

Levitation technique was used as shown in the Fig 2.2. A levitation copper coil was used in the high frequency induction furnace for the levitation melting. Ar gas was used to keep the quartz tube and the mould under inert atmosphere. After the levitation melting, melt was dropped in to the mould where it formed around 1mm thickness of casting. An s-type thermocouple was placed at the bottom of the mould to measure the melt temperature.
2.2.3 Metal mould casting (castmatic)

Fig 2.2: Schematic diagram of levitation casting

Fig 2.3: Schematic diagram of castmatic (metal mould) casting
Castmatic or metal mould casting contains melting and casting chambers as shown in the Fig 2.3. It is an automatic instrument. Initially air is removed from the both chambers and then Ar gas is filled into the melting chamber. It is usually performed three times to make sure the high purity melting environment. Then melting starts and continues for exactly one minute until it stops automatically and the melt flows into the mould which is in the casting chamber. Flow of the melt is facilitated by the gravity and the suction created by vacuum in the casting chamber.

2.3 Characterization of samples

Fe based microscopic samples were prepared and etched with 10 vol%HCl, 25 vol%HNO₃ and 65 vol% water. Light optical microscopy (LOM) analyses were performed by Leica DMRM microscope equipped with Qwin V3 image analyzer software. A JEOL-JSM840 Scanning electron microscope (SEM) was used to analyze microstructure and to perform composition analyses by energy dispersive spectroscopy (EDS). Selected area diffraction pattern, bright field image and EDS analyses were performed by Transmission electron microscopy (TEM-JEOL 2000EX microscope) operated at 200kV. X-ray analyses (XRD) were performed on the samples using Cu-Kα radiation. Differential scanning calorimetric (DSC) was used to analyze the samples and to perform heat treatment in a well controlled manner.
CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Rapid solidification of Fe based alloys

Fig 3.1: As-cast structure of 72Fe-8Cr-6Mn-5Si-4C alloy.

Initial investigation was performed with 72Fe-8Cr-6Mn-5Si-4C alloy by levitation casting and the as-cast and levitation sample micro structures are presented in the Fig 3.1. Micro structures contains primary M7C3 carbides, austenite and ledeburite matrix which contains
M$_7$C carbides and austenite. Then levitation experiment was performed in this alloy to investigate the effect of high cooling rate on this alloy. Optical micrograph sample of levitation casting sample is presented in Fig 3.2

![Levitation casting sample of 72Fe-8Cr-6Mn-5Si-4C alloy.](image)

Levitation sample shows a large portion of featureless area (no visible cast structures) at high cooling rate which is measured around 1600 K/s. Primary carbide particles surrounded by a eutectic structure was observed mostly close to the mould wall. It is believed that these carbides might have formed from a heterogeneous nucleation.

In order to avoid the formation of the carbide particles a series of experiments were performed with different carbon content (from 0.8C to 6C) with different RSP methods and the detailed study is presented in supplement-1. However no complete featureless was obtained for any of the carbon content and 3.2C and 4C content samples were showing some positive results. But neither of them showed any complete featureless for any experiment technique.
Fig 3.3: Melt spun ribbon of 72Fe-8Cr-6Mn-5Si-3.2C alloy.

Fig 3.4: Melt spun ribbon of 72Fe-8Cr-6Mn-5Si-5Mo-3.2C alloy.
In an attempt to increase the extent of the featureless phase, Mo was added into the alloy system. This alloying element was reported to increase degree of metastability in rapidly solidified Fe-Cr-Mo-Si-C alloys [27]. Kishitake et al. showed that an increase of the Mo content from 5 to 10wt% in the melt spun alloys containing 10wt%Cr, 1wt%Si and 4 to 5wt% C changed the microstructure from a predominant ε phase to fully amorphous structure at an estimated cooling rate of $6 \times 10^4$ K/s for a ribbon thickness of 80 μm. Another incentive for the introduction of large Mo atoms in the present work was to increase the atomic size mismatch between the elements involved. A high atomic size mismatch has been identified as a factor promotes the appearance of new dense-packed local atomic configurations in the melt, which hinders the reorganization of the atoms during solidification and prevents the formation of equilibrium crystalline structures [15, 28]. Free energy of the alloy system is defined as $\Delta G = \Delta H_f - T \Delta S_f$ where $\Delta H_f$ is enthalpy of formation and $\Delta S_f$ is entropy of formation. Meta-stable phase like glassy phase is achieved generally for low free energy transformation of liquid to solid. Since the multi-component alloy system with different atomic size would have more microscopic state, $\Delta S_f$ is expected to be high and this would ultimately favour the formation of metastable phase [29].

As stated in the literature 5 wt%Mo found to have positive influence of extending metastable phase in the melt spun ribbon as shown in the Fig 3.3 and Fig 3.4. Subsequent experiment with this composition yielded a maximum diameter of 2.85mm featureless rod at 1100K/s cooling rate in a metal mould casting. (Fig 3.5)
Continuous experiment with addition of Mo, Cr and Mn exhibited different size of complete featureless rod for certain compositions and a maximum of 7.5mm dia. rod was obtained for 63.8Fe-15Cr-6Mn-7Mo-5Si-3.2C alloy system as shown in the Fig 3.6-3.8.

Fig 3.7: Featureless phase of 6.5mm dia. rod of 72.8Fe-8Cr-6Mn-5Mo-5Si-3.2C alloy

Fig 3.8: Featureless phase of 7.5mm dia. rod of 63.8Fe-15Cr-6Mn-7Mo-5Si-3.2C alloy
3.1.1 Characterization of the featureless phase

Characterization of the featureless phase was done by DSC, SEM, TEM and XRD technique. DSC test performed on the featureless phase showed an exothermic peak around 600°C which was not observed the as-prepared sample and endothermic peaks observed at around 1100°C for both samples correspond to melting of the alloys as shown in the Fig 3.9. This exothermic peak could be associated with transformation of metastable phase into a stable crystalline phase [30].

EDS analyses performed by SEM analyses showed a homogeneous composition everywhere in the sample indicated that this featureless phase is single phase structure. Selected area diffraction pattern obtained by TEM and XRD analyses results features typical crystalline structure. However the identification of the exact phase by the experiment was not possible since the existing crystalline peaks and interplaner distance measured from TEM does not match with any existing phases. Details study of the XRD and TEM results are presented in supplement 1.
3.1.2 Heat treatment of featureless phase

Featureless samples of 72.8Fe-8Cr-6Mn-5Mo-5Si-3.2C alloy were heated to 590°C, 663°C and 693°C temperatures at 3 K/min heating rate to study the decomposition of the featureless metastable phase. These heat treatment temperatures correspond to the beginning, middle and end of the exothermic transformation observed in the Fig 3.9. Once the target temperature was reached, the samples were cooled at 20 K/min to room temperature. DSC graph pattern of heat treatment is shown in Fig 3.10.

Fig 3.10: DSC graph for heat treatment experiments performed on Castmatic samples of 72.8Fe-8Cr-6Mn-5Mo-5Si-3.2C, heated at 3K/min.

Featureless samples of 72.8Fe-8Cr-6Mn-5Mo-5Si-3.2C alloy were heated to 590°C, 663°C and 693°C temperatures at 3 K/min heating rate to study the decomposition of the featureless metastable phase. These heat treatment temperatures correspond to the beginning, middle and end of the exothermic transformation observed in the Fig 3.9. Once the target temperature was reached, the samples were cooled at 20 K/min to room temperature. DSC graph pattern of heat treatment is shown in Fig 3.10.

Fig 3.11: Optical micrograph of heat treated castmatic featureless (72.8Fe-8Cr-6Mn-5Mo-5Si-3.2C) at 663°C in DSC apparatus.
Microstructure analysis of the samples obtained at those three steps can give an insight into phase changes occurring during the exothermic transformation. A uniformly distributed micrometer scale needle like phases appeared in the featureless matrix. Density of the needles observed to be increasing with the heat treated temperatures. Fig 3.11 shows the needle like structure on heat treated sample at 663°C.

![Fig 3.12: Bright field TEM image for the castmatic sample heat treated at 663°C](image)

The TEM micrograph obtained from the same sample (Fig 3.11) clearly shows the needlelike phase in a uniform matrix. This needle like phases observed in the Fig 3.11 are actually composed of aggregates of parallel light colored fine plates, separated by featureless matrix as in the Fig 3.12. Some dark ovoid-shaped phases can be observed between the plates. This structure is typical that of upper bainite [31]. The aggregates of plates can be identified as sheaves of bainitic ferrite that formed from the featureless matrix. The dark ovoid particles situated between the ferrite plates are carbides precipitated after formation of the ferrite, due to partitioning of the carbon in the remaining matrix.

The gray shaded phase observed in the Fig 3.11 is composed of carbides that nucleated and grew in the carbon-enriched matrix. These carbides are nucleated along the grain boundaries of the matrix phase. These observations indicate that featureless phase decomposes with a structure of bainite and secondary fine carbides upon reheating.

Decomposition of metastable ε phase with a bainitic structure has been reported by Schmidt and Hornbogen in a splat-cooled hypereutectic Fe-C alloy of more than 4.31 wt% C at around 1x10³ K/s cooling rate [3]. However similar kind of fine bainitic structure was formed at low temperature heat treatment from austenitic phase of Fe-1.26Cr-1.89Mn-
0.26Mo-1.46Si-0.98C-0.09V alloy for 10 days [31]. Kishitake et al. reported that though ε and amorphous phase forms for 10Cr-5Mo alloy (rest Fe,~1wt%Si) for more than 4 wt% C at around 1x10^5 K/s, a metastable austenite was obtained for low carbon percentage for lower cooling rates [27]. Investigation of the Mn effect on the featureless phase did not give any promising results in extending the featureless phase. Mn is known to be an autenite stabilizer. These experimental results and the literature reviews indicate that this featureless phase could be a metastable ε phase or austenitic phase.

![Graph showing Vickers hardness values measured on the featureless phase for different Cr and Mo contents.](image)

Fig 3.13: Vickers hardness values measured on the featureless phase for different Cr and Mo contents.

It is generally observed that the hardness values increases with the Cr content except for the 5Mo-15Cr alloy system as shown in the Fig 3.13. 3Mo-10Cr alloy showed very lowest hardness since it was measured in the crystalline area. However hardness measured in the featureless phase showed slightly higher than this value. Addition of Mn into 7Mo-xCr(x-10, 12 and 15) alloy system showed reduction in the hardness values except for 7Mo-15Cr alloy as shown in the Fig 17. Mn was expected to reduce the hardness value by stabilizing austenitic phase which is harder than the ferrite. However the results showed otherwise.
3.2 Rapid solidification of Al based alloys

3.2.1 Al-Y alloy

Table 3.1: Average composition of the phases measured by EDS line analyses on the levitation sample.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Melt Temp.(°C)</th>
<th>Primary phase Avg. composition Al_{x}Y_{y}</th>
<th>Second. phase Avg. composition (Eutectic)</th>
<th>αAl Avg. composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al(wt%)</td>
<td>Y(wt%)</td>
<td>Al(wt%)</td>
</tr>
<tr>
<td>Sample-1</td>
<td>~1050</td>
<td>~44.5</td>
<td>~55.5</td>
<td>~86.7</td>
</tr>
<tr>
<td>Sample-2</td>
<td>~1150</td>
<td>~44.7</td>
<td>~55.3</td>
<td>~86.8</td>
</tr>
<tr>
<td>Sample-3</td>
<td>~1300</td>
<td>~49.8</td>
<td>~50.2</td>
<td>~84.6</td>
</tr>
</tbody>
</table>

Fig 3.14: Scanning electron micrograph of levitation experiment sample of Al-10Y -melt temperature around 1050°C (sample-1).

Identification of the phases was done with the help of EDS analyses by the SEM and the composition analysis results are listed in Table 3.1. As it is observed different kind of metastable phases formed for different melt temperature. In some cases peritectic transformation of the phases were observed as marked in the Fig 3.14.
Morphology of the primary phase changed from plate like structure to star like structure when the temperature of the melt was increased (Fig 3.5). Al rich primary phase is formed as the temperature reach 1300 °C and almost no αAl phase is observed in the matrix. EDS analyses shows that average composition of the eutectic structure contains less Al in sample-3 compared to sample -1&2.

As the melt temperature increases the structures become fine except for sample 2 where some long crystals were noticed. Q.Li et al. supported idea of chemical short range orders in the melt changes with temperature by their melt spinning experiment at two different temperatures. They also reported that inter atomic distance of Y-Al-Y system become smaller by expelling Al atom at high melting temperature [22]. Their argument was supported by our EDS analyses of the eutectic composition which shows decrease in Al concentration as the temperature increases. Grey layer of the eutectic structure would have had Y-Al-Y chemical short range order at low melt temperature and then this would have expelled few Al atoms when melt temperature was increased as suggested by Q.Li. However this was not supported by the primary crystal analysis and the results indicate high Al content as the temperature increases. Since Al₈Y₃ and Al₃Y crystal found in the low and high melt temperature respectively, one could expect that large size of cluster forms at low temperature and then decomposes in to smaller ones at high temperature. One could also suggest that Y atoms are expelled from Al-Y clusters when considering the EDS analyses results and these free Y atoms in the melt eutectic melt might change the eutectic composition to a lower Al concentration which is observed in eutectic structure. High temperature XRD analyses of the melt are required to prove this hypothesis.
3.2.2 Al-Si alloy

Fig 3.16: Levitation melting sample of Al-18Si cooled from ~850°C (left) and Al-25Si cooled from 1350°C (right)

Table 3.2: Number of primary Si crystals and the area percentage of primary crystal at different melt temperature for Al-18Si wt% and Al-25Si wt%

<table>
<thead>
<tr>
<th></th>
<th>~850°C</th>
<th>~1050°C</th>
<th>~1350°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-18%Si</td>
<td>~42</td>
<td>~62</td>
<td>~78</td>
</tr>
<tr>
<td>Area</td>
<td>Not measured</td>
<td>Not measured</td>
<td>Not measured</td>
</tr>
<tr>
<td>Al-25%Si</td>
<td>~74</td>
<td>~150</td>
<td>~265</td>
</tr>
<tr>
<td>Area</td>
<td>~12.66</td>
<td>~10.76</td>
<td>~9.98</td>
</tr>
</tbody>
</table>

According to equilibrium phase diagram only Si and Al phases can be formed during solidification. Primary Si and eutectic matrix of αAl and Si phases were observed in the Fig 3.16. Primary Si adopts different morphology during solidification, presumably, depending on the casting parameters. Facetted and fish bone structures of Si are formed in the 18%Si sample and the faceted crystals is surrounded by a small layer of αAl. There are small bright areas of primary αAl crystals observed mostly in the centre of the sample. Facetted crystals are formed only in low melting temperature sample and totally fish bone structures are observed in the high temperature melt sample. Primary Si and eutectic structure become fine when the temperature of the melt was increased (additional figures are in supplement 5). Edge of the sample which is close to the mould wall shows very fine structure of mostly eutectic and few primary crystals and the thickness of this region
increases as the melt temperature increases. This could be a characteristic of recalcenose of the crystals. However this could not be confirmed by the cooling curve since the temperature measurement frequency is not enough to record these changes.

Number of crystals formed in unit area is increasing as the temperature of the melt was increased in the both Al-18Si and Al-25Si samples and the difference is quite significant in the latter case (Table 3.2).

![Equilibrium phase diagram of Al-Si (continuous line) and expected non equilibrium phase diagram (broken line)](image)

Fig 3.17: Equilibrium phase diagram of Al-Si (continuous line) and expected non equilibrium phase diagram (broken line)

It was reported by W.Wang et.al that hyper eutectic Al-Si melt can form tetrahedral clusters of Si atoms in the melt above 850 °C which was observed by a pre-peak in X-ray analysis in which the melt is heated to maximum 1050°C[26]. Wang further reports that these tetrahedral clusters may decompose into free Si atoms at high temperature for Al-16Si alloy [24]. However the maximum super heat achieved was 110 °C in the experiment where density of the Al-16Si alloy was measured with different super heat.

Tetrahedral cluster decomposition could be supported by the increasing number of primary crystals with melt temperature as shown in Table-3.2. It seems that at low temperature there are many clusters in the melt which might form some agglomeration of the clusters. When the melt solidify at a high cooling rate, these clusters and agglomerates would act as a nuclei and form crystal by growing further by diffusion. This could be observed by a less number of large crystals at low melt temperature. Since these tetrahedral clusters decompose, as reported by Wang, in to free Si atom at high temperature there is no, may be few, tetrahedral Si nuclei to grow as crystal and probably new nuclei has to form during the cooling. This could be observed at high melt temperature samples which have large number of small Si crystals Fig 3.16(right).

Volume percentage of the Si crystals decreases with increasing melt temperature for Al-25wt%Si as shown in the Table-2. It was reported that the volume percentage of Si primary crystals decreases for Al-15Si, Al-18Si and Al-25Si as the melt temperature increases [33]. Al-Si system may not follow the equilibrium phase diagram when it is cooled rapidly. It is believed that equilibrium line of Al-Si phase diagram could be shifted as shown in the Fig.3.17 which would give a low amount of primary Si crystal in a high melt temperature sample as observed in the experimental result (Table 3.2).
4.1 Fe based alloy

The rapid solidification behaviour for alloys in the Fe-Cr-Mn-Si-Mo-C system was investigated for different system and cooling rates. Initially a complete featureless homogeneous phase was obtained for 2.85mm dia. rod for 72.8Fe-8Cr-6Mn-5Si-5Mo-3.2C alloy composition. In an attempt to extend the featureless phase by changing Mo, Cr and Mn yielded around 7.5mm dia. rod with complete featureless phase for 61.8Fe-15Cr-7Mo-8Mn-5Si-3.2C alloy composition. It is understood that featureless phase could be $\epsilon$ phase or austenitic solid solution through the experimental results and the literature review. However still an extensive crystallographic analyses should be performed to find out the exact phase. Heat treatment performed on the featureless phase revealed that bainite and secondary fine carbides starts to precipitate at low temperatures and almost complete around 700°C. Precipitation of bainitic ferrites and fine carbides reveals that the best use of this material could be achieved with suitable heat treatment. High hardness observed in the featureless phase could be exploited to use in high strength materials. Production of featureless powders by water atomizing shows that extension of the featureless phase could be achieved for large dimension by sintering them together. However effect of temperature during sintering has to be investigated.
4.2 Al based alloy

Melt temperature has an effect on the crystallization process of the Al-10at%Y, Al-18wt%Si and Al-25wt%Si alloy. Morphology changes were clearly observed both in Al-Y and Al-Si system as the temperature increases. It is believed that the temperature of the melt affects cluster formations and decomposition in the melt thereby forms different phases in the Al-10Y (wt %) system and also it affects the amount and the number of crystals formation.
CHAPTER 5

ELLIPTICAL LAMP FURNACE

5.1 Introduction
High energy lamps have been used in mainly lighting applications and cinema projectors. Due to its near point source of radiation compare to other lamps such as filament lamp, short arc lamp is well suitable for cinema projector applications. High energy lamps have been used in heating and melting in laboratory equipments [27-29]. In many cases filament lamp or mercury lamp were used since they are risk free compared to xenon arc lamp where high pressure xenon gas is used. C.Lockowandt et.al were using two 300 W filament lamps in a mirror furnace [27] designed by Swedish space agency in their experimental setup where different heating rates are used to analyze the phase transformation. Heating rate is controlled by changing the current through the lamp. D.Soupl et.al used two 5 kW xenon arc lamps to design a vertical optical floating zone furnace by using two ellipsoidal mirrors where floating zone was designed to be in the focal point of the two ellipsoidal mirrors [28]. In another experimental set up, three elliptical mirrors are used to heat the sample in a high temperature properties measuring instrument where sample is kept in the common focal point of the three mirrors [29].

In an attempt to improve the clean melting process to extend the featureless structure or to form amorphous phase by preventing external impurities into the melt, a high energy vacuum short arc furnace was designed in this study. Since the heating source is outside the melting chamber, chances of contamination of impurities from heat source are minimized compare to arc melting. As water cool copper mould was to use as melting
crucible, which can not normally used in induction melting, external contamination is very much low compared to ceramic crucibles. A combination of low vacuum, copper crucible and absence of heating source inside the melting chamber was expected to give a highly clean melting process. Necessary arrangement of the furnace set up and the design details of newly designed elliptical mirror are presented.

### 5.2 Experimental Setup

The short arc Xenon lamps require a special power sources to operate satisfactorily. Since the lamps are operated by direct current (DC), a rectifier which convert alternative current (AC) to direct current was used. The power system is designed by a rectifier power supply and an igniter which have to match with the characteristics of the lamp and the lighting system requirements. Since there were two different power lamps used (4 kW and 10 kW), two different power supply equipment were used in the set up. An elliptical mirror was used to focus the light waves from the lamp on to the sample which is at the focal point of the mirror. Initial experiment setup was designed as shown in Fig 5.1.

![Fig 5.1: Schematic diagram of the lamp furnace.](image)
5.3 Results and Discussions

![Figure 5.2](image1.png) As prepared and rod shaped sample made by using 10000 W lamp furnace

Experiment was performed with the setup shown in Fig 5.1 and the around 30 g of Fe based alloy was melted and cast as shown in the Fig 5.2. However the power needed to melt increased amount of alloy was not possible with this alloy within short time. Although it was possible to melt even more amount alloy, the existing cooling system was not efficient to run the experiment for long. So the furnace setup was replaced by the cinema projector with efficient cooling system. But the elliptical mirror received with the cinema projector was a cold mirror which does not reflect the infrared waves. Since the existing cold mirror has to be changed with another mirror, a new elliptical mirror was designed by considering lamp house space (cinema projector) and the radiation angle of the lamps. A detailed explanation, design details and discussion can be found in supplement 6.

5.4 Conclusion

Idea of using high energy short arc lamp in an elliptical mirror furnace is working well. A small quantity (~30 g) of high melting point alloy (1150°C) was successfully melted and cast as rod in a copper mould. Constructing new elliptical mirror, as designed above, and installing in the furnace setup will be the final step towards designing the lamp furnace. Compared to other melting furnaces including vacuum furnaces, where heating elements which may be the source for contamination are placed inside the melt chamber, this furnace will have clean melt since the heating source is placed out side the chamber. This can be used for bulk amorphous production where clean melt production is very much important.
ACKNOWLEDGEMENTS

I would like to express my deep and sincere gratitude to Prof. Hasse Fredriksson for giving me this opportunity to do PhD studies with an interesting topic. His vast knowledge, inspirational ideas and unique way of thinking have been great value for me.

I also would like to acknowledge Hugo Carlsson Stiftelse foundation and The Iron Matsters Association, Sweden for the financial support of this work. It would not have been materialized without them.

I would like to thank Asst.Prof. Steven Savage who was my one time co-advisor and a co-author during the work in supplement 1. I also like to thank Advenit Makaya for his good co-operation in completing work in the supplement 1, being a nice office mate and a good friend during the time.

My sincere gratitude to all my former and present colleagues at the materials processing division (casting of metals) especially to Bahman Korojy, Hani Nassar, Jonas Åberg and Jan Sarnet for their support and being friendly with me. I am very much thankful to Anders Eliasson for his help and advice during my experimental work.

I like to thank Lena Magnusson for all the help she provided throughout my studies and for kicking my butt in some occasions to wish me ”good luck”. Life would not have been easy in Sweden without her advices in many things.

I also would like to thank my friends who have helped me in various ways to accomplish my studies successfully.

I am very much thankful to my grandmother, aunts, uncles, especially my uncle S.U. Sivabaskaran, and cousins who have been supporting me throughout the studies. I would not have reached this level without their help, support and encouragement.

Last but not least, I express my deepest thanks to my mother and sister for always being there when I needed them most, and for their endless support and love through all these years.

Finally, I like to thank my wife for the patience, support and love she offered me during these years.
REFERENCES