

Solidification of Si and Si-alloys

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11.1 Introduction

Casting process parameters influence the mechanical properties and the product's homogeneity, which in turn affect product quality and cost. This chapter presents fundamental background knowledge on casting processes for MG–Si and iron-silicon alloys with more than 30 wt% Si. The first part covers the thermodynamics of solidification for different ferrosilicon alloys. The second part covers solidification processes, from traditional casting to new methods. The final part presents relevant industrial and academic results on the relationship between the solidification of silicon alloys and product properties.

11.2 Thermodynamics and phase diagram

The phase diagram of the Fe–Si system is shown in Figure 11.1. The temperatures and compositional ranges in this diagram cover the typical values found during tapping of liquid silicon ferroalloys. Recent measurement campaigns at silicon and ferrosilicon plants show that the temperature of silicon is between 1800–2000°C as it leaves the tap hole (Tangstad *et al.*, 2021). The alloy then cools rapidly, due to radiation losses and the low heat capacity of the liquid, reaching a temperature between 1500–1700°C in the ladle.

There are 4 solid phases in the range 30–100 wt.% Si:

FeSi: Often referred to as e-phase, *FeSi* melts at 1410°C.

Fe₃Si₇: This phase, also known as High Temperature *Fe₃Si₇* (HT-*Fe₃Si₇*) or ζ_a -phase in older literature, is characterized by vacancies left by approximately one out of six Fe atoms at elevated temperatures. It is stable between 948–1214°C.

FeSi₂: Stable below 996°C, *FeSi₂* is referred to as the Low Temperature *FeSi₂* (LT-*FeSi₂*) phase or ζ_b -phase in older literature. It can form, together with solid silicon, from the eutectoid reaction at 948°C from *Fe₃Si₇*. Alternatively, it can form from *Fe₃Si₇* together with *FeSi* in a peritectoid reaction.

Solid silicon phase: Solid silicon forms above 50 wt.% Si in the alloy, with pure Si being the nominal composition. Silicon dissolves less than 1 ppm Fe in the solid state (Nakajima and Usami, 2009).

The invariant points in the phase diagrams above 33 wt%Si are the following:

T: 1410°C; <i>FeSi</i> phase melts congruently	$FeSi_{(s)} = FeSi_{(l)}$
T: 1211°C; At 50%Si	$L \leftrightarrow Fe_3Si_7 + FeSi$ (eutectic)
T: 1214°C; At 57%Si	$L_2 \leftrightarrow Fe_3Si_7 + Si$ (eutectic)
T: 1215°C; <i>Fe₃Si₇</i> melts congruently	$Fe_3Si_{7(s)} = Fe_3Si_{7(l)}$
T: 996°C; wt% Si between 33–50%	$Fe_3Si_7 + FeSi \leftrightarrow FeSi_2$ (peritectoid)
T: 948°C; wt% Si above 57%	$Fe_3Si_7 \leftrightarrow FeSi_2 + Si$ (eutectoid)

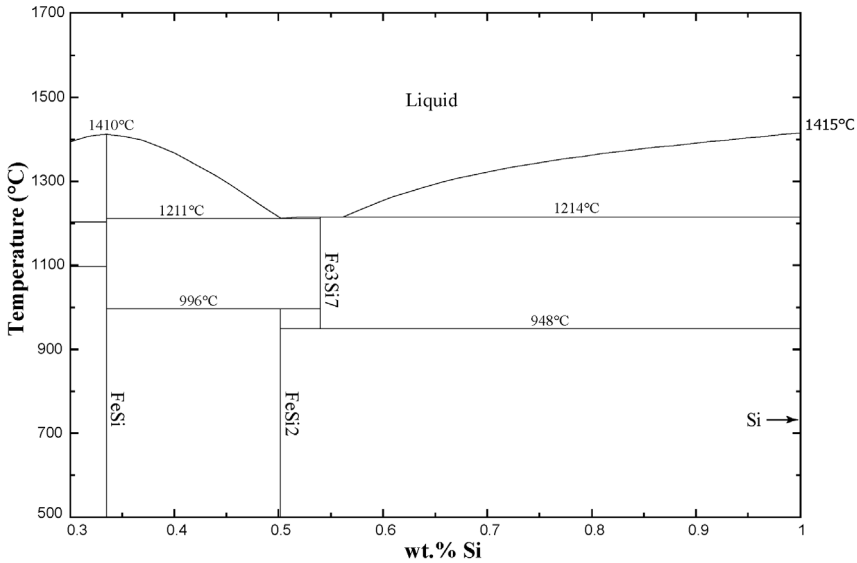


Figure 11.1 Phase diagram of the Fe–Si system (calculated in FactSage).

A solidification path is a diagram that shows the progressive change in the relative fraction of phases present over a temperature interval, as a liquid of known composition is cooled. In this section, the solidification paths for FeSi45, FeSi75 and FeSi92 are shown in Figure 11.2 and described. Other solidification paths may be illustrated using the lever rule in the Fe–Si phase diagram. Figure 11.2 a) shows the solidification path for the FeSi45 alloy, which at low temperatures ends up in the FeSi–FeSi₂ area. At 1295°C, FeSi begins to precipitate from the liquid, and the liquid gradually becomes richer in Si. At 1250°C, the liquid and FeSi are present in a ratio of 4:1. At 1211°C, the liquid is completely converted to Fe₃Si₇ and FeSi in a ratio of 56% to 44%. This situation remains constant until 996°C, where Fe₃Si₇ and FeSi transform into FeSi₂ through the peritectoid reaction.

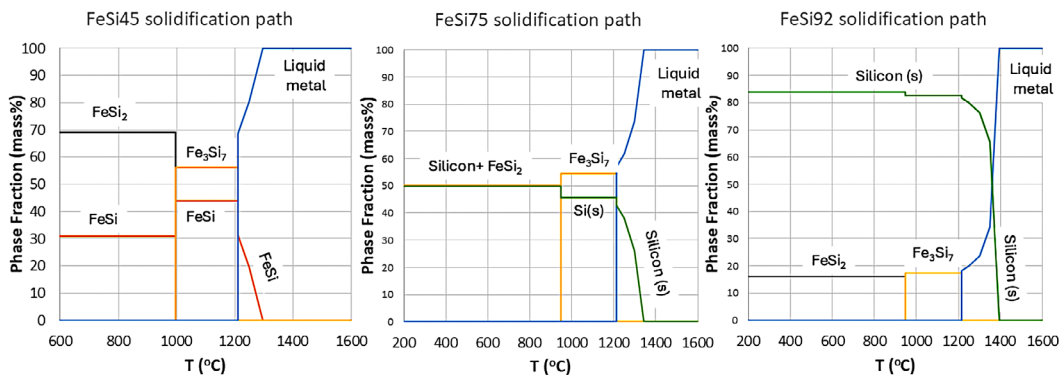


Figure 11.2 Solidification path for FeSi45, FeSi75 and FeSi92 (calculated by FactSage).

FeSi75 and FeSi92 both end up in the silicon and FeSi_2 area at low temperatures, as seen in Figure 11.2 b) and c). FeSi75 starts to precipitate solid silicon at 1344°C , whereas FeSi92 starts to precipitate silicon at 1395°C . Almost pure silicon precipitates due to the low solubility of iron in solid silicon. The liquid gradually becomes richer in Fe until it reaches the Fe_3Si_7 composition at 1214°C . Below this temperature, the liquid phase converts into solid Fe_3Si_7 , with the remainder being the Si phase. The eutectoid reaction from Fe_3Si_7 to FeSi_2 and silicon increases the amount of the Si phase.

Figure 11.3 shows the enthalpy of pure silicon and other FeSi alloys as a function of temperature. For 100% pure silicon, a large amount of thermal energy is released at 1414°C during the phase change from liquid to solid silicon. Normally, small amounts of trace elements like Al, Ca, Fe etc. create a small temperature range for solidification rather than a single point of solidification. The latent heat of silicon is about 7 times higher per ton compared to Fe, and hence, the latent heat of the alloy decreases dramatically when Fe is added to the alloy, as seen in Figure 11.3.

The enthalpy of pure Si at the melting point (1414°C) is 86 kJ/mol , with the latent heat being approximately 50 kJ/mol . Therefore, more than half of the energy is released during solidification, while the rest (approximately 36 kJ/mol) is released during cooling of the solid phase. The amount of thermal energy released during silicon solidification is about 9% of the electrical energy used in the process; hence, there are large possibilities for energy recovery in the industry.

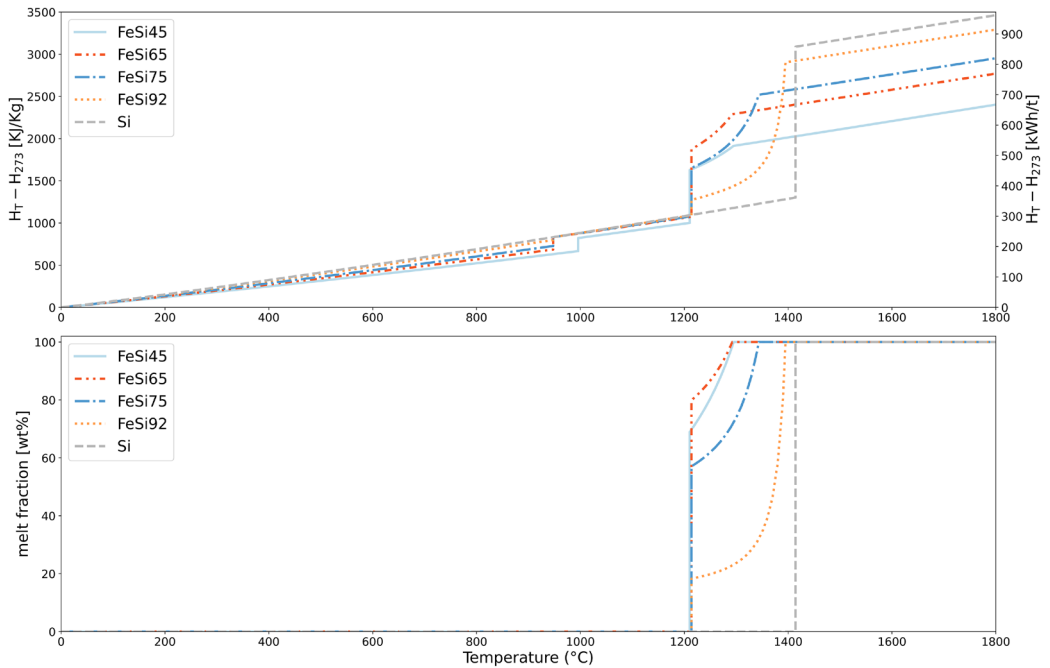


Figure 11.3 Enthalpy of silicon and silicon alloys and the melt fraction as a function of temperature (calculated in FactSage).

11.3 Solidification processes

Product Requirements

The main requirements for silicon alloys are high homogeneity, high strength, high purity and a tailored grain size distribution. Generally, a fast solidification process improves homogeneity and strength due to a smaller grain size and less segregation. Conversely, a slowly cooled cast results in more trace elements being concentrated in the centre of the ingot than at the edges, necessitating additional grinding and sieving steps (Andresen, 2006).

Ideally, shock freezing of the liquid would conserve the distribution of all the elements. However, the significant heat generated during solidification, recrystallization at the liquidus, and diffusion at temperatures above 400°C prevent the ideal distribution from being achieved in any industrial process

(Leblanc *et al.*, 2004). Smaller crystals are more abundant at grain boundaries, allowing a more even distribution of the intermetallic phases in rapid cooling technologies (Margaria, 1994; Baud and Margaria, 1995).

Traditional casting methods for FeSi and silicon

The two traditional casting methods for silicon and ferrosilicon currently in use are casting in iron molds and casting on a bed of Si/FeSi fines (or pieces, as practised in some plants in the USA). In both methods, the main cooling mechanisms are thermal conductivity to the mold and radiation from the top of the cast silicon.

Figures 11.4 and 11.5 show casting in an iron mold. A runner is sometimes used between the transport ladle and the iron mold to reduce the kinetic energy of the liquid metal stream. Casting molds can be either static or placed on belt machinery, with both circular and linear moving casters in use today. The size of the mold (also called beds) typically ranges from 0.5 to 2 meters, with a casting thickness of 5 to 30 mm. A cast iron mold is usually about 100 mm thick. Despite precautions such as using a runner, iron molds undergo significant thermal shock and wear. Additionally, the iron in the mold can dissolve into the Si/FeSi alloy, causing extra contamination.

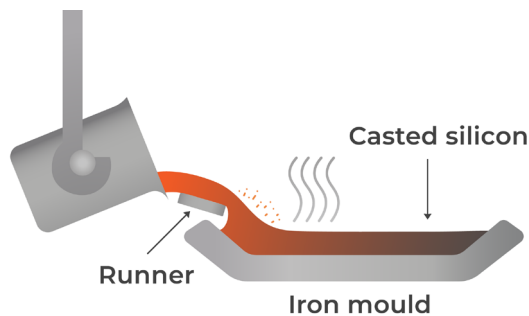


Figure 11.4 *Traditional casting in iron mold.*

Thin casting in beds filled with fines is the most commonly used casting method today. The fines range in size from 0–2 mm and come from the crushing steps of earlier casts (Møll, 2014). This method involves simply pouring

silicon from a ladle into a fines bed and allowing it to cool into a cake. The cake is removed from the mold as soon as possible, ready to be crushed and sieved, typically using a crane or forklift. Cooling of the cake to room temperature takes about 12 hours, according to Leblanc *et al.* (2004).

The lifespan of the mold increases when fines are placed in the bed. The fines protect the mold from wear and protect the alloy from Fe dissolution from the mold walls. However, as stated by Bullon and More, there are both advantages and disadvantages associated with using fines in the process (Bullon and More, 2002). Fines from earlier grinding steps are reused, minimizing waste as much as possible. The fines are recycled in the process because their market value is about 20% lower than that of sized silicon. Each cast can produce up to about 10% of fines. The use of fines, however, increases product inhomogeneity, as they typically contain a higher concentration of impurities. This is a concern for customers who seek the highest purity in their raw materials and want to minimize the fraction of fines. It has been observed that fines introduce more oxygen and impurities into the final product compared to copper casting techniques (Nygaard, 2006). Due to the low thermal conductivity of the fines, a large concentration difference within the ingot may arise. The casting is mainly cooled from the top by radiation and convection, which can induce segregation at the centre of the cast (Tveit, 1988).



Figure 11.5 *Traditional thin casting in mold with silicon fines (Møll, 2014).*

Other common features of traditional casting processes include:

- *Simplicity and Acceptable Quality:* The processes are simple, and the product quality is acceptable. Traditional casting strikes a good balance between product quality and cost. Among the currently available techniques, it requires the lowest initial capital investment in equipment and infrastructure.
- *Long Production Time:* The production time is quite long. It takes approximately 30 minutes to cast and cool the metal in a mold, and several hours before it is taken to the pre-crushing area. This is followed by two crushing processes and at least two sizing processes.
- *High Costs:* Although the initial investment is relatively low, the operating costs are high. It requires a lot of personnel, equipment, material movements, and results in losses (such as fines). This solidification technique is therefore most suitable for smaller, non-automated production where minimizing upfront investment is a priority.
- *Cooling Attempts:* There have been attempts to use water to cool down the cast iron mold. However, this method has proven to be neither practical nor safe for casting silicon (Nygaard, 2006).

Alternative casting methods

Copper casting technologies and water granulation are interesting processes because they offer a good balance between properties and costs. They provide higher homogeneity and cleanliness than traditional cast iron casting methods and require fewer grinding steps. These techniques rely on strong thermal shock during solidification. This can trigger a 'self-grinding' process in the product, influence grain size, and reduce the impurity level. However, it is difficult to find the right balance between the number of grain boundaries and the amount of intermetallic phases (Nygaard, 2006). When it is not possible to tune the particle size through the intrinsic properties of the alloy, a grinding step must be introduced into the process.

Advanced cast-to-shape methods such as atomization or air-granulation technologies are believed to provide higher quality than copper casting. However, they are difficult to implement at industrial scale, due to high maintenance and production costs.

Copper casting

Copper casting consists of casting silicon alloys onto a cooled copper plate. This technique gained attention at the beginning of the 2000s, as described by Bullòn *et al.* (2007). It is defined as ‘the adaptation of the continuous casting technology in steel to the silicon industry’. The ladle is connected to a tilting device, which allows the melt to fall continuously onto the plates. A runner distributes the metal across the full width of the plate. The molten metal meets water-cooled copper and starts to solidify. Vibration of the copper plate causes the metal to move forward. At this point, the metal is already solid (about 1100°C at the bottom surface). When it falls from the copper plate to the first iron plate, the metal starts to break up. Vibrations are then adjusted to transport the alloy along the iron plate while breaking it into pieces. When the silicon leaves the machine, its temperature drops to 500°C. The copper and iron plates remain perfectly clean, and no fines are incorporated into the product. Figure 11.6 shows how the copper casting machine looked in 2002 at the Ferroatlantica plant in Sabon, Spain.

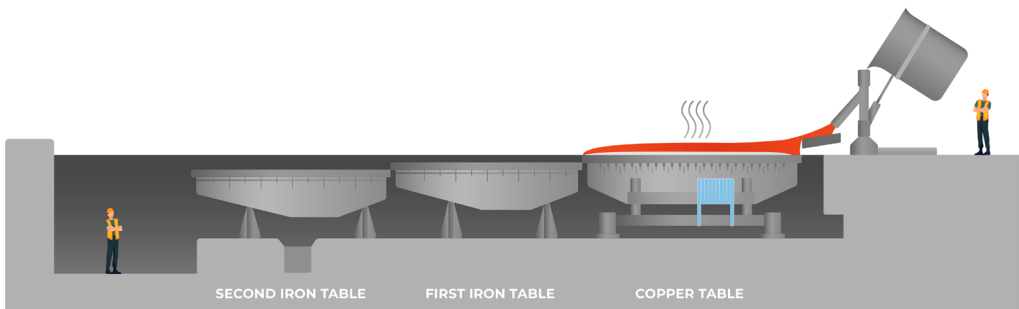


Figure 11.6 Schematic of the copper casting machine at Ferroatlàntica's Sabon plant (Bullòn *et al.*, 2007).

The copper casting process has several advantages:

- *The solidification time is very short.* The whole process takes about 15 minutes, from the ladle to sizing and storage. Solidification on the copper plate takes 30 seconds, the metal then moves from the copper plate less than 5 minutes later, and the remaining time is spent along the remaining two iron plates. By comparison, complete solidification of a single thin cast on fines takes approximately 30 minutes.

- *Copper casting does not have challenging crushing and sieving steps.* Vibration of the copper plates and the strong thermal gradient trigger a 'self-grinding' process. As a result, the expensive and time-consuming grinding steps are not carried out.
- *Copper casting gives a comparable solidification rate to the water granulation* (Andresen, 2006). This implies that copper-cooled silicon does not allow impurities sufficient time to segregate, thereby improving uniformity. In the copper casting machine, grains follow the cooling direction, whereas traditional fines casting results in disorganized crystals with random orientation.
- *No fines are used, and less fines are produced.* A direct consequence of not adding fines is a lower oxygen content in the material, resulting in reduced oxidation caused by fines. In addition, the amount of fines produced by self-crushing is lower. Bullòn and More (2002) report the formation of 3% fines below 5 mm and 1% fines below 1 mm with the copper casting machine, which is significantly lower than the 10% and 4% respectively for < 5 mm and < 1 mm fractions estimated in their study for conventional casting.
- *Improved slag segregation thanks to a slower ladle tilting process.* Thanks to the higher slag viscosity and density, slag remains in the ladle or on the runner instead of falling onto the copper plate, giving a slag content of about 1.22% in the silicon. The percentage of slag fragments in the material larger than 5 mm is lower.
- *The life span of the copper plates is higher compared to the traditional casting technique.* Bullòn and More reported that the machine did not experience significant mechanical erosion after more than 1,000 casts (approximately 40,000 tons of silicon). Primary maintenance involves replacing or turning the copper plate. Due to its symmetry, flipping the plate once it is worn out is sufficient. It was estimated that copper plate replacements add about €15 per ton to the cost of silicon.
- *The installation is easy to automate and optimize.* This implies reduced costs related to personnel, equipment, material movements, and losses in fines. A grinder could be added at the end to achieve finer granulometries. In addition, a load cell was applied under the ladle to tune the flow rate of silicon being cast onto the copper plate. These improvements are described in Bullòn *et al.* (2007).

Water granulation

Water granulation can be used both for silicon and ferrosilicon casting. The process is based on controlled teeming of metal into water. The metal stream from the ladle is split into droplets before reaching the water. The granules are continuously removed from the bottom of the granulation tank for dewatering and drying, before they are screened, stored, and shipped (Leblanc *et al.*, 2004). Plants have operated with either flowing water or still water. Figure 11.7 shows the principal process for water granulation.

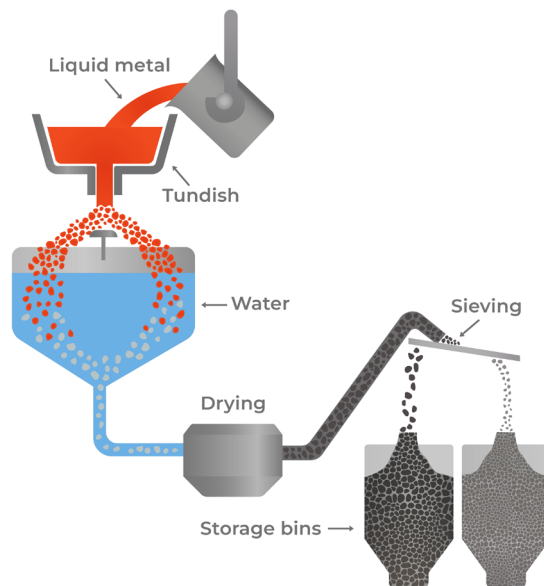


Figure 11.7 Water granulation principle.

The main features of the process can be listed as:

- *Water granulation gives fast solidification compared to other techniques* (Andresen, 2006), resulting in higher product homogeneity and shorter production times. The high heat-transfer rate, combined with the small size of the metal droplets, provides quick solidification and a strong alloy.
- *Water granulation avoids both fines and lumps formation.*

- *There have been problems related to hydrogen formation* since the 1970s, which created uncontrollable explosions (Nygaard, 2006). Studies on the drop formation energy and its effect on the product size distribution were carried out (Nygaard and Brekken, 1994). The intensity of the explosion and the degree of fragmentation during water granulation depend on the Al/Ca content in the molten drop (Hildal *et al.*, 2000). Alloyed specimens release more hydrogen than pure silicon drops, as a higher amount of Al or Ca in the Si-metal enhances the oxidation reaction. The increased level of impurities will, however, prevent steam explosions. Molten silicon drops with small content of Ca and Al descend in the water tank twice as fast as pure silicon drops. The reason for these events is not yet explained; however, this is why many water granulation installations have been shut down.

Cast to shape process

Elkem developed the first cast to shape process in 1995 at Fiskaa Silicon, Norway. Liquid silicon was poured into several rod-shaped molds, machined into the surface of a rotating copper roller. The small rods broke into pieces when they fell out of the molds.

The cast to shape technology was also ‘blended’ with copper casting to further increase the cooling rate. This technique was presented in 2004 by Leblanc *et al.* Sixteen identical copper segments form a huge horizontal rotating wheel. The copper is water cooled through internal channels. Just before one complete rotation, silicon is pushed off the wheel and down into a bin. When the product falls into the bin, it will break ‘as a china plate falling on a hard floor, and very little small splinters or powder will occur’ (Leblanc *et al.*, 2004).

These two casting methods aimed to avoid crushing and screening, and thereby to improve product yield and quality compared to traditional fines casting. The processes looked promising, but high costs were the main reason why cast to shape technology was not brought to industrial scale (Nygaard, 2006). Another issue is the continuous exposure of the casting equipment to immense heat. These casting methods may require stricter temperature and mass flow control, leading to higher levels of automation, more advanced technologies, and greater initial investments.

Atomization in inert gas or air

The atomization process consists of spraying silicon from an atomizer. The droplets freeze very quickly, and a high proportion of intermetallic phases forms at the grain boundaries rather than in primary silicon. A small-scale test for atomization, or ‘granulation in air’, was carried out at Wacker-Chemie in 1992. An air-blowing pipe was directed horizontally towards the liquid silicon, which was falling between the tapping spout and the ladle. As the velocity of the air was increased, the liquid silicon stream began to granulate. Most of the liquid silicon was converted into small drops, which froze to an average size of around 1 mm.

Some features of the atomization process are listed as:

- *It is difficult to tune the silicon particle size with high precision.* Nygaard (2006) quotes, as an example, a plant in Brazil producing about 40% of its particles with a size between 50–200 μm . The rest was coarser than 200 μm and therefore needed a subsequent milling step.
- *The potential properties could not defend the costs,* despite large savings from avoiding casting, crushing and milling. In fact, the technology was implemented at industrial scale without success.
- *Finally, water, air and oxygen must be eliminated* when using inert gas atomization. If they are not removed correctly, drops will be covered in a thick layer of oxide. Oxidation of the final product decreases product quality and brings extra maintenance and machinery costs to the solidification unit.

11.4 Solidification and product properties

Solidification processes

Structure index number (QF) and cooling rate

The chosen solidification process is directly related to the cooling rate. Since the cooling rate cannot be measured in absolute terms, Pachaly (1994) introduced the concept of the Structure Index Number (QF). The higher the QF, the faster the solidification rate and the higher the homogeneity of the material. QF is defined as the ratio between the area portion of the intermetallic phases at the grain boundaries and the area portion of intermetallic phases

in primary silicon. The value is computed after analyzing the structure of silicon samples by image analysis. QF therefore reflects variations in average grain size as the solidification technique changes. Table 11.1 lists some of the QF values estimated by Pachaly for most of the silicon solidification processes described in this book.

Table 11.1 *Structure index number as a function of solidification procedure describing the ratio between the area portion of the intermetallic phases at the grain boundaries and the area portion of inter-metallic phases in primary silicon (Pachaly, 1994).*

Solidification process	QF
Mold cast 50 cm on thick fines layer in isolated mold	0.10
Mold cast 50 cm on thin fines layer in isolated mold	0.25
Mold cast 40 cm on thick fines layer	0.26
Mold cast 40 cm on thin fines layer	1.58
Mold cast 30 cm on thin fines layer	2.34
Mold cast 10 cm on thin fines layer	6.02
Continuous cast 10 mm on copper	10.09
Water granulated 10–15 mm	23.21
Water granulated 5–10 mm	29.55
Air granulated 2–3 mm	42.60
Atomized	63.92

Solidification speed and grain growth in silicon rich-alloys

A model for grain growth has been reported by Kattamis *et al.* (1967). A smaller grain radius has a greater impact on surface tension than a larger grain radius. As shown in Figure 11.8, the dendrite arms are considered to consist of one arm with radius a and a thinner arm with radius r_o . This model appears to accurately represent grain growth in silicon-rich ferro-alloys.

It was found that grain coarsening occurs between 1412.8°C and 1396°C for MG–Si (Kinoshita and Champier, 1981), which is close to the melting point.

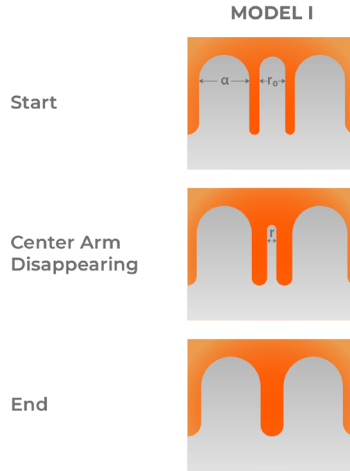


Figure 11.8 Model for coarsening of a dendrite grain structure (adapted from Kattamis *et al.*, 1967).

As grain radius increases, a composition gradient develops in the liquid phase: it is steeper outside a smaller grain than outside a larger grain, which makes the larger grain more stable. In 75% ferrosilicon, the silicon content is higher near the surface of a smaller grain than near the surface of a larger grain. Consequently, silicon diffuses from the smaller grain to the larger grain, stimulating silicon precipitation at the larger grain. Conversely, the reduced silicon content at the surface of the smaller grain may induce some melting of the smaller grain. This process is crucial to the formation of the alloy structure. Kattamis *et al.* (1967) calculated the correlation between the solidification time t_c and the dendrite or grain size d . The effect of the equation on microstructure is illustrated in Figure 11.9.

$$t_c = kd^3 \quad [11.1]$$

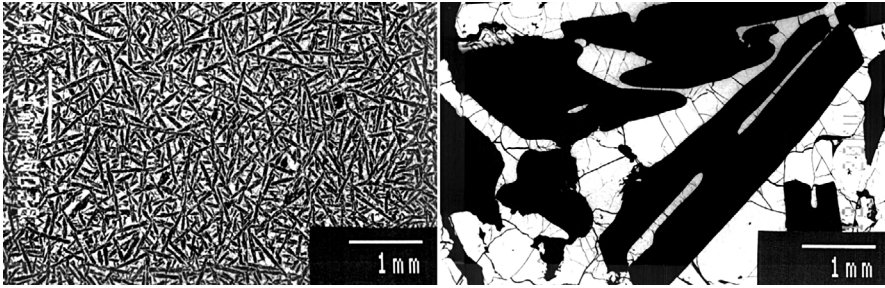


Figure 11.9 Left: Grain size of rapidly solidified ferrosilicon (1170°C/min). Ref. the 1 mm length line. Equivalent grain size is measured to be 59 μm . Right: Grain size of very slowly solidified ferrosilicon (0.21°C/min). Ref. the 1 mm length line. Equivalent grain size is measured to be 784 μm .

By increasing the cooling rate by a factor of 10^4 , the morphological spacing for silicon-rich alloys decreases by an order of magnitude. The relationship is shown in Figure 11.10, which gathers results from Tveit (1988) and Forwald (1997). The cooling rate varied over a long range, either by looking into industrial production or by varying the efficiency of the insulation of the ferrosilicon cast.

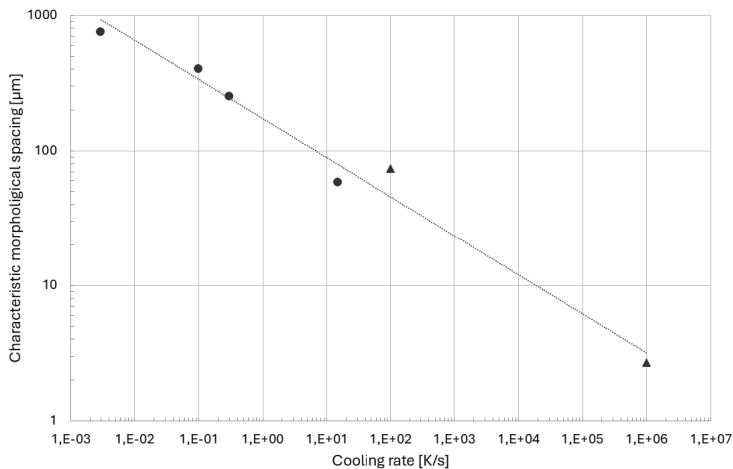


Figure 11.10 Morphological spacing vs. cooling rate for some Si-rich alloys (Forwald, 1997). Legend: 'spheres' = results from (Tveit, 1988); 'triangles' = results by (Forwald, 1997).

The final effect of the cooling rate on the grain size distribution is seen in Figure 11.11. The graph shows the grain size distribution of iron mold cast, water granulated and thin cast silicon metal. The curves for iron mold casting and thin casting are wide compared to water granulation, which has a very steep particle size distribution curve. A steep curve corresponds to more uniform particle size distributions and to a lower fines percentage. Most of the fraction for water granulation is below 3 mm, while the majority for iron mold and fines casting is between 10–100 mm or 7–10 mm, according to the product chosen.

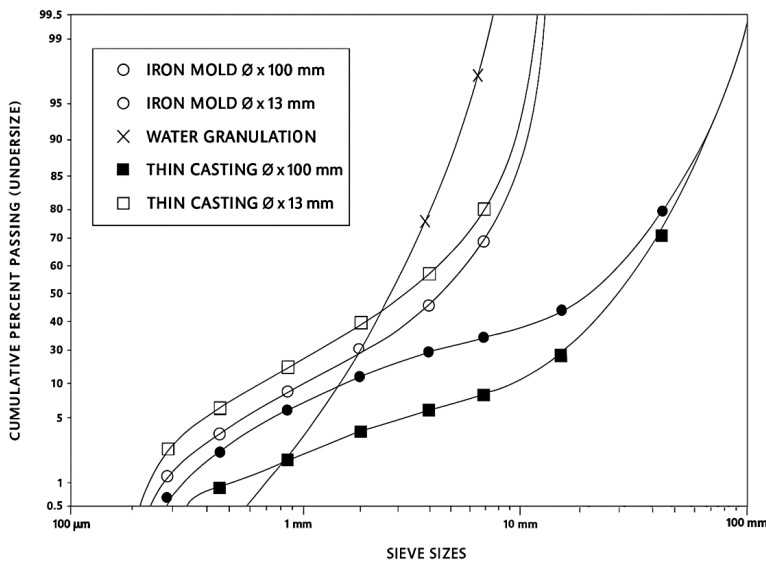


Figure 11.11 Size distribution of conventional casting, water granulation and thin casting (Leblanc et al., 2004).

Casting MG-Si in fines

Most of the impurities in a 10 cm thick cast are found close to the centre, between 5.0–7.5 cm from the top of the cast. It was found that this zone corresponds to the area where the temperature is still high after about 20 minutes of solidification, as shown in Figure 11.12. The position of the impurities is related to the cooling rate at different positions. Møll modelled the temperature at different positions in a 10 cm thick cast during solidification

(Figure 11.13). The positions close to the top and the bottom surface cool fast initially (10 cm, 9 cm, 7.5 cm, 0.5 cm and 1 cm), while the central portion of the cast (3 cm, 4 cm, 5 cm) keeps a higher temperature for longer. The results were also confirmed by characterization of silicon casts at different positions. Figure 11.14 shows the microstructure at the top, the centre and the bottom of the cast. The liquid silicon at the bottom is found together with the impurities, which increase the liquid density (Møll, 2014). Material coming from the top and the bottom zones in the cast has higher purity compared to the central part, where segregation and lower cooling rates are favored.

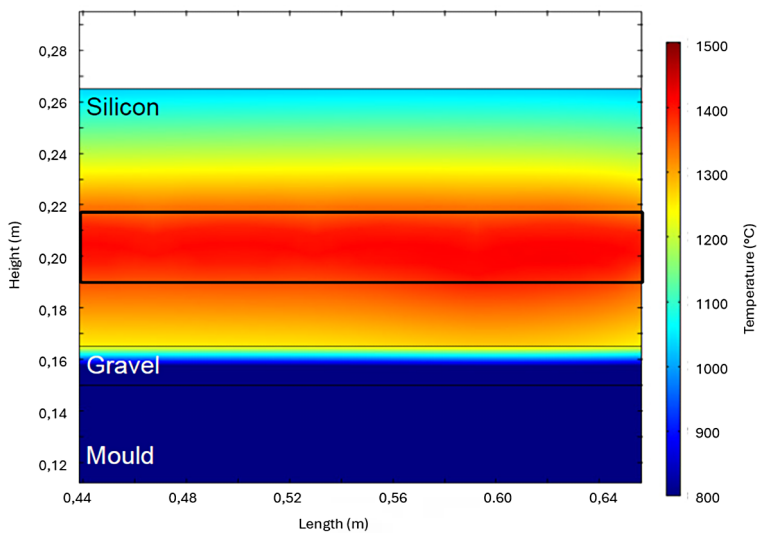


Figure 11.12 Surface plot, 1250 seconds (about 20 minutes) after the start of solidification obtained by the COMSOL model. Regions with temperatures below 800°C are illustrated in dark blue. The area inside the rectangle corresponds to the sample extracted 5.0–7.5 cm from the top of the cast. The microstructure in the black rectangle zone is comparable to Figure 11.14b (Møll, 2014). [Used with permission from Maria F. Møll].

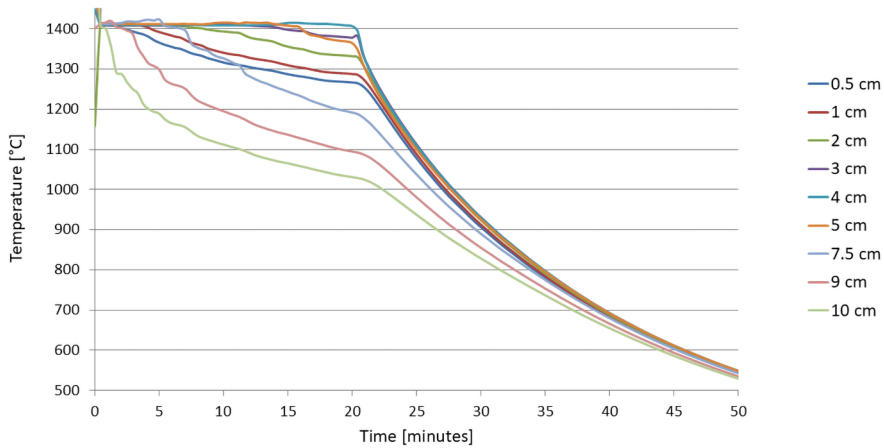


Figure 11.13 Temperature in different positions from the bottom of the 10 cm modelled cast. It is seen that when the position was close to the top or bottom surface, the temperature decrease is fast initially, but slow subsequently due to the heat from other areas that must be transported through the surfaces (Møll, 2014). [Used with permission from Maria F. Møll].

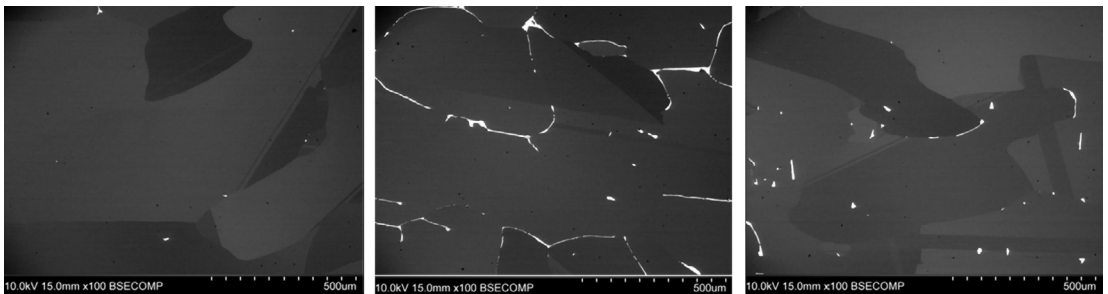


Figure 11.14 Microstructure of thin cast samples at top (a), centre (b) and bottom (c) of the cast. The concentration of intermetallic phases is highest at the centre of the cast (Broggi, 2015) [Used with permission from A. Broggi].

The amount of heat to be removed increases with the height of the cast (Møll, 2014). Figure 11.15 shows the temperature–time profile of casts of different heights, modelled at 1 cm above the fines. For thicker casts (> 5 cm), the cooling rate is quite similar in the temperature range where the silicon grain size is affected (1414–1396°C), highlighted by the blue rectangle. However,

for thinner casts, the cooling rate is faster, and the coarsening temperature interval is crossed very quickly, resulting in a smaller average grain size.

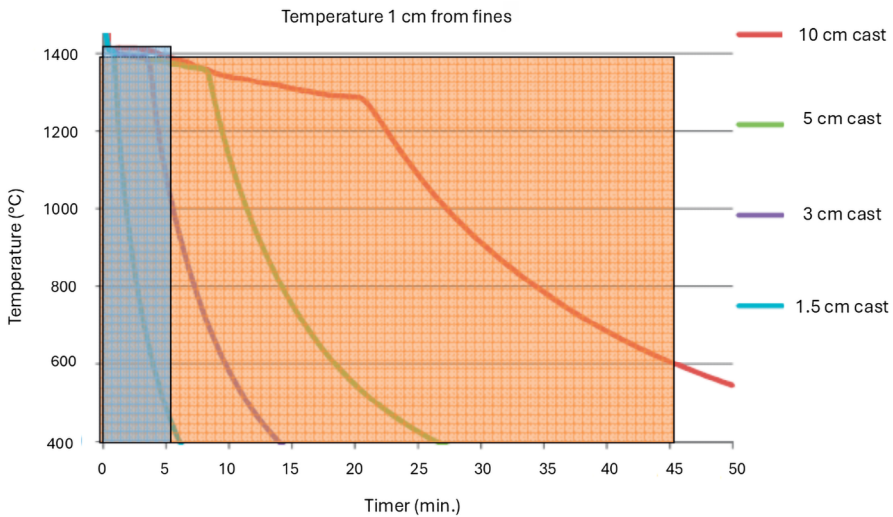


Figure 11.15 Temperature 1 cm from the fines layer in 1.5, 3, 5 and 10 cm cast. Notice the large variation in the cooling rate within the blue rectangle length for the different casts (Møll, 2014). [Used with permission from Maria F. Møll].

Transformation below the melting point of silicon

Heat treatments: effect on microstructure

Product homogeneity can be influenced by adjusting the cooling rate below the melting point of silicon, or by performing heat treatments once silicon has solidified, without affecting the grain size. The shape and number of intermetallic phases change when the cooling rate decreases after the solidification of primary silicon (Rong, 1992). Broggi and Tveit (2016) confirmed changes in microstructure after maintaining a desired temperature over time.

Heat treatments are effective when the temperature crosses the melting point of intermetallic phases. Figure 11.16 shows the cooling ranges for the most common intermetallic phases in MG–Si. These are the temperature ranges where the intermetallic phases can remelt during heating, or precipitate during cooling.

Common impurities in silicon include Al, Ca, Fe and Ti, as discussed in Chapter 10. These impurities form intermetallics at the grain boundaries of the silicon phase and affect the solidification temperature and structure. In an overview of literature on the topic, Møll (2014) concluded that there is a consensus on the typical intermetallic phases found in MG–Si, as listed in Figure 11.16. Calculations by Dons showed a solidification range of these intermetallic phases between 1100°C and 660°C. (Dons, 2009).

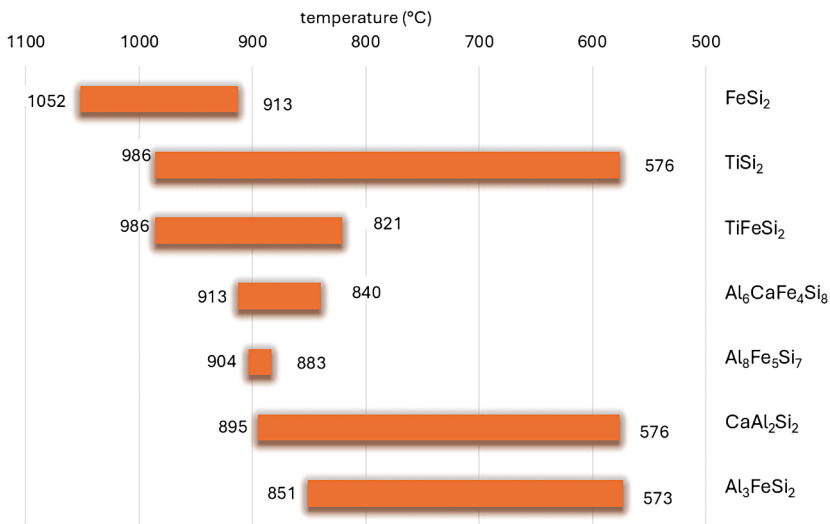


Figure 11.16 Cooling ranges of intermetallic phases summarized by Dons (2009). The temperatures delimiting the melting range are written on the side of each bar. (Broggi and Tveit, 2016). [Used with permission from A. Broggi].

It was found that the intermetallic phases change their microstructure after heat treatments at a temperature above 800°C. The intermetallic phases in the centre of the cast follow the grain-boundary profile. Their aspect ratio (a geometrical parameter, which decreases towards 1 as a shape is more circular) before the heat treatment can reach values between 5–13 (Broggi, 2015). After the treatment, the phases remelt, their aspect ratio decreases towards 2, and product homogeneity increases. There are radical changes in terms of average intermetallic particle size, aspect ratio and number of intermetallic phases per mm². The heat treatments are effective at above 900°C and durations exceeding 30 minutes.

The change in microstructure is attributed to a minimization of surface energy through splitting and coarsening (Broggi, 2015). At short holding times, the intermetallic phases will split. The number of intermetallic phases will increase through the cast, especially close to where the solidification fronts used to meet during solidification. At longer holding times, the intermetallic phases will coarsen and the particle number will decrease.

Cracking of intermetallic phases can affect product homogeneity. This phenomenon was also noticed by several authors (Møll, 2014; Broggi, 2015; Gueneau *et al.*, 1995; Ott, 2003). This effect might be meaningful in different downstream processes that are influenced by the intermetallic phase size distribution. During crushing and sieving, cracks would propagate; therefore, the intermetallic phases tend to end up in finer fractions. Møll (2014) found that in the + 0.3 mm fractions the trace elements were quite stable; however, in the –0.05 mm fraction, the level of trace elements was approximately doubled compared to the average value in the cast after crushing and sieving.

Margaria *et al.* (1992) found that the amount of four intermetallic phases CaSi_2 , $\text{FeSi}_{2.4}$, $\text{Al}_6\text{Fe}_4\text{CaSi}_8$ and CaAl_2Si_2 respectively reaches an ‘equilibrium point’ after heat treatments at 925°C (Figure 11.17). This reaction is believed to increase the product purity in MG–Si and Fe–Si, as pure silicon is produced. The suggested phase equilibrium may be written:

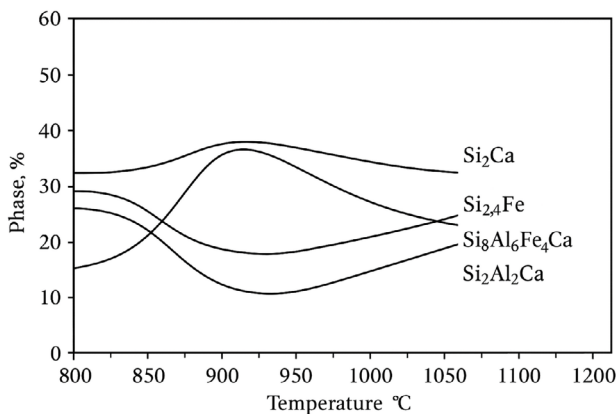
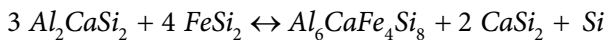
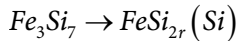


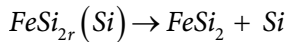
Figure 11.17 Effect of annealing on the relative fractions of intermetallic compounds (Margaria *et al.*, 1992).

Another solid-state chemical reaction is the formation of tertiary silicon in Fe–Si alloys. The mechanism is suggested to be a two-step reaction (Boomgard, 1972):

1. Fe_3Si_7 transforms first into the phase $\text{FeSi}_{2r}(\text{Si})$ while cooling down. This phase has an excess of Si atoms and is therefore supersaturated.



2. Silicon precipitates out of the supersaturated phase.



This reaction creates a volume increase by 0.6% in the alloy (Holdhus, 1962). This volume change may also justify the disintegration of ferrosilicon and the formation of cracks. The difference in the expansion coefficient of Si and Fe_3Si_7 creates thermomechanical stress while the alloy cools. If the cast is thick and the volume expansion is limited by the surrounding solidified alloy, this reaction may practically lead to a self-crushing situation.

Tertiary silicon has a characteristic feather-like look, as seen in Figure 11.18 (Anisdahl, 1987). The reaction seems to nucleate at grain boundaries or matrix irregularities. The structure is finer than the typical grain structure found in 75% ferrosilicon. It was found that the kinetics of formation of tertiary silicon are too slow compared with the rapid solidification rates used in industry (de Huff, 1969). Figure 11.19 shows that the reaction starts if the metal is at 787 °C for 10–15 minutes. The optimum condition for completing the reaction (i.e. lowest temperature and shortest time) is approximately 718 °C with a holding time of 3 hours. The measured reaction heat is approximately 30 kJ/kg FeSi_2 (Tveit, 1988).

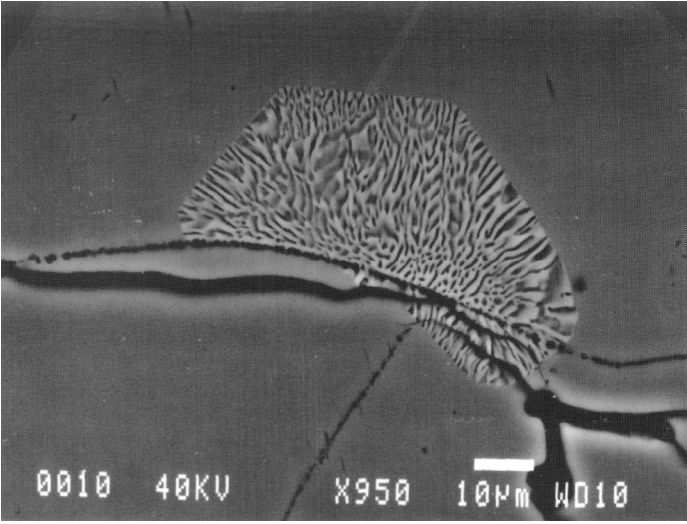


Figure 11.18 Microscope image of tertiary silicon and FeSi₂ from solid-state reaction (Anisdahl, 1987).

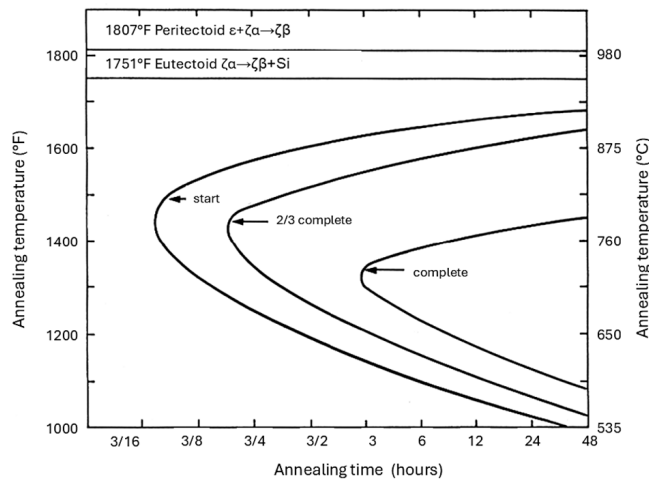


Figure 11.19 Temperature-time diagram for the reaction ζ_a -phase $[\text{Fe}_3\text{Si}_7] \rightarrow \text{FeSi}_2 + \text{Si}$ (de Huff, 1969).

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