METALLURGY OF CAST IRONS
Out-of-furnace processing of molten cast iron

Study support

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1 INTRODUCTION

Cast irons as construction material are still maintaining the standard of usability, because they provide a wide range of usable properties and also because they require less expensive metallurgy, or technology, and in many cases they provide a more economically convenient solution. The following table gives an overview of the product mix of foundry materials in the year 2001 in percentages according to individual countries compared to the Czech Republic. [1]

Table 1 – The product mix of foundry materials in selected countries

<table>
<thead>
<tr>
<th>Country</th>
<th>Alloys of iron [%]</th>
<th>Alloys of aluminum [%]</th>
<th>Others [%]</th>
<th>Total production [tons/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CILG</td>
<td>CISG</td>
<td>Cast steel</td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>82</td>
<td>53</td>
<td>35</td>
<td>12</td>
</tr>
<tr>
<td>Japan</td>
<td>80</td>
<td>80</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>Germany</td>
<td>81</td>
<td>81</td>
<td>13</td>
<td>6</td>
</tr>
<tr>
<td>Austria</td>
<td>64</td>
<td>64</td>
<td>26</td>
<td>10</td>
</tr>
<tr>
<td>Poland</td>
<td>90</td>
<td>90</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>83</td>
<td>62</td>
<td>13</td>
<td>25</td>
</tr>
</tbody>
</table>

The table above shows that alloys have an important status as a foundry material (CILG – cast iron with lamellar graphite, CISG – cast iron with spheroidal graphite). At the same time, however, it points out the low portion of CISG in the Czech Republic compared to other countries. The position of cast irons in the table is the result of a long-term research of cast irons crystallization, in other words the transition from liquid phase to solid phase, with all the consequences for utility properties of castings. This research has been able to incorporate cast irons to an equivalent position of mechanical properties as cast steels, or eventually forgings and stampings.

One of the possibilities of controlling the transition from liquid phase to solid one is the so-called out-of-furnace processing of molten cast iron, based on the methods of processing the cast iron using magnesium or other elements as calcium, aluminum, or eventually the rare earth metals. The processes of out-of-furnace processing lead to improvement of the utility properties of cast irons and it is possible to describe them as progressive methods in the field of cast irons metallurgy. The present state of knowledge cannot be considered as final, as it is constantly developing especially in the field of using the thermodynamic relations in the metallurgy of steels.

In this material, we will present the basic problems of these processes and therefore the material can also help the workers in metallurgy in foundry operations.
2 SOLUTIONS OF MOLTEN METALS

Contents of the chapter

✓ Properties of molten metals
✓ Basic concepts of solutions
✓ Composition of liquid solutions
✓ Concentration of solutions
✓ Basic types of solutions
  o Real solutions, thermodynamic activity
  o Coefficients of activity in multicomponent system, interaction coefficients
✓ Solutions of molten cast irons
✓ Conclusion

Time to study: individual

Aim After studying this chapter, you will be able to:

- Define the basic types and properties of cast irons.
- Explain the importance of the activity of elements in the cast irons of multicomponent metal systems.
- Define the importance of interaction coefficients in multicomponent systems

Presentation

2.1 Properties of molten metals

From the physical and chemical point of view, the molten metals belong to liquids. During the melting, their volume increase by about 2÷6%

- that applies for the metals with tight arrangement of crystalline lattice.
The physical and chemical properties of molten metals, such as the density, thermal capacities, thermal expansion coefficients, electrical and thermal conductivity all get near the properties of solid crystalline metals, if they are close to the melting temperature.

Based on the study of the molten metals structure using the X-rays, theories about the arrangement of basic particles in the molten metal solutions have been formulated:

**Quasi-crystalline theory** [2] – distinguishes the differences in the degree of arrangement of the basic structural particles of the solid and molten metals according to the short-range and long-range arrangement. The properties of metals, which have a long-range arrangement change abruptly during the melting. On the other hand, the properties dependent on a short-range arrangement are subject to only small change and that is why the metals with tighter arrangement show only minimal changes of volume during melting or during the temperature increase of the melt, in contrast to metals with free arrangement, the volume of which increases considerably. The properties of all these molten metals are more similar to one another than to the properties of solid metals.

**Theory of clusters or sibotaxies** [3, 4, 5] – this theory better describes the structure of melts than the previous ideas about the short-range arrangement in the direct surroundings of the particle. Groups of particles (clusters or sibotaxies) may occur in the melts. They have the same arrangement as the crystalline lattice in the solid state. These groups are unevenly dispersed throughout the volume of the melt (liquid) and their structure changes with time and decrease in temperature. Atoms belonging to one group transfer to another one newly created with totally different symmetry parameters (e.g. various concentrations of carbon). The viscosity of the melt is then given by the amount of ever emerging and disappearing arranged areas.

**Theory of vacancy structure** – this theory is closely related to the previous ones. It was developed by J.J.Frenkel [6, 7]. According to the theory of electron, in crystalline as well as in liquid state, each metal consists of positively charged atomic residues (“ions”) and freely moving common electrons (“electron type”) in the outer valence layers. These electrons are constantly moving between the positively charged atomic residues and they make the strength of the metallic bond. The movement of atoms depends on temperature, while on the other hand, the movement of electrons is maintained even at the absolute zero and is not very dependent on temperature.

When melting solid substances, small local cracks are created in the melt. J.J.Frenkel called them holes or cracks. There are many such cracks in the melt and they move during the melting process. The idea of a crack in the melt has a completely different meaning than the idea of atoms moving in the crystalline lattice, where the “crack” means an unoccupied nodal point in the lattice (vacancy).

The melting of metals is associated with an increase in their volume. According to the theory of vacancy structure, this increase cannot be understood as a simple increase of volume as a consequence of the increase of interatomic distances. The difference of volume of the substance in liquid and solid state is given by the sum of volumes of all the cracks that are present in the liquid.

This has been confirmed experimentally by measuring the coefficient of compressibility of the liquids, which at low values of pressure fluctuate considerably, while at pressure of hundreds of MPa, this coefficient does no change.
These theories are currently accepted and confirmed by further experiments but also in practice.

2.2 Basic concepts of solutions

Solutions in general are solid, liquid or gaseous homogeneous systems, consisting of at least two components. Any macroscopic part of the solution that is in the state of thermodynamic equilibrium has the same composition as the whole solution. That is the difference between solutions and mechanical mixtures, which are not homogeneous.

During the melting, most of the metallurgical reactions take place in the molten bath consisting of many components.

Unlike chemical compounds, whose composition is given by laws of permanent and quantitative weight ratios, the composition of solutions might vary continuously within certain limits. [8]

The study of physical and chemical properties of solutions has therefore a considerable importance for the theory and practice of the molten metals.

2.3 Composition of liquid solutions

The most important feature of solutions is their composition, which determines the qualitative (which components are a part of the solution) and quantitative (in what relative quantities are the individual components contained in the solution) properties.

Usually, the solution composition is given in weight percentages or in weight fractions. For the purposes of the theory of melts metallurgy, it is far more precise to represent the concentration of individual components using the atomic and molar fractions instead of weight percentages.

Example: a melt, whose composition is represented by the following weight percentages 20 % Al, 20 % Mn, 60 % Fe will have the atomic percentages of [8]:

<table>
<thead>
<tr>
<th>element</th>
<th>Weight percentage</th>
<th>Atomic percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>20 %</td>
<td>34 %</td>
</tr>
<tr>
<td>Mn</td>
<td>20 %</td>
<td>16.7 %</td>
</tr>
<tr>
<td>Fe</td>
<td>60 %</td>
<td>49.3 %</td>
</tr>
</tbody>
</table>

2.4 The concentration of solutions

Concepts called partial molar quantities, were introduced for the theoretical elaboration of technically important properties of solutions (melts among them).

Example: the volume occupied by 1 gram atom of molten iron in the pure state and in a binary melt with silicon is different and the molar volume of iron in the Fe-Si melt
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is changing with its concentration. It has to do with the fact that real solution, unlike the ideal solutions, have the real volume lower or higher than the correspondent sum of volumes of individual components. The same applies for other thermodynamic state quantities (thermal capacity, entropy, enthalpy).

It follows that the partial molar quantities are not properties, but they are changes in properties, and therefore can be positive and negative. The numerical calculation of the value of any partial molar solution has to specify its composition.

For practical metallurgical analysis, we are only interested in the difference in chemical potentials (Gibbs chemical potential), which related to the free enthalpy of the given substance in the pure state and we denote it $\Delta G$, by which we represent the relationship of this quantity with other partial molar quantities of the given melt solution.

2.5 Basic types of solution

In metallurgy, liquid solutions consist of systems of molten metals and slags. From the physical and chemical point of view, a convention is usually used, that says that the solvent in these solutions of metals is the component that is in substantial excess. [9]

Similar to the existence of only the real gases, only the real solutions exist as well. To express the properties of the solutions, the model of infinitely dilution of the solution (Henry's law) is used, the model of an ideal solution based on the Raoult's law, and the model for real solutions are used. See Fig.1.

![Figure 1 – Visual representation of Raoult's law and Henry's law](image)

2.5.1 Real solutions, thermodynamic activity

Real solutions exhibit deviations from Raoult's and Henry's laws, as depicted on Figure 2. For a quantitative depiction of these deviations and maintaining simple mathematic formulations of both laws, we are introducing the concepts of activity and activity coefficients.
To clarify these concepts, we consider a real solution with a positive deviation from the Raoult's law (Figure 2) in the area of concentration where Raoult's nor Henry's law are fulfilled.

![Figure 2 – Visual representation of activities and coefficients of activity](image)

For the $x$ concentration of a component of solution ($0 < x < 1$):

- $p$ – is the vapor pressure of the component of the real solution,
- $p_R$ – is the vapor pressure of the component according the Raoult's law,
- $p_H$ – is the vapor pressure of the component according the Henry's law,
- $a_R$ – is the activity of the component according the Raoult's law,
- $a_H$ – is the activity of the component according the Henry's law.

The activity represent the so-called effective concentration, a quantity, that needs to be installed in the simple mathematical formulations of Raoult's or Henry's law so that the vapor pressure of the real solution component is obtained.

The activity has the same role in real system as the concentration in ideal systems [9]. Activities are therefore the quantities, which after installing them in the equilibrium constant instead of concentration, enable using the law of active matter even for real systems.

To be able to quantitatively express the activity of any solved substance in a solution, it is necessary that its presence in the solution is related to a well-defined standard state, in which the given substance has exactly defined chemical activity at given temperature and pressure. This is the relation of activity of a random substance $i$ in a solution:
$a_i = \frac{\text{chemical substances efficiency } i \text{ in solution}}{\text{chemical substances efficiency } i \text{ in standard state}}$ (1)

These two states are used as a standard state:

a) state of pure substance

b) state of substance in an indefinitely diluted solution

In metallurgy, activity and the coefficient of activity is very often used in relation to the Henry’s law while selecting the standard state of 1% solution in weight percentage. The following then applies:

$$a_H^* = \frac{p}{p_{1\%}} \quad T = \text{const.}$$ (2)

and the following applies for the coefficient of activity

$$f^* = \frac{a_H^*}{\%X} = \frac{p}{\%X \cdot p_{1\%}} \quad T = \text{const.}$$ (3)

if the coefficient of activity is known, then

$$a_H^* = f^* \cdot \%X$$ (4)

where:

$\ p = $ vapor pressure of the component of the real solution

$p_{1\%} = $ vapor pressure of the 1% solution in weight percentage

$\%X = $ concentration of the component

Activities and activity coefficients are determined experimentally by various methods: measuring the vapor pressures, measuring the speed of evaporation, determining the phase diagrams, etc. The concentration dependencies from these experiments are expressed by various empirical and semi-empirical relations.

The activity should only, exactly if possible, characterize and reflect the observed facts and from the practical point of view obtain the data to improve the theory of real solutions.

### 2.5.2 Activity coefficients in multicomponent systems, interaction coefficients

In a polycrystalline system represented by a molten melt with the components A,B,C,D,E... we consider the component A (Fe) to be the solvent. In this system, the activity coefficient of the B component can be expressed in relation to the Henry’s law as follows:

$$f_B^{A,E...} = f_B^* \cdot f_B^C \cdot f_B^D \cdot f_B^E \quad T = \text{const.}$$ (5)
where: $f^*_B$ is the activity coefficient of the component B in a binary system A – B

$$f^*_B = f^C_B \cdot f^D_B \cdot f^E_B$$

expresses the influence of components C, D, E on the activity coefficient of the components B in the binary system A – B.

In diluted systems it is possible to define a so-called interaction coefficient of the ternary system A-B-C using the following relation:

$$\varepsilon_B^C = \frac{\partial \log f_B^C}{\partial [\% C]} \quad T = \text{const.} \quad (6)$$

The following then applies for the activity of the component B in the system A . . . E:

$$a^*_B = f^{A..E} \cdot [\% B] \quad (7)$$

The interaction coefficients of a variety of elements, especially in molten iron, are tabulated. For a molten melt, these quantities are still subject of further specifying.

At present, it is possible to also use the coefficients of second order, see chapter 3. [11]

E.g.: molten cast iron with its high content of carbon is significantly different from the majority of iron melts, which can be with a certain simplification considered infinitely dilute solutions.

**2.6 Molten cast iron solutions**

In terms of previously mentioned concepts about the melts properties, it is possible to consider a molten cast iron as a polycomponent solution. From the perspective of chemical composition, the solutions of cast irons have high content of carbon (up to 3.8 %), silicon (up to 2.8 %), phosphorus, sulfur and manganese.

The high content of C and Si significantly differs the cast iron from steel melts also from the viewpoint of physical properties such as surface tension, viscosity and volume changes.

Physical and chemical reaction in the cast iron (especially when processing the cast iron with magnesium) start at the interphase of the mutually contacting phases – in this regard, from the metallurgical point of view, it is necessary to know the influence of individual elements on the surface tension of molten iron (cast iron).

Therefore, we speak of surfactants (or inactive) elements.

Example: The results of measuring of the surface tension in binary and pure iron melts with carbon show that carbon decreases the surface tension of iron (cast iron), but considerably less than oxygen or sulfur. [12, 13]. With lowering temperature, the surface activity of carbon increases slightly.

In ternary systems, where the presence of third component influences the activity of the second component, the ratios are much more complicated. Oxygen and sulfur exhibit high
surface activity even in ternary systems \( \text{Fe} - \text{C} - \text{S} \) or \( \text{Fe} - \text{C} - \text{O} \). [11] On the contrary, the surface activity of C, Si, P in the systems of \( \text{Fe} - \text{C} - \text{S} - \text{Si} - \text{P} \) is low. The addition of magnesium and calcium (in the modification) to the molten cast iron causes the increase in surface tension of the cast iron. This is caused by the deoxidizing and desulfurizing action of these elements.

The values of surface tension in steels is at about 1000 dyn.cm\(^{-1}\) (rarely up to 1800 dyn.cm\(^{-1}\)), in cast irons and pig irons the reach the values between 800 and 1400 dyn.cm\(^{-1}\). [11]

**Viscosity** mainly influences the fluidity of cast iron and therefore the filling of the mold with molten metal. The viscosity of molten cast iron may hinder the casting and emergence of slag (as a consequence of modification, or inoculation of the cast iron). The viscosity decreases with increasing temperature.

Experiments have shown that carbon and silicon considerable lower the viscosity (improve fluidity) of the cast iron. [14, 15, 16, 17]

The addition of elements (alloying) in contents above 1% generally increases the viscosity of cast iron – the elements include Cu, Ni, W, V and Mn.

**Example:** Cast iron with addition of Cu = 10 % (0.064 poise at 1550 °C) has the maximum viscosity.

<table>
<thead>
<tr>
<th>Viscosity of:</th>
<th>the cast iron at 1400 °C</th>
<th>is</th>
<th>0.015 P</th>
</tr>
</thead>
<tbody>
<tr>
<td>steel</td>
<td>at 1600 °C</td>
<td>is</td>
<td>0.02 – 0.04 P</td>
</tr>
<tr>
<td>pure Fe</td>
<td>at 1550 °C</td>
<td>is</td>
<td>0.062 P</td>
</tr>
</tbody>
</table>

**Volume changes** are expressed by the changes of specific volume of the melt for given temperature and content of C, Si. It is possible to express them using the following calculation [18]:

\[
V_m^{1600°C} = V_{Fe}^{1600°C} + 0.003142 \cdot \%C_{free} + 0.000478 \cdot \%C_{bounded} + 0.001089 \cdot \%Si
\]  (8)

**Example:** The specific volume of pure iron at 1600 °C is 0.144 cm\(^3\).g\(^{-1}\). Steel at \( T = 1600 \, ^\circ C \), \( C = 0.3 \, % \), \( Si = 0.4 \, % \) has the specific volume of 0.14559 cm\(^3\).g\(^{-1}\), in other words an increase of 1.1 %. A cast iron with lamellar graphite (carbon is freely dispersed) at \( T = 1600 \, ^\circ C \), \( C = 3.5 \, % \), \( Si = 2.5 \, % \) has the specific volume of 0.15747 cm\(^3\).g\(^{-1}\), which represents an increase in specific volume of the melt of 9.3 %. [11, 18]

The structure of molten cast iron can be described [19] using the theories based on the existence of chemical non-homogeneity caused by additions. The molten cast iron contains areas enriched with carbon, so-called carbon clusters \( C_n \).

Since the cast iron contains also a high percentage of silicon apart from the high content of carbon, there are local areas in the melt with SiC crystals, which are particularly rich in C and Si. Due to the high solubility of Si and comparatively low solubility of C, which is further lowered due to the influence of silicon, there is a melt rich in Si around the dissolving SiC crystals. This results in formation of graphite.
The zones of “SiC-graphite”, rich in silicon and saturated with carbon, become the areas that contain graphite in the form of porous “graphite sponge”, impregnated with melt. Apart from them, there is a certain amount of carbon agglomerated, which also have their limited durability. It depends first of all on the temperature and the diffusion and does not depend on convection. The durability of carbon agglomerates is also influenced by trace elements, such as S, which may slow down the dissolution of graphite.

In agglomerates of the graphite phase, which may endure in the melt for a longer period, it concerns mainly the \( C_n \) molecules. These \( C_n \) clusters are not directly receivable on the metallographic sections, but they are provable based on their influence on the graphitization nuclei. This influence lasts for as long, until the \( C_n \) clusters fall apart through the \( C_n \) molecules to atoms. Only these represent the ideal state for nucleation of graphite.

If \( C_n \) clusters exist, then the content of ideally dissolved carbon in iron is lower than the analytically determined (total) content of carbon. Depending on how many undissolved \( C_n \) clusters there are, the formation of primary austenite occurs at higher temperature. That means that the \( C_n \) clusters may not only be the driving force in creating graphite nuclei, but they should also influence the austenite crystallization.

This issue is further elaborated in the chapter about the inoculation of cast irons.

Collaud published a different opinion about the molten cast iron [11, 20, 21]. He considers the cast iron to be a colloid solution, where pure iron is the solvent and colloids are created by the molecules of chemical compounds of the basic elements like oxides, nitrides, phosphides, sulphides and carbides.

The author divides the colloids [20] according to the size to gross, -1÷2, medium-fine-3÷4, fine -4÷5 and atomic-5 see Figure 3.

These colloids on Figure 3 with dimensions of \( 10^{-3} \) and \( 10^{-4} \) mm may form the nucleation stage of graphitization. The dimensions are approximating those of atomic solution. On the other hand, the inclusions of the size \( 10^{-2} \) mm form a suspension in the cast iron melt.
The condition of minimal occurrence of non-favorable inclusions is the quality batch material, which contains minimum of the, such as the pig iron of the Pignod type or deep-drawing sheet.

Collaud considers the molten cast iron to be a colloid or suspension solution depending on the size of present colloids or suspensions.

Molten cast iron is a heterogeneous solution, on which we can apply the model of real melt solution. Therefore, it represents a heterogeneous melt, containing metallic and non-metallic inclusions (graphite, sulphides, phosphides, etc.).

This does not apply for the cast iron with spheroidal graphite, the properties of which are closer to the Raoult’s law, because the content of these elements (apart from C and Si) is in tenths and hundredths of percent. That is why the cast iron with spheroidal graphite has properties similar to steel, such as the increase surface tension and viscosity.

**Terms summary**

- Mentioned in the „Contents of the chapter“ part
Questions

- What are the basic types and properties of solutions of ferroalloy?
- What is the importance of the activity of elements in the melts of multicomponent metal melt systems?
- What is the importance of the interaction coefficients in multicomponent systems?
3 USING THE LAWS OF THERMODYNAMICS IN APPLICATION ON MOLTEN CAST IRON

Contents of the chapter

✓ Formulas used to calculate activities
✓ Solubility of oxygen in a melt
✓ Significant reactions of elements contained in inoculants and modifiers
✓ Interaction of carbon – silicon
✓ Using the thermodynamic relations to conduct melting in coreless induction furnace
✓ Principles of melting conduction, limiting the formation of bubbles in castings

Time to study: individual

Aim  After studying this chapter, you will be able to:

- Define describe the solubility of oxygen in a melt
- Describe significant reactions of elements contained in inoculants and modifiers
- Use the thermodynamic relations to conduct melting in coreless induction furnace
- Calculate the equilibrium temperatures for the given ration of silicon and carbon when melting in electric induction furnaces.
- Apply the dependence between the exposure time and the degree of overheating of the melt in furnace

Presentation

The application of thermodynamic laws for molten cast iron gain importance, because they clarify the physical and chemical processes occurring during the melting and determine the thermodynamic stability or instability of possible reactions during melting. Mutual behavior of elements present in the melt is given by their weight representation expressed by concentration as a percentage, by the melt temperature and by the activity that is derived from them.

The activities of elements in molten cast iron are evaluated and from them the reaction between them are derived. Free energies of these reactions are defined and interaction coefficients of the 1st (e) and 2nd (r) order are determined. After that, the activity coefficients are calculated. In annex 1, the important interaction coefficients are listed.
From this point of view, we are interested in chemical reaction of elements present in the melt and further also of the elements we are adding to the melt during the out-of-furnace processing. These are the main elements we are interested in: C, Si, Mg, Ca, Al, Ba, Sr, etc. and not in the last place, the gases present in molten melt (oxygen, nitrogen, hydrogen), which significantly influence the seeding. In annex 2, there is a list of elements present in cast irons and their influences on the structure and properties.

Definitions of individual reactions will be described in chapter about inoculation and modification of the cast iron. Gases in the molten cast iron, in particular oxygen and possibly nitrogen and hydrogen form a substantial portion of chemical reactions.

Using the interaction coefficients, we are able to define the influence of gases on the molten cast iron and their influence on the final properties of cast iron castings. In the following table we are showing the informative contents of gases in molten cast irons in ppm.

Table 2 shows that the content of gases in molten cast iron is given by the melting unit and desired chemical composition. The lower the content of carbon and silicon, the higher the content of gases in molten cast iron. The content of these gases is much lower than in steel. For example, the content of oxygen in molten steel is around $10^3$ ppm. It is similar with hydrogen and nitrogen. The presence of oxygen in molten cast iron has negative but also positive effects. The negative effect is the creation of bubbles in castings (endogenous and exogenous bubbles), creation of an enormous amount of slag and creation of solid inclusions that disrupt the homogeneity of the structure of the basic metallic matter of the cast iron. The positive effect of oxygen is the formation of nuclei phase of graphite in the form of oxides, nitrides – heterogeneous nucleation that supports the stable solidification of the cast iron [22, 23]. Created oxides and nitrides, mainly $\text{SiO}_2$, strongly support the graphitization of the cast iron during crystallization.

The formation of seeds of graphite takes place during the transition from melt to solid state and particularly intensely during the eutectic delay. During this time, the optimal amount of free oxygen and possibly nitrogen must be available, as they cause the creation of seeding phase. The instant status can be determined from the DTA [8] by calculating the crystallization heat of the eutectic reaction (further analysis of the cooling curve will be given in later chapters) or by analyzing the slag, especially the ratios of acidic and basic components of slag, for example, from the ratio we refer to as the degree of oxidation of the melt:

$$S = \frac{\text{SiO}_2}{\sum (\text{FeO}, \text{Fe}_2\text{O}_3) + \text{MnO}} = 0.4 - 0.8$$

Lower values of this ratio cause the risk of shrinkages and opacities. On the other hand, higher values lead to the emergence of slag and endogenous bubbliness in castings.
Table 2 – Approximate content of gases in molten cast iron

<table>
<thead>
<tr>
<th>Melting aggregate</th>
<th>material</th>
<th>oxygen ppm</th>
<th>hydrogen ppm</th>
<th>nitrogen ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>cold-blast cupola</td>
<td>Blackheart CITG</td>
<td>64 – 104</td>
<td>1.0 – 1.1</td>
<td>101 – 103</td>
</tr>
<tr>
<td>cold-blast cupola</td>
<td>CILG for automobiles</td>
<td>14 – 26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cold-blast cupola</td>
<td>CILG</td>
<td>42 – 86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hot-blast cupola</td>
<td>Whiteheart CITG</td>
<td>23 – 52</td>
<td>1.0 – 2.0</td>
<td>111 – 114</td>
</tr>
<tr>
<td>hot-blast cupola</td>
<td>Coquille – centrifugal casting</td>
<td>5 – 7</td>
<td>0.8 – 0.9</td>
<td>11 – 17</td>
</tr>
<tr>
<td>Cupola lined with acidic material</td>
<td>CILG for automobiles</td>
<td>10 – 14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cupola lined with fireclay</td>
<td>CILG for automobiles</td>
<td>5 – 6</td>
<td>1.0 – 1.3</td>
<td>58 – 63</td>
</tr>
<tr>
<td>duplex – electric furnace</td>
<td>Blackheart CITG</td>
<td>14</td>
<td>0.9</td>
<td>100</td>
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<tr>
<td>duplex – electric furnace</td>
<td>CITG</td>
<td>35 – 43</td>
<td>1.8 – 2.0</td>
<td>80 – 94</td>
</tr>
<tr>
<td>Induction furnace</td>
<td>Alloved CILG</td>
<td>120</td>
<td>5.2 – 6.6</td>
<td>110</td>
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<td>Induction furnace</td>
<td>CILG</td>
<td>10 – 34</td>
<td></td>
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<tr>
<td>Electric arc furnace</td>
<td>Austenite cast irons</td>
<td>4</td>
<td>0.9</td>
<td>1700 - 1800</td>
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<tr>
<td>Electric arc furnace</td>
<td>CILG</td>
<td>29 – 63</td>
<td></td>
<td></td>
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<tr>
<td>Electric arc furnace</td>
<td>CISG</td>
<td>9 – 64</td>
<td></td>
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<tr>
<td>Blast furnace</td>
<td>PI</td>
<td>5 – 15</td>
<td>1.1 – 2.7</td>
<td>18 – 105</td>
</tr>
<tr>
<td>Drum rotary furnace</td>
<td>CILG</td>
<td>133 - 148</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CILG – cast iron with lamellar graphite      CISG – cast iron with spheroidal graphite
CITG – cast iron with tempered graphite    PI – pig-iron

3.1 Formulas used to calculate activities [8, 9]:

Activity

$$a_x^* = f_x \cdot \frac{\% X}{100}$$  \hspace{1cm} (10)

The reaction is defined by the free energy according to the following relation:

$$\Delta G = A + B \cdot T$$  \hspace{1cm} (11)

$$\Delta G_0^T = R \cdot T \cdot \ln K$$  \hspace{1cm} (12)
where: $\Delta G_0^T$ - Gibbs free energy

$R$ – gas constant $= 8.31441 \text{ J.K}^{-1}\text{.mol}^{-1}$

$= 1.98719 \text{ Cal.K}^{-1}\text{.mol}^{-1}$

The transition of decimal logarithm to a natural one

$$\log x = 2.3 \cdot \ln x$$

(13)

The equilibrium constant of the reactions

$$\log K = \frac{\Delta G_0^T}{R \cdot T \cdot 2.3}$$

(14)

### 3.2 Solubility of oxygen in the melt [24]

Solubility of oxygen in the melt depends on the temperature and can be determined as follows:

$$\frac{1}{2} \text{O}_2 \rightarrow [\text{O}] \quad \Delta G_T^O = -28000 - 0.69 \cdot T$$

and then

$$\log[\text{O}] = -\frac{1458}{T} - 0.0359$$

where: $T \text{ [K]}$

(15)

$$a_0^0 = f_0 \cdot [\%\text{O}]$$

Solubility of oxygen in the melt, depending on the temperature, is determined from the following relation

$$f_0 = \log e_0^O \cdot [\%\text{C}]$$

(16)

Based on these formulas, it is possible to create a diagram that shows the dependence of oxygen activity on the temperature in pure iron, as shown on Figure 4.
The activity of oxygen causes the creation of seeds based on oxides, which become unstable at higher temperatures and can dissociate or coagulate and then flow in the slag under certain conditions (temperature, time, melt viscosity). With decreasing temperature of the melt from the liquid temperature, the oxygen activity decreases until the start of eutectic reaction. With the influence of crystallization heat of the eutectic reaction, the oxygen activity increases again. [24, 25] At the liquid temperature, the oxygen activity increases due to the crystallization heat of the emerging austenite while at the same time the remaining melt is being enriched with carbon. Good conditions are thus created for the formation of graphite seeds and its crystallization.

3.3 Significant reactions of elements contained in inoculants and modifiers

In this chapter, we are listing the reactions of important elements, which are contained in inoculants and modifiers that are used during the out-of-furnace metallurgy as well as some important reactions with oxygen and carbon, which take place in molten cast iron.

**Carbon reaction**

\[
(\text{FeO}) = [\text{Fe}] + [\text{O}] \quad \Delta G_T^0 = 121000 - 52.38 \cdot T
\]

\[
\log K_p = \left( \frac{-\Delta G}{R \cdot T} \right) = \frac{-6315.24}{T} + 2.73
\]

\[
\text{C (g)} + \frac{1}{2} \text{O}_2 = \text{CO (g)} \quad \Delta G_T^0 = -119748.2 - 83.11 \cdot T
\]

\[
[\text{C}] = C_{(s)} \quad \Delta G_T^0 = 22609.8 - 42.28 \cdot T
\]

\[
[\text{O}] = \frac{1}{2} \text{O}_2 \quad \Delta G_T^0 = -117236.1 - 2.88 \cdot T
\]
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\[ [C] + [O] = \text{CO}_g \]
\[
\log K_p = \left( -\frac{\Delta G}{R \cdot T} \right) = \frac{-1311.15}{T} + 1.98
\]

\[
\frac{1}{2} \text{O}_2 = [O] \]
\[
\log K_p = \left( -\frac{\Delta G}{R \cdot T} \right) = \frac{6120}{T} + 0.15
\]

More important reactions:

**Ca-C**

\[ \text{C}_g + \frac{1}{2} \text{O}_2 = \text{CO}_g \]
\[ \Delta G_T^0 = -119748 - 83.11 \cdot T \]

\[ 2\text{C} + \text{Ca} = \text{CaC}_2 \]
\[ \Delta G_T^0 = -213000 + 61 \cdot T \]

\[ \text{Ca} + \frac{1}{2} \text{O}_2 = \text{CaO} \]
\[ \Delta G_T^0 = -790000 + 194 \cdot T \]

\[ \text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO} \]
\[ \Delta G_T^0 = 457252 - 216.11 \cdot T \]

\[
\log K_{\text{CO}} = \log P_{\text{CO}} = -\frac{23864.93}{T} + 11.28
\]

**Mg-C**

\[ \text{C}_g + \frac{1}{2} \text{O}_2 = \text{CO}_g \]
\[ \Delta G_T^0 = -119748 - 83.11 \cdot T \]

\[ 2\text{C} + \text{Mg} = \text{MgC}_2 \]
\[ \Delta G_T^0 = -498000 + 102 \cdot T \]

\[ \text{Mg} + \frac{1}{2} \text{O}_2 = \text{MgO} \]
\[ \Delta G_T^0 = -729000 + 204 \cdot T \]

\[ \text{MgO} + 3\text{C} = \text{MgC}_2 + \text{CO} \]
\[ \Delta G_T^0 = 559452 - 185.11 \cdot T \]

\[
\log K_{\text{CO}} = \log P_{\text{CO}} = -\frac{29199}{T} + 9.66
\]

**Al-O**

\[ 3 [\text{O}] = 3 [\frac{1}{2} \text{O}_2] \]
\[ 1: \Delta G_T^0 = 117000 - 2.89 \cdot T \]

\[ 2 [\text{Al}] = 2 \text{Al} \]
\[ 2: \Delta G_T^0 = 628000 + 23.8 \cdot T \]

\[ 2\text{Al} + 3 \frac{1}{2} \text{O}_2 = \text{Al}_2\text{O}_3 \]
\[ 3: \Delta G_T^0 = -1681000 + 324 \cdot T \]

\[ 2\text{Al} + 3 \text{O} = \text{Al}_2\text{O}_3 \]
\[ 4: \Delta G_T^0 = 1204400 - 380.2 \cdot T \]

and then

\[
\log K_{\text{Al}O_3} = \log [\text{Al}]^2 \cdot [\text{O}]^3 = -\frac{62876}{T} + 19.8
\]

\[
\log [\text{O}] = \frac{K_{\text{Al}O_3}}{3} = -\frac{2}{3} \log \text{Al} + 1.17 \text{Al}
\]
3.4 The interaction of carbon - silicon

The importance of both these elements lies in their mutual influencing of the crystallization process, in other words, the activity of Si increases the activity of C, and the creation of seeds in melt is influenced by that.

The influence of the activity of silicon on the activity of carbon can be expressed in the following way:

With the given chemical composition and temperature, we calculate the activity of carbon from the above mentioned relations

\[ e_C^C = \left( \frac{158}{T} + 0.058 \right), \quad r_C^C = \left( \frac{8.94}{T} + 0.0026 \right) \]

\[ \log f_C = e_C^C \cdot [\%C] + r_C^C \cdot [\%C]^2 \]

\[ a_C^C = f_C \cdot [\%C] \]

We will express the influence of the activity of silicon on the activity of carbon by calculating the logarithm of the activity coefficient of silicon from the relation (16) using the interaction coefficients of 1st and 2nd order:

\[ e_{Si}^C = \left( \frac{162}{T} + 0.008 \right), \quad r_{Si}^C = \left( \frac{1.94}{T} - 0.003 \right) \]

(17)

\[ \log f_{Si} = e_{Si}^C \cdot [\%Si] + r_{Si}^C \cdot [\%Si]^2 \]

and then by adding the result to the logarithm of carbon activity and calculate the carbon activity influenced by the presence of silicon.

\[ \log f_{C}^Si = \log f_C + \log f_{Si} \] (18a)

\[ a_C = f_{C}^Si \cdot [\%C] \] (18b)

Example: chemical composition of the cast iron C = 3.5 %, Si = 2 %, at 1600 °C and 1153 °C.

Calculation of EGM for the eutectic temperature (1153 °C):

\[ EGM = C_{anal} - C_E + 0.17 \cdot (Si + P) = C_{anal} - 1.81 + 0.17 \cdot 2 = 2.02\% \]
For the temperature of 1600 °C:
\[ \log f_C = 0.498 + 0.095 = 0.596 \quad \text{and then} \quad a_C = f_C \cdot [\%C] = 13.8 \]
\[ \log f_{Si} = 0.1889 - 0.00392 = 0.18106 \]
\[ \log f_{C_{Si}} = \log f_C + \log f_{Si} = 0.77706 \quad \text{and then} \quad a_C = f_C \cdot f_{Si} \cdot [\%C] = 20.95 \]
This implies that the graphitization ability of carbon has increased almost by 52 %.

For the temperature of 1153 °C
\[ \log f_C = 0.592 + 0.111 = 0.703 \quad \text{and then} \quad a_C = f_C \cdot [\%C] = 17.66 \]
\[ \log f_{Si} = 0.244 - 0.00655 = 0.237 \]
\[ \log f_{C_{Si}} = \log f_C + \log f_{Si} = 0.940 \quad \text{and then} \quad a_C = f_C \cdot f_{Si} \cdot [\%C] = 30.48 \]
This implies that the graphitization ability of carbon has increased almost by 73 %.

Increase in the activity of carbon to eutectic amount of C compared to the value of EGM:

Graphitization ability = \((\text{EGM}_R / \text{EGM}_{\text{TEO}}) \cdot 100 = 1.73 / 2.02 \cdot 100 = 85.64 \% \)

In the example, there are extremely different temperatures of reaction, so that the graphitization ability of the cast iron is compared at higher (1600 °C) and lower temperature (eutectic temperature 1153 °C) at the same chemical composition of the cast iron. The graphitization ability of the cast iron, even with the high carbon activity, is lower at higher temperature (13.8 %) compared to the activity at lower temperature (17.66 %). At high temperature, the seeds are instable due to the lower carbon activity and the graphitization ability is lower. On the other hand, at eutectic temperature, the graphitization ability is considerable higher. The influence of silicon at eutectic temperature is also higher, which corresponds with the calculated values (20.95 % to 30.48 %) and with practical knowledge.

The example implies the discovery that the values of activity of carbon and silicon increase with decreasing temperature, thereby increasing the graphitization ability of the cast iron as well.

All the above mentioned chemical reactions are dominant, because they can proceed not only during the melting of the cast iron, but also during its further out-of-furnace processing. The activities of barium and strontium to oxygen will be given in the chapter about inoculation.

3.5 Using thermodynamic relations to conduct melting in coreless induction furnace.

When melting electrical induction coreless induction furnace, higher melting temperatures are reached than when melting in cupolas. These temperatures reach the values of 1580 °C, especially during the production of cast iron with spheroidal graphite. The
process of melting influence the quality of cast iron. Incorrect conduction of melting may cause defects of castings.

Furthermore, the processes of reactions between silicon and oxygen and between silicon oxide and carbon are described. These reactions were published in literature before [22, 27] and presently, there are various values of free energies that somewhat change the original thermodynamic calculations.

**Reaction of Si - O :**

According to literature [24, 28, 29]:

\[
\begin{align*}
[Si] + 2[O] &= (SiO_2)_{(s)} \\
\Delta G^0_T &= -587018 + 227T \quad \text{J.mol}^{-1}.\text{K}^{-1}
\end{align*}
\]

For the value of gas constant \( R = 8.31441 \text{ J.K}^{-1}\text{.mol}^{-1} \) the value of equilibrium constant can be determined:

\[
\log K_p = \left( \frac{a_{SiO_2}}{a_{Si} \cdot (a_{O})^2} \right) = \frac{30645}{T} - 11.85
\]

From the equation (19) we can then determine the equilibrium between the content of oxygen and silicon for the given temperature.

On the Figure 5 there are the isotherms for 1300, 1350, 1400, 1450 and 1500 °C.

E.g. for the equilibrium temperature of 1450 °C, and the silicon content of 2 %, the equilibrium content of oxygen is 8 ppm.

Figure 5 shows the bond between silicon and oxygen at various temperatures and the formation of SiO\(_2\). This SiO\(_2\) comes to the slag and can cause the lowering of slag basicity, which leads to the increase of fluidity of the slag, which can easily reach into the castings. The degree of this oxidation can be the cause of other defects of castings.
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Figure 5 – The course of isotherms of the oxidation of silicon by oxygen, forming SiO₂

Reaction SiO₂ – C:

These reactions, according to literature [28], define the influence of carbon on the reduction of SiO₂ in molten cast irons:

\[
\text{[Si]} + 2\cdot \text{[O]} = \text{(SiO₂)}_{(g)} \quad \Delta G^0_T = -587018 + 227 \cdot T \quad [\text{J.mol}^{-1}.\text{K}^{-1}]
\]

\[
2 \cdot \text{[C]} + 2 \cdot \text{[O]} = 2 \cdot \text{CO}_{(g)} \quad \Delta G^0_T = 2 \cdot (-25122 - 37.93 \cdot T) \quad [\text{J.mol}^{-1}.\text{K}^{-1}]
\]

\[
\text{(SiO₂)} + 2\cdot \text{[C]} = \text{[Si]} + 2 \cdot \text{CO} \quad \Delta G^0_T = -536774 + 302.86 \cdot T \Delta \quad [\text{J.mol}^{-1}.\text{K}^{-1}]
\]

For the value of gas constant \( R = 8.31441 \text{ J.K}^{-1}.\text{mol}^{-1} \) it is possible to determine the value of the equilibrium constant \( K_{\text{Pco}} \).

\[
\log K_{\text{Pco}} = \left( \frac{a_{\text{[Si]}} \cdot (p_{\text{CO}})^2}{a_{\text{(SiO₂)}} \cdot (a_{\text{[C]}})^2} \right) = \frac{-28073}{T} + 15.84
\]

(20)

From the equation (20) we can determine the relation for the calculation of partial pressure CO, where we need to know the value of equilibrium constant \( K_{\text{Pco}} \) and the contents of silicon and carbon in percentages. If the SiO₂-C reaction proceeds to the right, the gaseous carbon monoxide is created, the partial pressure of which can be calculated according to the equation (21).
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\[ p_{co} = \sqrt{\frac{K_{pco} \cdot [\%C]^2}{[\%Si]}} \]  
\[ \text{[atm]} \]  
\[ (21) \]

By adjusting the formula according to the publication [30] it is possible to calculate the value of equilibrium temperature \( T_R \) for a certain percentage content of carbon and silicon and the correspondent partial pressure of CO.

\[ T_R = -\frac{28074}{\log \frac{Si}{C^2 \cdot (p_{co})^2}} - 15.84 \]  
\[ \text{[K]} \]  
\[ (22a) \]

\[ t_R = -\frac{28074}{\log \frac{Si}{C^2 \cdot (p_{co})^2}} - 273 \]  
\[ \text{[°C]} \]  
\[ (22b) \]

When installing the percentage values of silicon and carbon content in the relation (22), when the value of partial pressure of CO will be equal to 1atm, we gain the dependence displayed on the Figure 6.

On the Figure 7 there is the dependence of equilibrium temperature on the ratio \( (Si/C^2) \) at various partial pressure of CO.

![Figure 6](image)

Figure 6 – The course of equilibrium temperatures for the given ratio between silicon and carbon and the partial pressure of CO \( (p_{co} = 1 \text{ atm}) \).

Using the pictures (Figure 6 and Figure 7) it is possible to determine the equilibrium temperature and the correspondent partial pressure of CO, based on the content of carbon and
silicon in the melt. The partial pressure of CO is in equilibrium with the pressure conditions of melting in the way that when melting in a furnace without a lid, it is equal to the sum of the atmospheric pressure and ferrostatic pressure, which is given by the height of the column of molten cast iron in a crucible furnace. When using a lid, with respect to its tightness, the pressure can increase by tenths of atmospheres.

$$\text{(SiO}_2) + 2 \text{[C]} = \text{[Si]} + 2 \text{CO}$$

![Diagram](image)

**Figure 7** – The diagram of the dependence of the equilibrium temperature on the ratio (Si/C^2), at pressure of CO 0.25 atm; 0.5 atm; 0.75 atm and 1 atm.

From the point of view of the partial pressures of CO we are also interested in carbon boiling temperature ($t_{BP}$), where the deoxidation by carbon takes place. We can obtain the boiling point by calculation from the formula (23), mentioned in literature [30].

$$t_{BP} = 0.7866 \cdot t_E + 362 \quad [^\circ \text{C}]$$  \hspace{1cm} (23)

- $t_{BP}$ – boiling point temperature ($^\circ \text{C}$)
- $t_E$ – equilibrium temperature ($^\circ \text{C}$)

To evaluate these temperatures we have the melting temperature of the molten cast iron in the furnace. In the range of temperatures equilibrium temperature $\leq$ overheating temperature $\leq$ boiling point, the melt will be able to absorb more oxygen. The source of oxygen may be a heavily contaminated batch by iron oxides, oiled batch and also the oxygen from the atmosphere of the furnace. The highest and fastest saturation of cast iron with oxygen will take place under the boiling point, where there will be no creation and evaporation of CO. The process of saturation of the melt with oxygen will proceed more intensively when the melt stays longer on the correspondent melting temperature, thus increasing the portion of FeO and MnO in the slag.

On Figure 8 there is the solubility of oxygen for various contents of silicon, dependent on the temperature.
The mentioned dependence implies that the lower the content of silicon, the higher the value of oxygen solubility in the melt and vice versa. On the figure, there is a highlighted area, when decarburization occurs due to the reaction:

\[ C + O = CO \]
\[ \Delta G^0 = -25122 - 37.99 \cdot T \quad [\text{J.mol}^{-1}.\text{K}^{-1}] \]  \[28\]

Figure 5 also implies that when the cast iron is molten with lower content of silicon, the melt will contain more oxygen.

E.g. at 1500 °C, and the content of silicon of 1% the content of oxygen is equal to 22 ppm. At the same temperature and the content of silicon of 2.5%, the content of oxygen is equal to 13 ppm.

These values, obtained by reading from the given dependence, correspond with reality, because when melting cast irons in induction furnaces, the total amount of oxygen is indicated between 8 to 25 ppm.

Figure 8 – The dependence of the solubility of oxygen on the temperature for the silicon contents of 1% and 2.5%.

If we consider the SiO₂-C reaction as a reaction of deoxidation of the melt by silicon, then it is necessary to define the relations between the overheating temperature and the period of exposure to such temperature. Since we know the percentage contents of silicon and carbon and the value of exposure period, we can define the overheating temperature as the difference of temperatures (melting temperature – equilibrium temperature), which we call the degree of
overheating. The value of equilibrium temperature can be determined by calculation according to the formula (22) or by reading it from the Figure 8.

The exposure period at the correspondent melting temperature plays an important role in the deoxidation by carbon. The longer the melt stays at the melting temperature, the more oxygen can dissolve in the melt. The dependence between the overheating temperature and the exposure period is given by the equation (24), according to the literature [30].

\[(T_T - T_R)^2 \cdot \tau_1 = (T_{p1})^2 \cdot \tau_1 \leq 6800\]  

\(T_T\) – melting temperature \([K]\) \hspace{1cm} \(T_{p1}\) – overheating temperature \([K]\) 
\(T_R\) – equilibrium temperature \([K]\) \hspace{1cm} \(\tau_1\) – exposure period \([\text{min}]\) 

\[6800 \approx (82)^2\] – upper limiting value of overheating \([K]\)

The relation (24) is visually depicted on the Figure 9.

![Figure 9](image)

Figure 9 – The dependence between the exposure period and the degree of overheating of the cast iron in the furnace

The dependence has an exponential character, the exposure period \(\tau_1\) in minutes is on the horizontal axes, the degree of overheating in Kelvins is on vertical axis. The more we are moving above the value of 6800, the more the melt will be enriched by oxygen and the bigger the risk of formation of endogenous bubbles in the castings.

Figure 9 further shows that these two variables are dependent – the higher the degree of overheating, the shorter the time we have to keep the melt in the furnace aggregate and vice versa, in order to avoid the formation of bubbles. These bubbles have endogenous character, in other words they are formed directly in the cast iron during the melting and casting.

The practical use of the formula (24) and the dependence depicted on Figure 9 is mentioned in the following example.
Example: We are melting a grey cast iron with the content of \( Si = 2.2 \% \), \( C = 3.5 \% \), \( T_T = 1480 {^\circ}C = 1753 \, K \), partial pressure of CO = 1.2 atm, the period of keeping the melt in furnace \( \tau_1 = 3.5 \) min. From the relation (22) we determine the value \( T_R = 1709 \, K \). We use the relation (24) for the calculation:

\[
(T_T - T_R)^2 \cdot \tau_1 = (T_p^1)^2 \cdot \tau_1 \leq 6800
\]

\[
(1753 - 1709)^2 \cdot 3.5 = (44)^2 \cdot 3.5 \leq 6800
\]

\[
6776 \leq 6800
\]

The value of the left side of the equation is lower than the right side, meaning that the bubbles should not be formed in the castings.

If the value on the left side of the relation (24) is higher than 6800, it will be necessary to use deoxidizing products to decrease the content of oxygen, or create conditions for reaching the boiling point of the cast iron.

Conditions for boiling of the cast iron can be determined from the relation (25), according to the literature [30].

\[
(T_p^2) \cdot \tau_2 \leq \sqrt{(T_p^1)^2 \cdot \tau_1} - \frac{6800}{218}
\]  

(25)

\[
T_p^1 = T_T - T_R \quad \text{- degree of overheating in a ladle} \, [K]
\]

\[
T_p^2 = T_T - T_{BV} \quad \text{- overheating temperature for the boiling area} \, [K]
\]

\[
\tau_1 \quad \text{- exposure period} \, [\text{min}]
\]

\[
\tau_2 \quad \text{- exposure period in the boiling area} \, [\text{min}]
\]

The following example shows the use of the relation (25) in practice.

Example: We are melting a grey cast iron with the content of \( Si = 2.2 \% \), \( C = 3.5 \% \), \( T_T = 1480 {^\circ}C = 1753 \, K \), partial pressure of CO = 1.2 atm, the period of keeping the melt in the furnace \( \tau_1 = 5 \) min. From the relation (22) we determine the value \( T_R = 1709 \, K \). We will use the relation (24) to calculate the value.

\[
(T_T - T_R)^2 \cdot \tau_1 = (T_p^1)^2 \cdot \tau_1 \leq 6800
\]

\[
(1753 - 1709)^2 \cdot 5 = (44)^2 \cdot 5 \leq 6800
\]

\[
9680 \nleq 6800
\]
The value of the left side of the equation is higher than the right side of the equation, meaning that the content of O$_2$ may further increase in the cast iron. Therefore, there is a danger of formation of bubble in the castings. To decrease the content of oxygen and thus prevent the formation of bubbles in castings, it is possible to create conditions for a carbon boiling of the cast iron, determined by the formula (25).

\[
(T_p^2) \cdot \tau_2 \leq \sqrt{(T_p^1)^2 \cdot \tau_1} - \frac{6800}{218}
\]  

(25)

\[
T_{BV} = 0.7866 \cdot t_R + 362 + 273 = 1764 \ [K]
\]

\[
(1764 - 1753) \cdot \tau_2 \leq \sqrt{(44)^2 \cdot 5} - \frac{6800}{218}
\]

\[
11 \cdot \tau_2 \leq 67.19
\]

\[
\tau_2 \leq 6.11 \ [\text{min}]
\]

To successfully decrease the content of oxygen in the melt, and thus decrease the possibility of formation of bubbles in the castings, it is necessary to increase the melting temperature by at least 11 °C, in other words increase the temperature to the boiling point and the exposure at this temperature should not exceed 6.1 minutes.

**Principles of conducting the melting, which limit the formation of bubbles in the castings:**

1) Controlling the input batch material – pollution, humidity, lumpiness.

2) Ensuring as little contact of the melt with atmosphere as possible during the melting – melting under a lid.

3) If the points 1) and 2) are accomplished, we may keep the melt temperature ± 30K around the equilibrium temperature. This exposure should be longer than 15 minutes.

   If the points 1) and 2) are not accomplished, it is necessary to use deoxidation products before casting.

   It is not recommended to keep the melting temperature closely under the boiling point of carbon.

### Terms summary

- Mentioned in the „Contents of the chapter“ part  

### Questions

- What determined the solubility of oxygen in the cast iron?
- How do the reactions of elements contained in the inoculants and modifiers with the cast iron proceed?
- What is the purpose of the thermodynamic relations for conducting the melting
<table>
<thead>
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<th>in coreless induction furnace?</th>
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<tr>
<td>• How do we calculate the equilibrium temperature for the given ratio of silicon and carbon when melting the cast iron in electrical induction furnace?</td>
</tr>
<tr>
<td>• What is the interpretation of the dependence between the exposure period and the degree of overheating of the cast iron in furnace?</td>
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4 CRYSTALLIZATION OF CAST IRONS

Contents of the chapter

✓ Eutectic crystallization
✓ Graphite crystallization
✓ The mechanism and kinetics of graphitization
✓ Calculation of EGM

Time to study: individual

Aim After studying this chapter, you will be able to

- Describe the Fe-C and Fe-Fe₃C diagrams.
- Explain the crystallization of an eutectic in an cast iron.
- Describe the process of cast irons solidification using the cooling curve.
- Describe the types of eutectic cells and the morphology of cast irons solidification.
- Explain the mechanism and kinetics of the formation of graphite in cast irons.

Presentation

The transition from liquid to solid state, while crystals are being formed, is called crystallization, which is an integral part of the out-of-furnace (after furnace processing, ladle metallurgy). The crystallization takes place from the temperatures of the liquid to the temperature of the surrounding environment. At higher temperatures – from the liquid temperature to the solid temperature, the crystallization is called solidification. From the temperature of solid till the temperature of surrounding environment, the crystallization is called cooling off.

The crystallization of cast irons at higher temperatures from the temperature of the liquid to the temperature of the solid is called primary crystallization and from the temperature solid to the temperature of surrounding environment, it is called the secondary crystallization. The final structure of the casting is formed during an eutectoid reaction. [27, 31, 42, 43, 47]

The final structure can be divided to:

1. basic metal matrix – ferrite, perlite and other structural components
2. high-carbon phase – graphite, ledeburite

The conditions of crystallization are guided by the equilibrium diagram Fe-Fe$_3$C, Fe-C – Figure 10.

![Equilibrium diagram Fe-Fe$_3$C, Fe-C](image)

Figure 10 – Binary diagram Fe-C and Fe-Fe$_3$C

The influence of silicon on the critical points of the diagram is also recorded in this diagram.

A fundamental difference between crystallization of steel and a cast iron is that the cast iron crystallizes either in a metastable state – in this case a high-carbon phase is released in the form cementite (the cast iron is referred to as white); or it crystallizes in a stable state – then the high-carbon phase is released in the form of graphite (the cast iron is referred to as grey). At certain conditions, both form of high-carbon phase coexist at the same time (the cast iron is referred to as poppy or half-hearted).

The decisive conditions for one form or the other are these:

1. chemical composition
2. Cooling Speed

It follows that the individual types of cast iron cannot be characterized only by chemical composition, as in the case of steel, but we have to consider other conditions, which are decisive for the final structure of cast iron – the cooling conditions.

Cast iron crystallization differs from the steels by the eutectic delay, which occurs during the solidification. The difference between the crystallization of steel and cast iron results from the schematic cooling curves shown in Figure 11. While steel crystallizes in the range of temperatures between the liquid temperature and the solid temperature without delay, in cast iron an eutectic is formed during crystallization. In this eutectic, the melt is equilibrium and the solid phase consists of austenite and graphite or cementite. \([44, 45, 46]\). Cementite eutectic is called ledeburite. The eutectic reaction widens the range of crystallization temperatures and contributes to the final structure of the cast iron. According to the content of carbon in the cast iron, we divide them into hypoeutectic \((C<4.3\%)\), eutectic \((C=4.3\%)\), and hypereutectic \((C>4.3\%)\). In an hypoeutectic cast iron, the austenite is mainly released – mostly in a dendritic form. In an hypereutectic cast iron, the high-carbon phase is released (primary cementite, graphite). In eutectic cast irons the austenite, graphite and ledeburite crystallize at the same time. During the eutectic reaction, the melt, austenite, graphite and ledeburite are all in equilibrium.

\[ T_L - \text{liquid temperature; } T_S - \text{solid temperature; } T_E - \text{eutectic temperature} \]

Figure 11 – Cooling curves of steel (A) and cast iron (B)

### 4.1 Crystallization of the Eutectic

The formation graphitic or ledeburitic eutectic depends on the thermodynamic and kinetic conditions of crystallization. \([44, 45]\)

Thermodynamic conditions are given by the change of free energy of the stable and metastable system, as shown on the Figure 12. The change free energy \(\Delta G\) in pure cast iron Fe-C has the following form:

\[
\Delta G = -L \cdot \frac{\Delta T}{T_E} \quad [J.mol^{-1}.K^{-1}] 
\]
where: \( L \) latent heat of crystallization of graphite or ledeburite
\( T_E \) equilibrium temperature of the eutectic
\( \Delta T \) undercooling value

The temperature of a stable equilibrium eutectic is 1153 °C, for a metastable eutectic, it is 1147 °C, \( \Delta T = 6 \) °C.

![Diagram of ΔG vs Temperature](image)

Figure 12 – The influence of undercooling on the crystallization of the cast iron

Stable crystallization, in other words the activation of graphite seeds, does not need a high value of \( \Delta G \), excretion of graphite takes place already at low degrees of undercooling (around 8÷10 °C).

With lowering content of carbon in the cast iron, the value of undercooling becomes higher.

During the crystallization of spheroidal graphite CISG, a high value of \( \Delta T \) (around 60 °C) is necessary, which is explained by the change of physical and chemical properties of the cast iron processed by the modification with magnesium. If the undercooling is high, the melt temperature reaches lower temperature than the metastable temperature – the melt will crystallize without precipitation graphite (see alternative in Figure 13c,13d).
The interval between the stable and metastable temperature is decisive for the graphitization ability of the cast iron. This interval is influenced by the presence of other elements in the cast iron (Figure 14). Elements that widen the interval between $T_S$ and $T_M$ will support graphitization and vice versa (Figure 15). The eutectic is defined as a eutectic cell. A stable eutectic cell has an appearance according to the graphitization conditions and it is related to the change of shape of the graphite (lamellar – vermicular – spheroidal).
Metallurgy of cast irons. Out-of-furnace processing of molten cast iron. 2014

In the Figure 16 there are the types of eutectic cells:

a) cast irons with lamellar graphite
b) undercooled cast irons with lamellar graphite
c) cast irons with spheroidal graphite
d) white cast irons

The effect of chemical composition on the crystallization of the eutectic is associated with its influence on the activity of carbon in the melt of the Fe-C-X alloy as follows:

The saturation of the carbon in molten iron depending on the temperature can be determined using the following equation:

\[ \%C_{SAT} = 0.649 + 2.53 \cdot 10^{-3} \cdot T \]  \hspace{1cm} \text{temperature in K} \tag{27} \]

The activity of carbon in the solution can be determined using the activity coefficient \( f_C \) for a given temperature and carbon content:

\[ \log f_C = \frac{158}{T} + 0.0581 \cdot [\%C] + \frac{8.94}{T} \cdot 0.0026 \cdot [\%C]^2 \]  \tag{27a} \]
where:  \( T \) is the temperature in K
\( \%C \) is the carbon content in the solution in \%

For example, at 1250 °C the concentration of C = 4.5 %, the correspondent coefficient of activity is \( \log f_C = 0.42 \) (according to the equation 27). According to the equation 27a the activity \( C > 1 \) in the Fe-C system, carbon will be released in the form graphite.

In doing so:

\[
 a_C = f_C \cdot \left[ \%C \right]
\]

The effect of a third element on the change of activity \( a_C \) can be calculated using the interaction coefficients \( e_C^x, r_C^y \). The effect of these elements can be divided into two groups:

1/ **carbide forming** (Zr, Ti, V, Mo, Cr, W, Mn) – increase the solubility of C and decrease its activity

2/ **graphite forming** (Si, Al, P, Cu, Ni, Co) – decrease the solubility of C and increase its activity

With the change of activity of carbon comes the change of its concentration in the solution depending on other present elements in the molted cast iron.

\[
 C^x = m \cdot x
\]

where:  \( C^x \) is the change of solubility of carbon in %
\( m \) is the coefficient of the effect of element x on the activity of carbon (see. Table 3)
\( x \) is the concentration of element x in %

<table>
<thead>
<tr>
<th>element</th>
<th>m</th>
<th>x (wght. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>- 0.40</td>
<td>0.4</td>
</tr>
<tr>
<td>P</td>
<td>- 0.33</td>
<td>3.0</td>
</tr>
<tr>
<td>Si</td>
<td>- 0.31</td>
<td>5.5</td>
</tr>
<tr>
<td>Al</td>
<td>- 0.22</td>
<td>2.0</td>
</tr>
<tr>
<td>Cu</td>
<td>- 0.074</td>
<td>3.8</td>
</tr>
<tr>
<td>Mn</td>
<td>+ 0.027</td>
<td>2.5</td>
</tr>
<tr>
<td>Cr</td>
<td>+ 0.063</td>
<td>9.0</td>
</tr>
<tr>
<td>Ti</td>
<td>+ 0.14</td>
<td>-</td>
</tr>
</tbody>
</table>

From that it is possible to determine the real content of carbon in the eutectic.

\[
 C_{c'} = \frac{C}{Fe - C} - \sum_{i=1}^{n} \Delta C_i^x
\]  \( (28) \)
therefore

\[ C'_c = 4.26 - \sum_{i=1}^{n} (m_i \cdot x_i) \quad [\%] \]  

and after substituting

\[ C'_c = 4.26 - 0.31 \cdot Si + 0.33 \cdot P + 0.027 \cdot Mn - 0.4 \cdot S \]  

The degree of eutectiveness (\( S_c \)) can be calculated from the following relation:

\[ S_c = \frac{C}{C_c} = \frac{C}{4.26 - 0.31 \cdot Si - 0.33 \cdot P + 0.027 \cdot Mn - 0.4 \cdot S} \]  

where \( C \) is the analytically determined total carbon in the cast iron according to the ČSN and in practice, this formula is simplified to the form of:

\[ S_c = \begin{cases} > 1 & \text{hypereutectic cast iron} \\ = 1 & \text{eutectic cast iron} \\ < 1 & \text{hypoeutectic cast iron} \end{cases} \]

The carbon equivalent (\( C_{ekv} \)), which determines – similarly to the \( S_c \) – the position of the cast iron in the Fe-C diagram, will be determined from the following relation:

\[ C_{ekv} = C + \sum_{i=1}^{n} (m_i \cdot x_i) \quad [\%] \]  

\( C_{ekv} \) corresponds with \( S_c \).

The above mentioned information imply the influence of chemical composition of the cast iron on the process of crystallization of the eutectic.

Another important factor influencing the crystallization of cast irons is the cooling speed of molten cast iron, in other word the speed of transition between the liquid state and the solid state.

The influence of this factor is expressed by isothermal and anisothermic transformation of the eutectic transition [31].

Figure 17 and Figure 18 show the mechanism of effect of the cooling rate on the final structure of the cast iron. Temperatures \( T_1 \) and \( T_2 \) and the correspondent cooling rates \( v_1 \) and \( v_2 \) provide the conditions for the transformation of structural components of the final structure of the cast iron. In the temperature range between \( T_1 \) and \( T_2 \), both high-carbon phases are formed at the same time. The resulting form is mottled structure, where two carbon phases coexist together – graphite and cementite (mottled cast iron).
Metallurgy of cast irons. Out-of-furnace processing of molten cast iron. 2014

Figure 17 – Curves of isothermal transformation

- $G_s$ - the beginning of crystallization of the graphitic eutectic
- $G_f$ - the end of crystallization of the graphitic eutectic
- $L_s$ - the beginning of ledeburitic crystallization
- $L_f$ - the end of ledeburitic crystallization

Figure 18 – Curves of anisothermic transformation
In terms of the morphology of the solidification, the cast irons have mutual difference that is related to the processing of the melt. They solidify differently when comparing the graphitizing cast irons and white cast irons. The graphitization is also various, e.g. in CILG or CISG.

In the Figure 19 there is the schematic visualization of the solidification of CILG and CISG. This picture shows the difference between the solidification of CILG eutectic and a CISG cast iron. While in CILG an eutectic cell is formed during the austenite crystallization, in CISG the austenite crystallization prevails over the formation of eutectic cell.

This different morphology of solidification of graphitizing cast irons is especially important for the formation of shrinkages of these cast irons.

4.2 Graphite crystallization

Crystallization of graphite constitutes an individual chapter because the crystallization determined the shape, amount, size and method of graphite release.

Graphite may be released in the cast iron either through direct or indirect paths:

- In the direct path, carbon is the seed of graphitization. Carbon is present in a sufficient concentration in the melt, and therefore it increases the activity of the reaction towards the seeding of graphite. So-called homogeneous nucleation takes place.

- The indirect path of graphite crystallization leads through the formation of cementite, its break up with the formation of carbide, oxide and nitride seeds, which support the seeds of graphite – a so called heterogeneous nucleation.

<table>
<thead>
<tr>
<th>Direct path:</th>
<th>Indirect path:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{solution}} \rightarrow C_{\text{graphite}}$</td>
<td>$C_{\text{solution}} \rightarrow Fe_{3}C + \text{Austenite} \rightarrow C_{\text{graphite/p}}$</td>
</tr>
</tbody>
</table>
4.2.1 The mechanism and kinetics of graphitization

If we consider the indirect path, then the graphitization includes the following processes:

- Break up
- Diffusion
- Free graphite crystallization
- Dissolving
- Slowed down graphite crystallization

These processes can be thermodynamically described through the so-called coefficients of diffusion, dissolution, break up and crystallization.

\[
\text{graphite crystallization} = \frac{\left[\%C\right]_{\text{STABLE}} - \left[\%C\right]_{\text{METASTABLE}}}{1 + \frac{1}{K_{DC}} + \frac{1}{K_D} + \frac{1}{K_{KR}}} \tag{34}
\]

where:
- \(\left[\%C\right]_{\text{STABLE}}\) – concentration gradient
- \(K_{DC}\) – the coefficient of dissociation of cementite in the melt
- \(K_D\) – the coefficient of carbon diffusion
- \(K_{KR}\) – The coefficient of crystallization (free – in the melt, slowed down – in the solid state)

In the denominator the mentioned processes take place simultaneously. The process that is the slowest in this period is the limiting one. For example, during the crystallization of CILG, the graphite is surrounded partly by austenite and the ends of lamellas are in contact with the melt, that is why the graphite lamella grows faster in the longitudinal direction than in the transverse direction, where the carbon diffuses into lamellae through austenite.

In the case of spheroidal graphite, the graphite grows uniformly, because more carbon gets to the graphite crystal only through diffusion through an austenite envelope, that is why it grows in all directions with the same speed. From the point of view of graphitization kinetics – homogenous and heterogeneous – the speed of growth of seeds depending on time is considered.

On the Figure 20 the graphitization kinetics is visualized. The temperature is on the horizontal axis and the number of nucleus is on the vertical axis.
The mechanism of graphitization can be influenced by external procedures – inoculation, modification, or alloying.

**Calculation of EGM**

Original form:

\[
EGM_{TEO} = C_{an} - C_E + 0.1 \cdot (Si + P)
\]  (35)

\(C_{an}\) – analytically determined value of total carbon  
\(C_E\) – maximum solubility of the carbon influenced by silicon (constant value of 2% Si)

\[
EGM_{TEO} = C_{an} - 1.3 + 0.1 \cdot (Si + P)
\]  (36)

Present form:

\[
EGM_{TEO} = C_{an} - C_E + 0.17 \cdot (Si + P) = C_{an} - 1.81 + 0.17 \cdot (Si + P)
\]  (37)

EGM calculated in this way can be considered as theoretical (EGM_{TEO}) – determined only based on the content of C, Si, P.

\[
\text{Graphitization ability} = \left( \frac{EGM_{R}}{EGM_{TEO}} \right) \cdot 100 \quad \text{[\%]} \]  (38)

\(EGM_{R}\) - real EGM determined experimentally
The above mentioned basic knowledge about the crystallization of the cast iron give an idea about the complexity of this process and at the same time they enable us to understand the basic laws of transition of melt from liquid state to solid state with the possibility to influence this process.

The method of releasing the eutectic is decisive during the crystallization, because in this period, there is the formation of graphite nucleus and by that the influence of the graphitization ability of the molten cast iron. In CILG, the period of crystallization of the eutectic is proportional to the carbon content – the lower the carbon content, the lower the amount of eutectic and also the lower the graphitization ability of the cast iron. In CISG the eutectic has the largest portion of the crystalline phase, because the carbon content is at high levels around 3.7÷3.9 %C.

**Term summary**

– Is mentioned in the „Contents of the chapter“ part

**Questions**

- Describe the Fe-C and Fe-Fe\textsubscript{3}C diagrams
- Explain the eutectic crystallization in the cast iron
- Describe the course of solidification of cast irons using the cooling curve
- Describe the types of eutectic cells and the morphology of cast iron solidification.
- Explain the mechanism and kinetics of the graphite formation in cast irons
5 INFLUENCING CAST IRONS CRYSTALLIZATION

Time to study: individual

Aim After studying this chapter you will be able to:

- Describe the cooling curve (CC) of cast irons
- Explain the use of 1st derivation of the normal CC and the areas PA, EA, ER.
- Apply the calculation of the oxidation degree of the cast iron
- Interpret the analysis of furnace and ladle slag

Presentation

Current knowledge about the cast iron crystallization permit the modifications of this process especially of the graphite crystallization – graphitization. The main task of a metallurgist of cast iron is to preventively determine the graphitization ability of the cast iron – the extent to which the carbon presence in the cast iron will activate the creation of graphite nucleus.

One of many methods according to which the graphitization ability of a cast iron can be determined, is a thermal analysis of the curves of 1st and 2nd derivation of temperature-time. [44, 45, 46, 53] An example of a typical cooling curve is on the figure below.
Figure 21 – Typical cooling curve of a cast iron solidifying in a stable way

On the Figure 21 there is a typical cooling curve of a cast iron solidifying in a stable way and its first derivation.

The cooling curve compared to the theoretical cooling curve $T_0 = k \cdot \sqrt{\tau}$ enables us to calculate the amount of released phases (the bottom portions marked PA, EA and ER) based on the crystallization heats of the austenite and graphite. On the curve it is possible to determine the critical temperatures of the transition of cast iron from the liquid to solid phase.
Metallurgy of cast irons. Out-of-furnace processing of molten cast iron. 2014

$T_L$ temperature of the liquid  
$T_0$ temperature of the solid  
$T_{eu}$ bottom eutectic temperature  
$T_{eo}$ top eutectic temperature  
$T_X$ beginning of the austenite release  
$PA$ amount of released austenite  
$EA$ starting amount of eutectic ($T_K$)  
$ER$ residual amount of eutectic ($T_s$)  
$R$ recrystallization related to the theoretical temperature by the eutectic

Figure 21 on the right, marked $VK_1$ and $VK_2$

$$T_E = 1153 + 6.7 \cdot [\% Si]$$ (39)

To assess the metallurgical quality of the cast iron, it is possible to use (Figure 22) the proportion of residual eutectic to the starting amount of eutectic, which also expresses the kinetics of the graphite seeding, because, as was already mentioned, deoxidation, degasification and formation of graphite seeds are the core processes of inoculation.

$$\frac{ER}{EA} = 0.4 \div 0.6$$ low value, tendency to shrink

$$\frac{ER}{EA} = 1 \div 1.2$$ optimal, good quality

$$\frac{ER}{EA} = 1.6 \div 2$$ high value, slaginess, gassiness of the castings

This ratio can also be expresses based on the analysis of the slag through the ratio of $\frac{SiO_2}{FeO + MnO}$. If this ratio is high, then the slag and oxygen content is also high. If it is low, then there is high tendency to shrink. The ratio $\frac{SiO_2}{FeO + MnO}$ is called the degree of oxidation of the melt.

The analyses of slags from a cupola and a casting ladle can be used as an example – table 4.
Figure 22 – The dependence determining the metallurgical quality of the melt

Table 4 – Analysis of the slags from cupola and pouring ladle

<table>
<thead>
<tr>
<th></th>
<th>$SiO_2$</th>
<th>$\sum FeO + MnO$</th>
<th>$\frac{SiO_2}{FeO + MnO}$</th>
<th>marking</th>
</tr>
</thead>
<tbody>
<tr>
<td>slag cupola</td>
<td>46.9</td>
<td>2.7</td>
<td>17.3</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>50.2</td>
<td>4.0</td>
<td>12.5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>52.8</td>
<td>5.1</td>
<td>10.3</td>
<td>3</td>
</tr>
<tr>
<td>slag ladle</td>
<td>43.32</td>
<td>53.96</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>42.3</td>
<td>39.7</td>
<td>1.07</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>51.2</td>
<td>42.7</td>
<td>1.2</td>
<td>3</td>
</tr>
</tbody>
</table>

The melt marked with number 1 „slag-ladle“ has an optimal degree of oxidation, melt n.3 “slag-pan” tends to have defects like slag or higher content of gases.
Table 5 – The degree of oxidation during modification

<table>
<thead>
<tr>
<th>Method</th>
<th>( \text{SiO}_2 )</th>
<th>( \sum \text{FeO} + \text{MnO} )</th>
<th>( \frac{\text{SiO}_2}{\text{FeO} + \text{MnO}} )</th>
<th>marking</th>
</tr>
</thead>
<tbody>
<tr>
<td>glazing Fe Si Mg5</td>
<td>30.2</td>
<td>37.4</td>
<td>0.81</td>
<td>1</td>
</tr>
<tr>
<td>convertor 100 % Mg</td>
<td>17</td>
<td>16.6</td>
<td>1.02</td>
<td>2</td>
</tr>
</tbody>
</table>

Using pure magnesium during modification is more prone to defects of the slag type, or a gas content (marked 2).

The most used of various technological tests (chill) is the wedge test and the analysis of the fracture in this test. Apart from the chemical analysis, the above mentioned tests also complement the melt controlling during the melting process.

### Terms summary

- Mentioned in the „Contents of the chapter“ part

### Questions

- How do we obtain a cooling curve of a cast iron?
- Why do we use the 1st derivation of the cooling curve and what is the importance of the areas \( PA, EA, ER \)?
- How can we calculate the degrees of oxidation of the melt
- How can we interpret the chemical analyses of the furnace and ladle slags?
6 INOCULATION

Contents of the chapter

✓ Theory of inoculation
✓ The influence of oxygen on the process of inoculation
✓ The mechanism of inoculation effect
✓ The methods of inoculation

Time to study: individual

Aim After studying this chapter you will have the knowledge about:

- Theory of inoculation
- The mechanism of inoculation effect
- The influence of oxygen on the process of inoculation
- The methods of inoculation
- The comparison of the inoculation effect of various inoculants

Presentation

One of the main methods of after furnace processing of molten cast iron (influencing the final structure of the cast iron in a casting) is inoculation, meaning the formation of sufficient amount graphitization nucleus. A bigger number of nucleus softens the graphite, prevents the release of free cementite and by that it decreases the tendency to chills. The precondition of this process in the first phase of melting (in the furnace) is that the molten cast iron has a sufficient nucleation potential for the next inoculation process given by the composition of the batch. [29, 34, 39]

The essence of inoculation is the heterogeneous nucleation, which is supported by the introduction of inoculates, usually based on FeSi into the molten cast iron.

We use inoculation when we want to reach an increase of exogenous graphitization nuclei and by that reach the softening of the released graphite, prevent the formation of free cementite and decrease the occurrence of chill in the critical sections of the casting (sections under the width of 8 to 4 mm).

The used inoculants and inoculation techniques will be listed in more detail in the following chapters.
Inoculation is a complex process influenced by a number of variable factors such as: keeping the temperature, basic chemical composition, a suitable type of inoculant, grain structure. The process is used to influence the structure of the basic metal matrix (in CISG) and to influence the method of release of graphite (in LLG).

For example, in a cast iron with lamellar graphite (CILG), the inoculation influences the size and amount of graphite lamellas. In a cast iron with vermicular graphite (CIVG) it influence the structure of the basic metal matrix and in a cast iron with tempered graphite (CITG), we use the inoculation to shorten the period of tempering.

In this way like this:

- **Inoculation**
  - Improves the mechanical properties of the cast iron
  - Decreases stresses in thin walled castings
  - Increases the graphitization ability of the molten cast iron and decreases chill in castings from CISG or in castings cast into metallic forms
  - The chemical composition of the cast iron practically does not change
6.1 Theory of inoculation

Inoculating has become the subject of research of many experts who tried to explain the process of nucleation taking place during the crystallization of cast iron and determine the rules for the methods of inoculation, so that the scope of nucleation was preserved as much as possible. Research of nucleation from 50 years of the last century has changed the views on the scope of nuclei added to the melt. The resulting hypotheses until now can be divided into the following groups:

a) **physical and chemical nature** of inoculation, in other word the role of the surface tension of the melt, the crystalline structure of the inoculant and the affinity of the parameters of the crystalline lattice.

b) **thermodynamic nature** of inoculation and the related nature of homogeneous and heterogeneous nucleation, the formation of oxides, or other compounds constituting the heterogeneous nucleation phase.

c) this group contains **other** hypotheses, which define the state of the melt before inoculation, during it and they apply the knowledge from physical chemistry and thermodynamics

a) **Physical and chemical nature of inoculation**

Inoculants, inducing the formation of new nuclei, should have the same crystalline lattice as graphite, hexagonal, or at least one parameter of the crystalline lattice should have the same size as the parameter of the graphite lattice (deviation $\pm 5\%$). [32]

Figure 23 shows the ideas about graphite nucleation using CaC$_2$. That implies a positive influence of calcium on the formation of seeds. The formation of CaC$_2$ has been explained according the reaction Ca-C in chapter 3.3.

![Diagram of CaC$_2$ and graphite formation](image)

Figure 23 – The scheme of effect of the CaC$_2$ on graphitization during inoculation
Figure 23a shows the crystalline lattice of CaC$_2$ and graphite. Figure 23b shows the scheme of effect of CaC$_2$ on the seeding of graphite during the transition from the liquid phase to the solid phase. In this case, the condition of minimal deviation of the parameters of lattice is accomplisher (7.4Å in CaC$_2$ and 7.42Å in graphite). The angle of wettability $\delta$ on the interface between phases melt – alien seed – graphite seed has to be smaller than 180°, which is clear from the Figure 24. In that case, according to the relation on Figure 24, the alien seed is actively supporting graphitization. The interface tension is given by the physical and chemical properties of the melt, which change after adding the inoculant and this determines the wettability of the alien seed vis-à-vis the graphite seed. With an angle bigger than 180° the alien seed would be repelled from the graphite. [32]

Figure 24 – The influence of exogenous particle on the nucleation of graphite

b) Thermodynamic nature of inoculation

Using the thermodynamic laws, we are able to determine the processes of chemical reactions that take place during inoculation. The inoculant added to the melt in the solid state is melted and chemical compounds are being formed, mostly oxidic, which from the point of view of heterogeneous nucleation are the most effective (mostly SiO$_2$). Apart from these oxides, other compounds are formed such as carbides, nitrides and sulphides, which support the heterogeneous nucleation by their effects. To understand these laws, it is necessary to know about the physical and chemical parameters of these elements contained in inoculants:

Table 6a – Physical parameters of selected elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Melting temperature [°C]</th>
<th>Boiling temperature [°C]</th>
<th>Atomic weight [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1410</td>
<td>2355</td>
<td>28.1</td>
</tr>
<tr>
<td>C</td>
<td>3830</td>
<td>-</td>
<td>12</td>
</tr>
<tr>
<td>Ca</td>
<td>850</td>
<td>1484</td>
<td>40</td>
</tr>
<tr>
<td>Al</td>
<td>660</td>
<td>2460</td>
<td>26.98</td>
</tr>
<tr>
<td>Ba</td>
<td>710</td>
<td>1638</td>
<td>137.3</td>
</tr>
<tr>
<td>Sr</td>
<td>757</td>
<td>1364</td>
<td>87.6</td>
</tr>
<tr>
<td>Mg</td>
<td>650</td>
<td>1090</td>
<td>24.31</td>
</tr>
</tbody>
</table>
Table 6b – Thermodynamic parameters at the temperature of 1773 K (1500 °C)

<table>
<thead>
<tr>
<th>Element</th>
<th>Pressure of saturated vapors for the pressure of 1 bar</th>
<th>The content of the element at boiling point and the pressure of 1 bar</th>
<th>Equilibrium constant</th>
<th>log (O) for 1 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>1.0486</td>
<td>0.003</td>
<td>-11.0602</td>
<td>-7.0176</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>selected – 0.05</td>
<td>-11.9631</td>
<td>-3.4795</td>
</tr>
<tr>
<td>Ba</td>
<td>0.2014</td>
<td>0.0559</td>
<td>-9.3948</td>
<td>-3.0662</td>
</tr>
<tr>
<td>Sr</td>
<td>2.1721</td>
<td>0.0070</td>
<td>-10.2226</td>
<td>-6.2887</td>
</tr>
<tr>
<td>Mg</td>
<td>12.4290</td>
<td>0.0055</td>
<td>-9.4880</td>
<td>-5.3656</td>
</tr>
</tbody>
</table>

The following thermodynamic relations determine the amount of oxygen that is in equilibrium with the given element contained in the inoculant at the temperature of processing of the melt. Using these calculations, we can determine the influence of each inoculant on the formation of oxides and by that describe its influence on the formation of nucleation phase. [28]

**Ca:**

\[
\log(P_{Ca}^O) = -8082/T + 4.579
\]

\[
\log[Ca] = 1196/T - 2.192
\]

\[
\log Kp = -34104/T + 8.175
\]

\[
\log|O| = \log Kp - \log[Ca] - e_{o}^{Ca} \cdot |Ca| - \frac{e_{o}^{Ca} \cdot 2.3 \cdot Kp}{|Ca|^2}
\]

**Al:**

\[
\log Kp = -62876/T + 23.5
\]

\[
\log|O| = \frac{1}{3} \cdot \log Kp - \frac{2}{3} \cdot \log|Al| + e_{o}^{Al} \cdot 2.3 \cdot Kp \frac{2.3 \cdot Kp}{|Al|^2}
\]

**Ba:**

\[
\log(P_{Ba}^O) = -7535/T + 3.554
\]

\[
\log[Ba] = -760/T - 0.824
\]

\[
\log Kp = -31318/T + 8.269
\]

\[
\log|O| = \log Kp - \log[Ba] - e_{o}^{Ba} \cdot |Ba| - \frac{e_{o}^{Ba} \cdot 2.3 \cdot Kp}{|Ba|^2}
\]
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Sr:

\[
\log(P_{Sr}^O) = -7422/T + 4.523 \\
\log|Sr| = -310/T - 1.98 \\
\log Kp = -32259/T + 7.972 \\
\log|O| = \log Kp - \log|Sr| - e_{Sr}^O \cdot |Sr| - \frac{e_{Sr}^O \cdot 2.3 \cdot Kp}{|Sr|^2}
\]

Mg:

\[
\log(P_{Mg}^O) = -6333/T + 4.666 \\
\log|Mg| = 970/T - 2.804 \\
\log Kp = -31375/T + 8.208 \\
\log|O| = \log Kp - \log|Mg| - e_{Mg}^O \cdot|Mg| - \frac{e_{Mg}^O \cdot 2.3 \cdot Kp}{|Mg|^2}
\]

Example: The Superseded inoculant – Si = 75 %, Ca = 0.1 %, Al = 0.5 %, Sr = 0.8 %. In case we batch in an amount of 0.7 % to mass of liquid metal, then the following amount will be put in the melt together with the inoculant:

Si = \frac{0.7 \cdot 0.75}{100} = 0.525\% \quad Ca = \frac{0.7 \cdot 0.1}{100} = 0.0007\%

Al = \frac{0.7 \cdot 0.5}{100} = 0.0035\% \quad Sr = \frac{0.7 \cdot 0.8}{100} = 0.0056\%

These values correspond to the equilibrium amount of oxygen listed in the table 7 at the temperature of 1485 °C.

Table 7 – Equilibrium state of oxygen at 1485 °C

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Ca</th>
<th>Al</th>
<th>Sr</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-4.6</td>
<td>-8.83</td>
<td>-3.8</td>
<td>-6.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.000025 %</td>
<td>0.0000000001 %</td>
<td>0.00016 %</td>
<td>0.0000003 %</td>
<td>0.000185301 %</td>
</tr>
</tbody>
</table>

The above mentioned value enable us to state that in case of calcium and strontium, their influence on the inoculation at given conditions is negligible. On the other hand, the influence of silicon and aluminum is significant, however, it is necessary to take into account that elements such as strontium and calcium can significantly influence the amount of sulfur (formation of sulfides). Due to the low boiling point of strontium, its evaporation may occur and it may positively influence the inoculation. The bond of calcium with carbon is more
important than with oxygen, because $\text{CaC}_2$ is formed. The reaction proceeds to the right and the higher the temperature the higher the possibility of creation of $\text{CaC}_2$.

c) Other hypotheses

According to the current theoretical knowledge, the influence of inoculant on the graphite nucleation is the following:

According to the author [23], the effect of FeSi and SiC as inoculant is schematically displayed on Figure 25. It is a comparison of the effect of these two compounds, wherein SiC has a very effective influence on the formation of graphitizing nuclei, but it cannot be used as an inoculant. SiC has a great importance in the first phase of the melting to increase the nucleation potential of the melt a by that improve the conditions of the subsequent inoculation process. Figure 25 shows that the effect of the inoculant in the melt is divided into three phases:

- Dissolving the Si applied to the melt by the inoculant
- Dissolving the formed graphite
- Dissolving the graphite clusters

The top part of the Figure 25 represents the mechanism of the influence of SiC, the bottom part represents the influence of FeSi. A layer of $\text{SiO}_2$ is formed around the layer of SiC, which causes an intensive release of graphite (30% of the total carbon released as graphite and the formation of molecules of C) so-called pre-inoculation effect.

During this mechanism, nucleation and growth of austenite take place as well as the releasing of graphite (inoculation effect) and releasing of cementite. The whole process take place slowly and it prolongs the inoculation effect. It is caused by the fact that the carbon clusters and carbon molecules easily dissolve in austenite and at the same time the graphite nucleation easily takes place. The formation of cementite is conditioned by the formation of atomic carbon.

When using FeSi, only 5% of the total amount carbon is used for the reaction and the formation of graphite is not as intensive. The dissolution of carbon clusters (the last part of Figure 25) to atomic carbon follows.

In general, it is possible to explain the inoculation effect in a cast iron by the influence of different concentration of silicon from the inoculant in the melt (high concentration around the grain of inoculant) [33]. This results in the formation of cast iron with hypereutectic composition in the areas of inoculant dissolution. The composition ensures the release of primary graphite when the temperatures are lowered. This hypothesis emphasizes the influence of the maximum dispersion of inoculant in the whole volume of the melt.

For the carbon to be released in the form of graphite, the activity of carbon has to be $a_C \geq 1$. If the value is lower than 1, graphite is not formed. The activity of carbon is therefore a condition of the formation of graphite. As the solution of cast iron is also composed of other elements, it is necessary to consider their influence on the activity of C.
**Figure 25** – The comparison of the inoculation effect of two different inoculants FeSi and SiC [23]

An example of a direct graphite nucleation

\[
[C] = C_{Gr} \quad \text{(40)}
\]

\[
\Delta G = R \cdot T \cdot \ln a_C \quad \text{(41)}
\]

Indirect graphite nucleation due to the breaking of Fe₃C

- e.g. Ca, Zr, Ti according to the reaction

\[
Fe_3C \rightarrow 3[Fe] + C_{Gr} \quad \text{(42)}
\]

\[
Ca + m \cdot Si + n \cdot C = p \cdot CaSi + g \cdot Ca_2Si + r \cdot CaC_2 \quad \text{(43)}
\]

The products of the reaction are dissolved and they form areas oversaturated with carbon and silicon and the direct release of graphite follows.

According to author [34] Figure 26 and Figure 27 the effect of inoculation can be described as follows:
The element reduces the solubility of carbon in the solution and does not form stable compounds (Figure 26). The inoculation effect can be determined from the angle \( \alpha \), the lower the angle, the bigger the inoculation effect. Furthermore, the inoculation effect is dependent on the concentration of carbon in the solution \( A = C_S - C_1 \). The concentration \( C_2 \) will not cause the inoculation effect because its concentration and therefore its activity is low. The activity of carbon \( a_c \) will depend on the character of element, generally called \( M \).

![Inoculation effect](image)

**Figure 26 – Inoculation effect, where the M element does not form compounds**

- \( \alpha \) – expresses the inoculation effect
- \( M, M_A \) – generally an element supporting the graphitization of carbon in the melt
- \( C_1, C_2, C_S \) – content of carbon in the melt in percentage

Figure 27 shows another example when the added element decreases the solubility of carbon in the solution, creates stable compounds, which can break up to form graphite. Figure 27 shows the example of silicon.

If we inoculate using the FeSi 75 % type inoculant, then the concentration of Si in the area of dissolution is 75 % and the SiC compound is formed, and it is stable at this concentration of silicon. During further dissolution, the concentration of Si decreases to the value of 22 %. At this concentration or lower, SiC breaks up and graphite is formed. If the concentration of Si decreases under 3 %, no inoculation effect takes place. That is why silicon is the base of graphitizing inoculants.

The following conclusion can be made [37]:

1/ Certain elements are capable of causing the releasing of graphite – they increase \( a_c \) - decrease the solubility of C in the solution. These are the elements: Al, Si, Cu, Co, Ni, P.

2/ Certain elements decrease the \( a_c \) and create stable compounds independent on concentration and temperature. These are the elements: Cr, Mn, Mo, V.
6.2 The effect of oxygen on the process of inoculation

As stated in literature [8, 25, 28, 36], various authors focus on the behavior of oxygen in the molten cast iron, as it is considered to be the determining factor for the inoculation effect. Many research works were made in this direction. They basically determine the dependence of the stability of formed oxides with regard on the presence of elements with high affinity towards oxygen. The dependence of the melt temperature and exposure time on melting temperature is being observed with regard to the technological conditions of melting.

According to Figure 28, authors [22] state the presence of oxides in the individual phases of casting. There is a formation of SiO₂ in the furnace, during casting out of furnace and inoculation in the casting pan, big amount of Al₂O₃ and a smaller amount of ZrO₂ are formed. After casting into a form, the presence of oxides is recorded in lower amount – meaning that the inoculation effects stops after pouring the melt into the form.
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Figure 28 – Changes of content of oxygen in the melt, in the furnace, in the ladle and for the inoculation in the casting

Figure 29 – Changes of the content of oxygen during overdosing the inoculant in the cast iron melt (samples taken from the side zone of the casting) [22]
Figure 29 shows the change of oxygen content depending on temperature. The maximum depletion of oxygen occurs at the temperature of 1570 °C and then it decreases. Lowering the amount of oxygen bound in oxides (O\textsubscript{SiO\textsubscript{2}}) culminates at 1570 °C, which is connected with the deoxidation of the melt by carbon.

![Oxygen content vs temperature graph]

Figure 30 – Gradual depletion of the melt from oxygen depending on the melting period at the exposure temperature of 1290 °C

Figure 30 shows the influence of delay time on the content of oxygen in the melt at T = 1290 °C, the delay time was from 0 to 260 min and the values of oxygen content lowered from original 70 to 5 ppm.

As shown in these pictures, 1600 °C is the limiting temperature. At these temperature, the carbon boiling occurs and during it there is a steep decrease of oxygen content (deoxidation by carbon).

The above mentioned dependencies show that the formation of oxides is important especially for heterogeneous nucleation. High overheating temperature influences this nucleation negatively, because the oxygen content can totally decrease and by that the amount of graphite seeds also decreases. The same goes for the exposure time at the given temperature.

The situation can be solved in the next stage of melt inoculation, so that the process of formation of oxides can be renewed again. In practice, this means the use of three steps method of inoculation, furnace- ladle, ladle - pouring ladle, pouring ladle- mould. In that case the total amount of used inoculant is divided into individual stages. The last phase has the lowest amount of inoculant. This arrangement permits variations.

Figure 31 is very important as it shows the influence of aluminum on the nucleation of graphite as well as the influence of aluminum on deoxidation of the melt. On the vertical axis there is the total amount of oxygen on the cast iron in the form of oxygen in ppm and on the horizontal axis there is the total amount of aluminum in the melt in ppm. With regard to the a possibility of deoxidation by aluminum, areas are shown in the Figure 31 where oxides
exceed considerably the content of aluminum, this area is defined as 25 % quality of the cast iron. When the total oxygen decreases, the bottom right case might occur, where for given oxides there will be aluminum in excess and that is the 35 % quality of the cast iron. The optimal content of aluminum for the given amount of oxides in the melt is marked by the middle area of 100 % quality of the cast iron. It is bordered by so-called minimum content $A_{\text{min}} = 8.6 \cdot [\%O]$ and then by $A_{\text{max}} = 24.1 \cdot [\%O]$.

![Diagram](image.png)

Figure 31 – Defining the areas for good metallurgical quality of cast iron depending on the amount of oxygen and aluminum (for deoxidation) in the melt. [28, 35]

Example: We have the total amount of oxygen of 15 ppm in the melt, the amount of aluminum in the melt before inoculation is 0.005 %. According to Figure 31 we can calculate the minimum amount of oxygen in the melt. The optimal amount of aluminum should be $15 \cdot 8.6 = 129 \text{ppm} = 0.0129 \% \text{Al}$. If we inoculate the melt by 0.7 % to mass of liquid metal then we will add by the inoculant with the content of 1.2 %Al, $0.7 \cdot 1.2/100 = 0.0084 \% \text{Al}$. The total amount of aluminum in the melt will then be $0.005 + 0.0084 = 0.0134 \% \text{Al}$. By inoculating, we have considerably improved the quality of the melt, so much, that we are now in the area of 100 % quality of the cast iron.
Example: The analytically determined total amount of oxygen in the melt is 25 ppm, the amount of aluminum is 0.006 %. The optimal amount of aluminum should be $25 \cdot 0.6 = 0.0206 \% \text{ Al}$. If we inoculate the melt with 0.6 % to mass of liquid metal then we will add, with the content of 1.2 % Al in the inoculant, $0.6 \cdot 1.2 / 100 = 0.0072 \% \text{ Al}$. The total amount of aluminum in the melt will then be $0.006 + 0.0072 = 0.0132 \% \text{ Al}$. In this case, we find ourselves in the top part (25 % quality of the cast iron), it is necessary to add the difference between the optimal and real value into the melt - $0.0215 - 0.0132 = 0.0083 \% \text{ pure aluminum}$.

Other authors [24, 25, 26, 49] state that there is a possibility of using the activity of carbon and the activity of silicon to explain the influence of the inoculation on the quality of the molten cast iron. The influence of inoculation on the quality is measured during a chill test.

In this method we calculate the activities of carbon and the activity of silicon on carbon from the melt prepared to inoculated, which has a certain temperature. We add the determined amount of inoculant and again calculate the correspondent change of activities caused by inoculation for the given temperature after inoculation. Before and after the inoculation we perform the chill test, because it is probable that the inoculation changed the activity of carbon, especially due to the silicon contained in the inoculant. This increase may be expressed as a multiplier or in percentage.

Authors [26, 49] have made a number of measurements of the influence of the activity on the depth of chill, and they have expressed these measurements in the dependencies in the Figure 32 and Figure 33.

![Figure 32 – The dependence $a_{C-Si}^{C-Si}$ depending on the chill depth before inoculation](image-url)
Figure 33 – The dependence of $a_C^{C-Si}$ depending on the chill depth after inoculation

### 6.3 The mechanism of inoculant effect

The above mentioned hypotheses suggest the following requirements for inoculants.

1) good solubility in the melt
2) content of elements increasing the activity of carbon, such as Si, Al and others
3) content of elements, which change the interphase tension by increasing the surface tension of the melt, such as Ba, Ca, Zr and others
4/ keeping the chemical composition of the inoculant in constant allowable limits according to the customer requirements is needed
5/ storage of the inoculants in closed metal containers in a dry environment is required.

The examples of chemical composition of some foreign manufacturers are listed in tables 8-11.

#### Table 8 – Foreign inoculants (fa ELKEM)

<table>
<thead>
<tr>
<th>Type</th>
<th>Si</th>
<th>Ca</th>
<th>Al</th>
<th>Ba</th>
<th>Zr</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foundrysil</td>
<td>73 – 78</td>
<td>0.75 – 1.25</td>
<td>0.75 – 1.25</td>
<td>0.25 – 1.25</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Superseed</td>
<td>73 – 78</td>
<td>max. 0.1</td>
<td>max. 0.5</td>
<td>–</td>
<td>0.6 – 1.0</td>
<td>0.6 – 1.0</td>
</tr>
<tr>
<td>F G Fe Si</td>
<td>74 – 78</td>
<td>0.4 – 1.0</td>
<td>1 – 1.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Zirconol</td>
<td>73 - 78</td>
<td>2 – 2.5</td>
<td>1 – 1.5</td>
<td>–</td>
<td>1.3 – 1.8</td>
<td>–</td>
</tr>
</tbody>
</table>
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Table 9 – fa Material Method Ltd.

<table>
<thead>
<tr>
<th>type</th>
<th>Si</th>
<th>Ca</th>
<th>Al</th>
<th>Zr</th>
<th>Mg</th>
<th>REM</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOKLAT 2</td>
<td>70 – 77</td>
<td>0.75 – 1.25</td>
<td>1.3 – 1.8</td>
<td>0.25 – 1.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NOKLAT 3D</td>
<td>74 – 78</td>
<td>1.3 – 1.8</td>
<td>1.25 – 1.75</td>
<td>0.6 – 1.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NOKLAT 18M*</td>
<td>65 – 70</td>
<td>0.8 – 1.5</td>
<td>0.8 – 1.5</td>
<td>–</td>
<td>1.25 – 1.75</td>
<td>0.05 – 0.15</td>
</tr>
<tr>
<td>ESCALOY</td>
<td>48 – 53</td>
<td>0.5 – 1</td>
<td>0.5 – 1</td>
<td>C = 30 – 35</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* special graphitizing inoculant for the cast iron with spheroidal graphite

Table 10 – Hempel Metals UK

<table>
<thead>
<tr>
<th>Si</th>
<th>Ca</th>
<th>Al</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>74 – 79</td>
<td>0.1 max</td>
<td>0.5 max</td>
<td>0.8 – 1.2</td>
</tr>
<tr>
<td>74 – 79</td>
<td>0.8 – 1.3</td>
<td>1.2 max</td>
<td>Ba</td>
</tr>
<tr>
<td>73 – 78</td>
<td>2.0 – 2.5</td>
<td>1.0 – 1.5</td>
<td>1.3 – 1.8</td>
</tr>
</tbody>
</table>

At present SiC 98 and SiC 84 inoculants are used

Table 11 – SiC type inoculants

<table>
<thead>
<tr>
<th>SiC</th>
<th>C free</th>
<th>Si free</th>
<th>Al pure</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC 98</td>
<td>98.5</td>
<td>0.23</td>
<td>0.62</td>
<td>0.04</td>
</tr>
<tr>
<td>SiC 84</td>
<td>83.7</td>
<td>5.06</td>
<td>0.06</td>
<td>0.3</td>
</tr>
</tbody>
</table>

6.4 Methods of inoculation

At present, various different methods are used to add the inoculant to molten cast iron. With the gradual change of methods of inoculation, also the requirements for inoculant types have changed:

1/ inoculation by liquid inoculant (less frequent method)

2/ inoculation by granulized inoculant (the most frequent method), the dimension of grains varies from 0.2 mm to 8-10 mm

3/ inoculation by compact bodies inserted to the pouring basin or to the reaction chamber in the gating system

4/ inoculation by filled profiles

One of the commonly used methods (not optimal) is to add the inoculant to the pouring channel of the melting furnace during the pouring of the liquid cast iron into the casting ladle,
or the inoculant can be placed on the bottom of the casting ladle before its filling. In case of inoculation in the ladle, it is necessary to fill the ladle with a certain amount of liquid metal before adding the inoculant. By this we prevent the inoculant from staying at the bottom of the ladle (uneven distribution of the inoculant in the melt). Both cases are methods without investment costs and are financially inexpensive. However, these methods carry a risk of decreasing the incubation period of the inoculation effect (shortening the effective period of the inoculant), the time limit of which was determined at around 20 minutes from adding the inoculant in the melt after casting the product.

That is why there is an effort to inoculate the melt immediately before casting or directly during the pouring into a casting mould. The amount of used inoculant is informatively set in the range of 0.1-1.2 % of the weight of liquid metal and it is totally individual according to the given conditions of casting and it is not possible to prescribe it.

Furthermore, some other inoculation methods will be listed according to the individual figures.

Figure 34 shows the inoculation using the compact inoculants placed in the gating hole. The body is inserted in the hole in such way, so that it is gradually melted away during the pouring process. This method is used when pouring the products of higher weight category and it has many advantages. First of all, it solves the problem of the incubation period of the inoculation effect, because the inoculation takes place immediately before solidification of the casting. The size and weight of the inoculating bodies are fixed for the given weight of the casting and type of cast iron, therefore the exact dosage is ensured. The bodies are produced in various categories of chemical composition.

This method of graphitizing inoculation is used in the production of massive castings from cast iron with spheroidal graphite with the use of so-called starting block.

Figure 34 – inoculation in the mould cavity – the layout.

Inoculation in the gating system is displayed on the Figure 35 and Figure 36. The inoculation chamber is divided by a dividing plane and a compact inoculant may also be used, or the granulized inoculant (Figure 36). This method has a number of advantages but also some disadvantages. Also in this case the conditions of keeping the incubation period and keeping the exact dosage of the inoculant for the weight of cast metal are complied with.
dynamic effect of flowing metal through the gating system ensures the good solubility of the inoculant. [37]

On the other hand, there is a risk of leakage of inclusions generated after inoculation into the casting. That is why it is recommended for pressurized castings (strained by the pressure of gaseous or liquid medium) to place a sieve or filter to the gating system with the corresponding cross-sectional dimension of the slag trap. Table 12 and 13 show the dimensions of the gating system according to Figure 35 and Figure 36.

Figure 35 – Inoculation in an gating system and using a compact inoculant.

Figure 36 – Inoculation in a gating system and using a granulized inoculant.
In irregularly shaped castings, especially in thin-walled, there may not be a total homogenization of the inoculant in the whole volume of the product during its pouring (by this method). It is necessary to pay attention to the construction of the gating system, which has to ensure an even filling of the mold cavity and which ensures the equal distribution of the dissolved inoculant. It is also necessary to ensure the control of the placement of the inoculant in the inoculation chamber. This method of inoculation is suitable for graphitizing inoculation of the cast iron with spheroidal graphite modified with pure magnesium.

The effort to inoculate the molten cast iron just before or during pouring into the mould lead to the construction of various batch meters for adding the inoculant. One of the methods of is injecting a very fine granulated inoculant into the stream of melt between the casting ladle and the mould cavity.

A special device connected automatically with the pouring machine will turn the injector on shortly after the beginning of the casting. This injector will use the compressed air and a feeder to inject the inoculant into the stream of melt, which entrains the inoculant into the mold cavity. This method is suitable for automatic moulding line with machine production of the moulds.

### Table 12 – Dimensions of the gating system according to Figure 35.

<table>
<thead>
<tr>
<th>Gate</th>
<th>Strainer</th>
<th>Reaction chamber</th>
<th>Drain area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b = diameter of the holes</td>
<td>r = top diameter</td>
<td>d = top diameter</td>
</tr>
<tr>
<td></td>
<td>b' = diameter of the holes</td>
<td>r' = bottom diameter</td>
<td>d' = bottom diameter</td>
</tr>
<tr>
<td></td>
<td>α = chamfer of the holes</td>
<td>f = height</td>
<td>g = depth</td>
</tr>
<tr>
<td></td>
<td>c = length of the holes</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Diameter | Cross section | Dimensions | |
|----------|---------------|-------------|
| e        | mm            | b E b' α c r  r' f d d' g |
| mm       | °             | mm          |
| 20       | 315           | 45 40,5 14 10 40 30 35 36 30 35 |
| 25       | 490           | 51 46,5 14 10 46 30 40 41 35 35 |
| 30       | 710           | 55 50,5 14 10 50 35 45 45 40 40 |
| 35       | 960           | 70 65 14 11 65 50 50 60 55 45 |
| 40       | 1260          | 80 75 14 11 75 60 55 70 65 50 |
| 45       | 1590          | 90 84 15 12 85 70 60 80 75 60 |

Moulds with low weight of the liquid metal in a flask are produced in a large number during a relatively long period of time and the melt inoculated in a holding furnace would lose its properties of an inoculated cast iron after some time.

During the last few years a new method is starting to be used. It also solves the above mentioned problems. It is the method of inoculation using filled profiles. In this method, the inoculant is pressed in a steel thin-walled pipe and is injected into the melt in the furnace using a feeding device. The speed of feeding has to be selected for the given conditions, so
that the dissolution of the core wire takes place near the bottom of the pan, which ensure the good spread of the inoculant in the whole volume of the melt. For large volumes, it is possible to increase the good spreading of the inoculant by purging it with an inert gas. This method is operative and exact. It is suitable to dose it just before casting into form – it moderately expensive.

Table 13 – Dimension of the gating system according to Figure 36.

<table>
<thead>
<tr>
<th>Gate diameter</th>
<th>Area</th>
<th>Maximum weight</th>
<th>Reaction chamber dimensions</th>
<th>Slag trap dimensions</th>
<th>Ingate area</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>E</td>
<td>m</td>
<td>d</td>
<td>d'</td>
<td>l</td>
</tr>
<tr>
<td>20</td>
<td>315</td>
<td>15</td>
<td>50</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>25</td>
<td>490</td>
<td>30</td>
<td>75</td>
<td>65</td>
<td>30</td>
</tr>
<tr>
<td>30</td>
<td>710</td>
<td>50</td>
<td>20</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>35</td>
<td>960</td>
<td>80</td>
<td>30</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>40</td>
<td>1260</td>
<td>120</td>
<td>75</td>
<td>65</td>
<td>30</td>
</tr>
<tr>
<td>45</td>
<td>1590</td>
<td>200</td>
<td>35</td>
<td>40</td>
<td>35</td>
</tr>
</tbody>
</table>

Figure 37 shows a diagram for determining the speed of feeding of the core wire (CW) depending on the weight speed of casting and the type of inoculating FP for the added amount 0.05 % of the weight of the liquid metal.

The feeding speed can be determined from the following formula:

\[
V = \frac{1}{100} \frac{m_o \cdot Z}{I \cdot \tau} \quad [\text{m.sec}^{-1}] \quad (44)
\]

where
- \( Z \) = addition of the inoculant (\%)
- \( I \) = the amount of inoculant (g/m)
- \( m_o \) = weight of casting in kg
- \( \tau \) = casting time (sec)
- \( V \) = feeding speed (m/sec)

The individual variations of the added profile is schematically illustrated in the following figures.
Figure 37 – The selected wire movement speeds depending on the feeding speed and the type of used inoculant IW (applies for CILG and the amount of inoculant in IW = 0.05% on weight of molten metal).

Figure 38 shows the possibility of adding the profile into the stream of metal during the casting from casting ladle through the beak.

Figure 38 – Inoculation by wire (FP): a) into the ladle b) into the stream
Figure 39 shows the disposition of feeding of a core wire into the ladle hanging on the casting crane.

![Feeding equipment](image)

**Figure 39 – Inoculation by a core wire on a casting crane**

Figure 40 shows the case of feeding the CW during the casting from the ladle with bottom outflow. The inoculation by core wire during the casting from holding furnaces is displayed in two variations on Figure 41 and Figure 42. Figure 41 shows the inoculation carried out in a semi-ladle equipped with a partition, which prevents the inflow of slag and products of inoculation into the form. Figure 42 shows the case when the filled core wire is fed directly through the stopper. The feeding device is controlled together with the controlling device dosing the needed amount of metal during the casting into the frame.
Figure 40 – Inoculating the FP into the stream of metal during casting

Figure 41 – Inoculating the FP in a semi-ladle during the casting
Figure 42 – Inoculating by FP during the casting from casting device using the stopper.

Filled profiles allow different combinations of inoculant composition, which is another advantage of this method of inoculation.

Table 4 shows the examples of composition of filled profiles and other important data such as the weight of the filling, total weight of the profile, diameter and thickness of the casing. This method is suitable for graphitizing inoculation during the production CISG, as will be described below.

Table 14 – Example of composition of filled profiles for graphitizing inoculation

<table>
<thead>
<tr>
<th>Title</th>
<th>Al</th>
<th>Ca</th>
<th>Mn</th>
<th>Si</th>
<th>Weight of the content g/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSi75</td>
<td>1.5</td>
<td>0.5</td>
<td>-</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>SUPERSEED</td>
<td>0.5</td>
<td>0.1</td>
<td>-</td>
<td>75</td>
<td>Sr 0.8</td>
</tr>
<tr>
<td>W 80</td>
<td>1.4</td>
<td>2.6</td>
<td>-</td>
<td>75</td>
<td>Zr 1.6</td>
</tr>
<tr>
<td>ZIRKOGRAF</td>
<td>1.3</td>
<td>1.5</td>
<td>6</td>
<td>66</td>
<td>Zr 6</td>
</tr>
</tbody>
</table>

The inoculation of cast irons is a very important intervention into the crystallization, by which we are influencing the final structure of the casting. Even if it is a quite long known method (since 1950s), it is becoming clear that it is necessary to pay due attention to it, because up until now this method is not totally theoretically mastered.

Gradually, the inoculation gets new importance and meaning, as there are new methods being developed and the quality of inoculants is improving.
The aim of metallurgists engaged in casting cast irons is to achieve even structure of the graphite and the basic metal matrix.

The effect of the inoculation depends on:

1. The properties of the inoculant – melting temperature of the inoculant, its chemical composition
2. the method of inoculation
3. the physical and chemical state of the melt
4. the amount of used inoculant
5. the timing of the inoculation
6. the purpose of the inoculation.

Terms summary

– Mentioned in the “Contents of the chapter” part

Questions

- What are the basic theories of inoculation?
- What is the mechanism of action of the inoculant?
- How is the effect of oxygen on the inoculation process demonstrated?
- What are the methods of inoculation?
- What is the effect of the inoculant based on FeSi and SiC?
7 MODIFICATION

Contents of the chapter

✓ Basic formulas for controlling the modification
✓ Conditions of modification
✓ Losses of magnesium when producing a cast iron with spheroidal graphite

Time to study: individual

Aim After studying this chapter you will be able to:

- Characterize the process of modification
- Apply the basic formulas for controlling the modification
- Define the conditions of modification
- Calculate the losses of magnesium during the production of a cast iron with spheroidal graphite

Presentation

We use modification to influence the shape of the graphite during its crystallization, so that the lamellar graphite changes to a spheroidal shape due to the influence of the modifier (noduliser). This considerably changes the utility properties of the cast iron but also the physical properties such as thermal conductivity, coefficient of thermal expansion and technological properties such as corrosion resistance, the possibility of welding and machining.

All these properties are expressed in Czech and European technical norms. The cast iron becomes tough with corresponding mechanical properties. The important thing is that these properties of cast iron with spheroidal graphite can be achieved in casted state or by subsequent heat treatment. That is why the modification has a long reaching importance for the utility of cast iron with spheroidal graphite as a construction material.

Theories existing and explaining the mechanism of modification can be summarized into these basic main views:

1. During the modification, evaporation of magnesium takes place, magnesium comes to atomic state and is absorbed on the surfaces of the existing graphite crystal, thus changing the speed of crystal surfaces growth.
2. During the modification, there is deoxidation, desulphurization, degasification of the melt – its refining, and because of this there is change of physical properties of the melt, influencing the graphite growth.

3. During the modification, nucleation conditions of the graphitization change, in other words, undercooling increases, and the temperature and length of eutectic delay changes.

Presently, metallurgically pure Mg (99.5 %) is used as a modifier – 42 % of the world production of CISG or pre-alloy Mg – 58 % of the world production, in which the concentration of Mg varies from 5 % to 35 % Mg.

Main elements are: Si, Ni, Cu, Fe – concentration of cca 40 - 55 %

Accompanying elements are: Ca, Al, Ce, or. REM – Σ concentration up to 7 %

Presently there are various compositions of the modifier, the selection of which depends apart from other things on the method of production of the cast iron with spheroidal graphite.

Tables 15 to 20 provide an overview of the used modifiers according to the methods of production of CISG produced by various European companies.

Table 15 – Overview of the used modifiers – LITVAR

<table>
<thead>
<tr>
<th>Mark</th>
<th>Mg</th>
<th>Cs</th>
<th>Si</th>
<th>Al</th>
<th>REM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 – 6</td>
<td>1 – 2.5</td>
<td>45 – 50</td>
<td>1.2</td>
<td>0.8 – 1</td>
</tr>
<tr>
<td>2</td>
<td>5 – 6</td>
<td>1 – 2.5</td>
<td>45 – 50</td>
<td>1.2</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>13 – 16</td>
<td>1 – 2.5</td>
<td>45 – 50</td>
<td>1.2</td>
<td>0.8 – 1</td>
</tr>
<tr>
<td>4</td>
<td>13 – 16</td>
<td>1 – 2.5</td>
<td>45 – 50</td>
<td>1.2</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 16 – Overview of the used modifiers – SKW

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Ca</th>
<th>Si</th>
<th>REM</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>VL 44</td>
<td>27 – 29</td>
<td>3.2 – 4.2</td>
<td>55</td>
<td>0.8 – 1.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>VL 62</td>
<td>42 – 45</td>
<td>4.5 – 6.0</td>
<td>45</td>
<td>0.8 – 1.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>VL 81</td>
<td>36 – 38</td>
<td>–</td>
<td>45</td>
<td>2.0 – 2.5</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Cs</th>
<th>Si</th>
<th>REM</th>
<th>NiMg</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Denodul 5</td>
<td>5 – 6</td>
<td>–</td>
<td>47</td>
<td>2.5 – 3.5</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Denodul 9</td>
<td>8 – 10</td>
<td>–</td>
<td>47</td>
<td>3 – 4</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Ca</th>
<th>Si</th>
<th>REM</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>VL 1</td>
<td>15 – 17</td>
<td>2.0 max</td>
<td>–</td>
<td>–</td>
<td>residue</td>
<td></td>
</tr>
<tr>
<td>FeNiMg</td>
<td>15 – 16.25</td>
<td>–</td>
<td>7.5 max</td>
<td>–</td>
<td>9.5 max</td>
<td>residue</td>
</tr>
<tr>
<td>FeNiMg</td>
<td>15 – 16.25</td>
<td>–</td>
<td>7.5 max</td>
<td>3</td>
<td>9.5 max</td>
<td>residue</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Cs</th>
<th>Si</th>
<th>REM</th>
<th>NiMg</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>VL 4</td>
<td>4.5 – 5.5</td>
<td>–</td>
<td>2.0 max</td>
<td>–</td>
<td>32 – 37</td>
<td>residue</td>
</tr>
<tr>
<td>VL 3</td>
<td>4.5 – 5.5</td>
<td>–</td>
<td>0.2 max</td>
<td>–</td>
<td>–</td>
<td>residue</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Cs</th>
<th>Si</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuMg</td>
<td>14 – 16</td>
<td>–</td>
<td>2.0 max</td>
<td>–</td>
</tr>
</tbody>
</table>
Table 17 – Overview of the used modifiers – Dušika Ruše - Slovenia

<table>
<thead>
<tr>
<th>modifikátor</th>
<th>Si</th>
<th>Mg</th>
<th>Al</th>
<th>Ca</th>
<th>Ce</th>
<th>Ni</th>
<th>Fe</th>
<th>grains [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-NOSTAND 5</td>
<td>45–48</td>
<td>5–6</td>
<td>1–1.2</td>
<td>1–1.5</td>
<td>0.8</td>
<td>–</td>
<td>+</td>
<td>6-40 / 0.5-6.0</td>
</tr>
<tr>
<td>R-NOSTAND 5S</td>
<td>46–47</td>
<td>0.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>+</td>
<td>1-5 /1-3</td>
<td></td>
</tr>
<tr>
<td>R-NOFORM</td>
<td>46–47</td>
<td>6–6.5</td>
<td>max. 0.8</td>
<td>max. 0.5</td>
<td>0.7–0.8</td>
<td>–</td>
<td>+</td>
<td>0.5-40</td>
</tr>
<tr>
<td>R-NOKOM</td>
<td>46–47</td>
<td>6–6.5</td>
<td>max. 1.0</td>
<td>0.7–0.9</td>
<td>0.9–1.0</td>
<td>–</td>
<td>+</td>
<td>3-8</td>
</tr>
<tr>
<td>R-NOSTAND 10</td>
<td>45–47</td>
<td>9–11</td>
<td>max. 1.0</td>
<td>1–1.5</td>
<td>0.7–0.9</td>
<td>–</td>
<td>+</td>
<td>6-40 / 0.5-6</td>
</tr>
<tr>
<td>R-NOSTAND 10S</td>
<td>max. 0.5</td>
<td>–</td>
<td>–</td>
<td>+</td>
<td>1-5 /1-3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 18 – Overview of the used modifiers – Material a Methods Ltd

<table>
<thead>
<tr>
<th>mark</th>
<th>Mg</th>
<th>Ca</th>
<th>Si</th>
<th>Al</th>
<th>Ce REM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5–4.2</td>
<td>0.5–1.25</td>
<td>45–50</td>
<td>0.5–1.0</td>
<td>1.4–1.6</td>
</tr>
<tr>
<td>2</td>
<td>5.5–6.0</td>
<td>2.0–2.5</td>
<td>42–47</td>
<td>0.5–1.0</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>3</td>
<td>3.7–4.2</td>
<td>0.1–0.6</td>
<td>45–50</td>
<td>0.5–1.0</td>
<td>1.0–1.5</td>
</tr>
<tr>
<td>4</td>
<td>5.0–7.0</td>
<td>0.2–0.7</td>
<td>45–50</td>
<td>0.5–1.0</td>
<td>0.4–0.6</td>
</tr>
</tbody>
</table>

1 - PROCALOY 25 for the Floret method,
2 - PROCALOY 62 for Sandwich,
3 - PROCALOY 42 for In Mold,
4 - PROCALOY 76

Table 19 – Overview of the used modifiers – Elkem

<table>
<thead>
<tr>
<th>Title</th>
<th>Si [%]</th>
<th>Mg [%]</th>
<th>Ca [%]</th>
<th>Al</th>
<th>RE</th>
</tr>
</thead>
<tbody>
<tr>
<td>BJOMET™  1</td>
<td>44-48</td>
<td>4.3-4.8</td>
<td>0.5-1.0</td>
<td>0.6 [%] max</td>
<td>0.4-0.6 [%]</td>
</tr>
<tr>
<td>BJOMET™ 2</td>
<td>44-48</td>
<td>5.0-6.0</td>
<td>0.8-1.2</td>
<td>1.0 [%] max</td>
<td>0.35-0.65 [%]</td>
</tr>
<tr>
<td>BJOMET™ 3</td>
<td>44-48</td>
<td>5.0-6.0</td>
<td>1.4-1.8</td>
<td>1.0 [%] max</td>
<td>0.7-1.0 [%]</td>
</tr>
<tr>
<td>BJOMET™ 4</td>
<td>44-48</td>
<td>5.0-5.6</td>
<td>1.9-2.4</td>
<td>1.0 [%] max</td>
<td>1.8-2.3 [%]</td>
</tr>
<tr>
<td>BJOMET™ 5</td>
<td>44-48</td>
<td>5.5-6.5</td>
<td>0.3-0.5</td>
<td>0.8 [%] max</td>
<td>0.1 [%] max</td>
</tr>
<tr>
<td>BJOMET™ 6</td>
<td>44-48</td>
<td>5.5-6.0</td>
<td>0.5-1.0</td>
<td>0.3 [%] max</td>
<td>0.8-1.0 [%]</td>
</tr>
<tr>
<td>BJOMET™ 7</td>
<td>44-48</td>
<td>5.5-6.5</td>
<td>0.5-1.0</td>
<td>1.0 [%] max</td>
<td>0.4-0.6 [%]</td>
</tr>
<tr>
<td>BJOMET™ 8</td>
<td>44-48</td>
<td>5.5-6.2</td>
<td>0.8-1.2</td>
<td>1.0 [%] max</td>
<td>0.8-1.2 [%]</td>
</tr>
<tr>
<td>BJOMET™ 9</td>
<td>44-48</td>
<td>5.7-6.7</td>
<td>2.5-3.5</td>
<td>1.0 [%] max</td>
<td>0.8-1.2 [%]</td>
</tr>
<tr>
<td>BJOMET™ 10</td>
<td>44-48</td>
<td>8.5-9.5</td>
<td>2.5-3.5</td>
<td>1.0 [%] max</td>
<td>0.8-1.2 [%]</td>
</tr>
<tr>
<td>BJOMET™ 11</td>
<td>44-48</td>
<td>9.0-10.0</td>
<td>0.8-1.2</td>
<td>1.0 [%] max</td>
<td>0.8-1.2 [%]</td>
</tr>
<tr>
<td>LAMETTM</td>
<td>44-48</td>
<td>5.0-6.0</td>
<td>0.4-0.6</td>
<td>0.8-1.2 [%]</td>
<td>La 0.25-0.4 [%]</td>
</tr>
<tr>
<td>REMAG®</td>
<td>44-48</td>
<td>2.75-3.5</td>
<td>0.2-0.5</td>
<td>1.0 [%] max</td>
<td>1.75-2.5 [%]</td>
</tr>
<tr>
<td>COMPACTMAG™</td>
<td>44-48</td>
<td>5.0-6.0</td>
<td>1.8-2.3</td>
<td>1.0 [%] max</td>
<td>5.0-7.0 [%]</td>
</tr>
</tbody>
</table>
Table 20 – Overview of the used modifiers – Hempel Metals UK

<table>
<thead>
<tr>
<th>Mg</th>
<th>Ca</th>
<th>Al</th>
<th>Si</th>
<th>TRE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0 – 4.0</td>
<td>1.0 – 1.5</td>
<td>1.0 max</td>
<td>45 – 48</td>
<td>1.0 – 1.5</td>
</tr>
<tr>
<td>4.5 – 5.5</td>
<td>1.5 – 2.0</td>
<td>1.0 max</td>
<td>45 – 48</td>
<td>1.5 – 2.0</td>
</tr>
<tr>
<td>5.0 – 6.0</td>
<td>1.0 – 1.5</td>
<td>1.0 max</td>
<td>45 – 48</td>
<td>1.0 – 1.5</td>
</tr>
<tr>
<td>2.3 – 3.5</td>
<td>0.5 – 1.0</td>
<td>1.0 max</td>
<td>45 – 48</td>
<td>1.5 – 2.5</td>
</tr>
</tbody>
</table>

7.1 Basic formulas for controlling the modification

\[
Mg_{YS} = \frac{\%Mg_{MOD} \cdot \%Q_{MOD}}{100} \quad \text{[\%]} \quad (45)
\]

\[
Q_{MOD} = \frac{0.76 \cdot \%S_v + \%Mg_{MIN}}{\%\eta_{MOD} \cdot \%Mg_{MOD}} \quad \text{[\%]} \quad (46a)
\]

\[
Q_{MOD} = m \cdot 0.76 \cdot \%S_v + \%Mg_{MIN} \cdot 100 \quad \text{[kg]} \quad (46b)
\]

\[
\eta_{MOD} = \frac{0.76 \cdot \%S_v + \%Mg_{ZBYT} \cdot 100}{\%Q_{MOD}} \quad \text{[\%]} \quad (47)
\]

\[
\eta_{Mg} = \frac{0.76 \cdot \Delta S_v + \%Mg_{ZBYT} \cdot 100}{\%Mg_{YS}} \quad \text{[\%]} \quad (48a)
\]

\[
\eta_{Mg} = \frac{\%Mg_{ZBYT} \cdot 100}{\%Mg_{YS}} \quad \text{[\%]} \quad (48b)
\]

Filled profiles

\[
Q_{Dr} = \frac{0.76 \cdot \%S_v + \%Mg_{ZBYT}}{\%\eta_{Dr} \cdot \%Mg_{Dr}} \quad \text{[\%]} \quad (49a)
\]

\[
Q_{Dr} = \frac{0.76 \cdot \%S_v + \%Mg_{ZBYT} \cdot 100}{\%\eta_{Dr} \cdot \%Mg_{Dr}} \quad \text{[kg]} \quad (49b)
\]

\[
Q_{Dr} = \frac{Q_{Dr}}{G_N} \quad \text{[m]} \quad (49c)
\]

\[
\eta_{Mg} = \frac{0.76 \cdot \Delta S_v + \%Mg_{ZBYT} \cdot 100}{\%Q_{Dr}} \quad \text{[\%]} \quad (50)
\]

\[
\eta_{Mg,Dr} = \frac{0.76 \cdot \Delta S_v + \%Mg_{ZBYT}}{\%Q_{Dr} \cdot \%Mg_{Dr}} \quad \text{[\%]} \quad (51)
\]
Calculation of the modifier dissolution in the flow method

\[ q = \frac{Q_K}{\tau} \] [kg.sec\(^{-1}\)]  
\[ \tau = \frac{Q_{MOD}}{q} \] [sec]  
\[ K_R = \frac{q}{S} \] [kg.sec\(^{-1}\).cm\(^{-2}\)]  
\[ \tau_{MOD} = \frac{\tau}{K_R} \] [sec]

Example: For 500 kg of metal, 10 kg of modifier, 50 sec casting and flow method of modification:

\[ q = \frac{500 \text{kg}}{50 \text{sec}} = 10 \text{ kg} \cdot \text{sec}^{-1} \]
\[ \tau = \frac{10 \text{ kg}}{10 \text{ kg} \cdot \text{sec}^{-1}} = 1 \text{ sec} \]
\[ K_R = \frac{10 \text{ kg/sec}}{300 \text{ cm}^2} = 0.033 \text{ kg} \cdot \text{sec}^{-1} \cdot \text{cm}^{-2} \]
\[ \frac{1}{K_R} = \frac{1}{0.033} = 30.3 \text{ sec} \]

\[ Q_{KMOD} = 0.033 \cdot 300 \cdot 30.3 = 297 \text{ kg} \] the amount of metal in which the modified has dissolved

\[ \frac{30}{50} \cdot 100 = 60\% \] the ratio of dissolution period and the flow time of the melt through the chamber

The meaning of symbols in formulas 45 - 55

\( \text{Mg}_{\text{MIN}} \) – the minimum amount of Mg in %
\( \text{Mg}_{\text{vs}} \) – the amount of used Mg in %
\( \text{Mg}_{\text{MOD}} \) – the amount of Mg in the modifier in
\( Q_{\text{MOD}} \) – the amount of used modifier in % on mass of liquid metal or in kg on mass of liquid metal
\( S_v \) – the initial content of sulphur in the cast iron in
\( \Delta S \) – the difference between the content of sulphur before and after the modification in %
\( m \) – the weight of modified cast iron in kg
\( Q_{\text{cw}} \) – the amount of used profile in % on mass of liquid metal or in kg on mass of liquid metal or in m on the weight of the cast iron
\( \text{Mg}_{\text{zbyt.}} \) – the amount of residual Mg after the modification in % (0.03-0.06)
The basic condition of a successful modification is the content of residual magnesium (marked \( \text{Mg}_{\text{rest.}} \)) after the modification at least 0.03 \%. That is why its yield will be important for the efficiency of the modification. This usage can be expressed using the above mentioned formulas, in which the usage of magnesium and the master alloy is considered and the same thing for the filled profiles. The content of sulphur in the cast iron is considered to be one of the main factors.

### 7.2 Conditions of the modification

Modification is an after furnace processing of the molten cast iron, which can be divided into:

1. Preparation of the cast iron for the modification: chemical composition and melting temperature
2. The processes taking place during the modification:
   - Physical
   - Chemical (refining the melt)

The properties of the cast iron designed for the production of CISG are somewhat different from the normal CILG, especially from the point of view of its chemical composition. [37, 59, 60]

Molten cast iron that we want to process by modification, has to have a high graphitization ability, because the modification is a refining process, it decreases the graphitization ability of the melt meaning that it increases the tendency of metastable hardening.

Chemical composition of the cast iron has to have a high content of C + Si, the elements supporting graphitization.

The recommended content of C = 3.5\(\div\)3.8 \% and the content of Si = max. 2.8 \%. The amount of initial silicon depends apart from other things on the type of used modifier. If this modifier contains silicon as the main element, the initial content of silicon in the melt is decreasing, because certain amount of silicon transits from the modifier to the melt. However, the decisive factor is the graphitizing inoculation which accompanies the modification.
Metallurgy of cast irons. Out-of-furnace processing of molten cast iron. 2014

It is possible to inoculate graphite during the process of modification and especially after the modification. The process has similar principles to the ones mentioned in previous chapter dealing with inoculation.

From the point of view of the content of carbon and silicon we choose \( S_C = 0.98 \pm 1.05 \), meaning \( C_{E_KV} = 4.2 \pm 4.3\% \) as optimal values.

This value is determined based on other properties that we require.

Figure 43 shows the relation between silicon and carbon with regards to the final properties of the cast iron with spheroidal graphite. E.g. with the content of \( C = 3.7\% \) the limiting factor, from the point of view of graphite flotation and low impact toughness, is the content of silicon.

According to Figure 44 the content of silicon for flotation for \( C = 3.7\% \) is:

\[
Si = (4.55 - 3.7) \cdot 3 = 2.55\%
\]

From the point of view of occurrence of shrinkages and chills the limiting content of \( Si \) for the given content of \( C = 3.7\% \).

\[
Si = (3.7 - 3.5) \cdot 7 = 1.4\%
\]

---

**Figure 43** – Determining the content of carbon in % depending on the silicon in %

**Figure 44** shows the influence of the module of the casting, content of carbon and silicon on the flotation of graphite.

The content of other basic elements – Mn, P and S is ranging in the values used in cast steels – \( Mn = 0.2 - 0.6\% \), \( P = 0.03 - 0.06\% \), \( S = 0.01 - 0.03\% \). More details about the influence of these elements will be given in following chapters. During the modification the
main role is played by trace elements, which may disturb the process of modification. We call these elements disturbing elements, they prevent the formation of spheroidal graphite. The disturbing elements get into the melt with the metal batch that may be polluted by these elements in various ways.

The disturbing elements are: Pb, Sb, As, Bi, Ti, Sn and others. [54]

![Diagram of the influence of C, Si and the module of casting (M) on the flotation of graphite](image)

The maximum permissible amount of interfering elements: Pb = 0.011÷0.016 %, Sb = 0.026 %, As = 0.08 %, Bi = 0.008 % in combination with Ti = 0.13 %, Te = 0.2 %

The influence of these elements can be controlled by the coefficient of certainty $K_2$ which is given by the following relation:

$$K_2 = \frac{K_1}{Mg} = 10 \div 25$$ (56)

where: $K_1 = 4.4 \cdot Ti + 2.2 \cdot As + 2.3 \cdot Sn + 5 \cdot Sb + 290 \cdot Pb + 370 \cdot Bi + 1.6 \cdot Al$

$Mg$ = required input amount of Mg in %

On the other hand, the molten cast iron can be suitable alloyed by V, Mo, Ni, Cu and increase its mechanical properties without influencing the shape of graphite.
The condition of successful modification of the cast iron is sufficiently high temperature of modification at which we are processing the melt with magnesium. The modification is accompanied by the decrease of temperature due to the melting and evaporation of magnesium. The decrease of temperature ranges from 40 to 70 °C from the practical experience.

7.3 The losses of magnesium during the production of cast iron with spheroidal graphite

The losses of magnesium occur during the modification and are related with the period of standing of the modified cast iron, with the period of casting and subsequently with the period of solidification of the molten cast iron in the form and with the thickness of the wall (casting module).

Literature [60] gives these loses as the total value of magnesium decrease in the molten cast iron after the casting has been finished.

Losses of magnesium during modification are:

a) physical – after the boiling point is reached (see chapter 8.1 Physical condition of the modification)

b) chemical
   - the bond of magnesium and sulphur, formation of MgS
   - the bond of magnesium and oxygen, formation of MgO

Further losses occur during the pouring of the melt into the form:

c) influence of the casting modulus

d) solidification time of the casting

Other losses:

e) slag removing

f) the transport of the ladle to the pouring field

g) casting period

These losses can be calculated from the following relations:

a) – these losses constitute 40 to 50 % of the input magnesium (according to operation experience)

b) – the losses of Mg on \( S = \Delta S \cdot 0.76 = \text{in} \% \), where \( \Delta S \) is the difference of the contents of sulphur in the melt before and after the modification

the losses of Mg on \( \frac{1}{2} O_2 = \Delta O \cdot 1.5 = \text{in} \% \), where \( \Delta O \) is the difference of the contents of oxygen in the melt before and after the modification (the losses on oxygen may be used only in the case of knowing the content of oxygen in the cast iron during modification)

c) – the influence of the modulus of the casting \( = 0.00015 \cdot M \text{[cm]} \), where \( M \) is the determining modulus of the casting
d) – the period of hardening depends on the temperature when pouring into the mould, on the coefficient of solidification and on the determining modulus of the casting according to the formula:

\[
M_{g_{ztr}} = \left[0.086 \cdot M \cdot \left(\sqrt{T_L - 1150} + \sqrt{250}\right)\right] - 0.001
\]

where 0.086 – solidification constant for bentonite molding mixture and CISG

(for CT forms and CISG, the constant has the value of 0.0742)

M – modulus of the casting

250 – change of temperature influenced by the crystallization heat of the graphitization

T_L – temperature of pouring

e), f), g) – we obtain these losses by observing the operation and they range from 5 minutes to maximum of 22 minutes, which is the value, when the effect modification vanishes.

Example: the amount of added magnesium to the melt \(M_{VS} = 0.13\%\), the amount of sulphur before modification \(S_{POC} = 0.025\%\), the temperature of metal poured into the form 1320 °C and the module of casting 1.7 cm

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation of magnesium</td>
<td>35 %</td>
</tr>
<tr>
<td>Initial content of sulphur</td>
<td>0.025 %</td>
</tr>
<tr>
<td>Modulus of the casting M</td>
<td>1.7 cm</td>
</tr>
<tr>
<td>Temperature of pouring T_L</td>
<td>1320 °C</td>
</tr>
<tr>
<td>The period of manipulation with the melt</td>
<td>18 min</td>
</tr>
<tr>
<td>Total losses of magnesium</td>
<td>(\sum M_{g_{ztr}} = 0.085245%)</td>
</tr>
<tr>
<td>Residual magnesium</td>
<td>(M_{g_{zbyt}} = 0.045%)</td>
</tr>
</tbody>
</table>

The formula from the Figure 44 is visually represented on Figure 45 and Figure 46, where the solidification time is given depending on the modulus of the casting and in the right part there are the corresponding losses of Mg depending on the period of manipulation with the liquid metal and the solidification time of the casting.
Figure 45 – Losses of Mg depending on the solidification time and the M of the casting.

Figure 46 – Losses of Mg depending on the solidification time and the M of the casting.

If there is a requirement for the lowering of the content of $Mg_{zbyt} = 0.035\%$, then $Q_{mod} = 9.67$ kg, which corresponds with the real consumption.

The practical utility of these relations require operational verification in the given conditions of a foundry. The time required for the manipulation and the casting time of the modified cast iron remain important factors.

These data will affect the total effectiveness of the modification.
Terms summary

Mentioned in the “contents of the chapter“ part

Questions

- What characterizes the process of modification?
- Which criteria are used with the basic formulas for controlling the modification?
- What are the basic conditions of the modification?
- How are the magnesium losses calculated during the production of cast iron with spheroidal graphite?
8 THE BASICS OF MODIFICATION THERMODYNAMICS

Contents of the chapter
- The basics of modification thermodynamics
- Physical condition of modification
- The definition of modification pressure
- Physical properties of calcium
- Chemical conditions of modification
- Mg-S reactions
- The influence of calcium on modification
- Deoxidizing effect of magnesium, calcium and aluminum during modification
- Evaluating the theoretical analysis

Time to study: individual

Aim After studying this chapter you will able to:
- Define the physical conditions of modification
- Interpret the definition of modification pressure
- Apply the chemical condition of the modification
- Explain the deoxidizing effect of magnesium, calcium and aluminum during the modification
- Evaluate the theoretical analysis of the modification process

Presentation

The thermodynamic nature of modification is totally different from the inoculation. While inoculation takes place during the calm dissolution of the inoculant in the molten cast iron, the modification takes place during a turbulent reaction of the modifier with the molten cast iron. It is caused by the physical properties of magnesium. Apart from that, magnesium has high affinity towards oxygen and sulphur, eventually carbon. These reactions change the physical and chemical nature of molten cast iron. The modification is accompanied by the refining of the melt with magnesium – deoxidation and desulphurization take place as well as the total decrease of the content of gases in the melt.

From the point of view of the content of carbon and silicon, the CISG has the character of a cast iron, however if we consider the amounts of manganese, phosphorus and sulphur, it
has the character of steel. It is therefore possible to apply some of the experienced gained for steel in defining the thermodynamic conditions of the modification.

### 8.1 Physical condition of modification

Physical properties of magnesium:
- Melting temperature 650 °C
- Evaporation temperature 1110 °C at pressure of 1.013 bar

The pressure of magnesium vapors depends on the temperature \( P_{\text{Mg}} = f(T) \) and can be calculated from the formulas (57÷60), listed on Figure 47. Mutual deviation of individual authors is negligible. [24, 35, 38, 39, 40, 41, 56] According to these relations, it is possible to calculate the corresponding pressure of magnesium vapors, in other words the pressure, for which the dissolved magnesium in the melt will be in equilibrium with the given melt temperature. If we increase this pressure for the given temperature, then the evaporation of magnesium will be suppressed and the magnesium will be in a liquid state in the melt solution. The above mentioned values apply for pure iron.

At lower pressure of the Mg vapors, than corresponds with the equilibrium values, there will be an intensive evaporation and great losses of magnesium during the modification.

\[
\begin{align*}
\text{B. Marinček} & \quad \log P_{\text{Mg}} = -\frac{7100 \pm 1090}{T} + 5.16 \quad [\text{bar}] \\
\text{K. Vaščenko} & \quad \log P_{\text{Mg}} = -\frac{7840}{T} - 1.22 \cdot \log T + 9.52 \quad [\text{bar}] \\
\text{K. Kulikov} & \quad \log P_{\text{Mg}} = -\frac{6333}{T} + 4.66 \quad [\text{bar}] \\
\text{Kubasewsky} & \quad \log P_{\text{Mg}} = -\frac{7555}{T} - 1.41 \cdot \log T + 12.79 \quad [\text{torr}]
\end{align*}
\]
Metallurgy of cast irons. Out-of-furnace processing of molten cast iron. 2014

Figure 47 – Pressure of magnesium vapors depending on the temperature according to various authors

Relation between the pressure of saturated vapor of $\text{Mg} (P_{\text{Mg}}^0)$, the temperature and the concentration of Mg in the solution [%Mg] is represented on the Figure 48.

Figure 48 – The pressure of magnesium vapors depending on the temperature and the corresponding concentration of magnesium in the melt in % (for pure iron).
Metallurgy of cast irons. Out-of-furnace processing of molten cast iron. 2014

Used formulas:

\[
\log \left[ \frac{Mg}{P_{Mg}} \right] = \frac{970}{T} - 2.804 \tag{61}
\]

\[
\log P_{Mg}^0 = -\frac{6333}{T} + 4.666 \quad [\text{bar}] \tag{62}
\]

It is assumed that at the pressure of 20 bar, 1 % of magnesium is in equilibrium in the solution.

Physical conditions of modification, meaning the pressure over the level of the melt and the melt temperature, are the basic factors determining the usage of magnesium or the modifier. Reactions listed on Figure 47 have a general character. If we want to further develop this relation, it is necessary to know the concentration of the magnesium in the solution [%Mg] for the given pressure of the magnesium vapors and the correspondent temperature. Thermodynamic conditions are given by the following relation:

\[
Mg_{pyn} = [Mg]_{1\%} \quad G_f^0 = -4440 + 12.37 \cdot T \quad [\text{J.K}^{-1}.\text{mol}^{-1}] \tag{63}
\]

then

\[
\log \left[ \frac{Mg}{P_{Mg}} \right] = \frac{970}{T} - 2.804 \tag{64}
\]

then

\[
[\%Mg] = P_{Mg} \cdot 10^{\frac{970}{T} - 2.804} \quad P_{Mg} = [\text{bar}] \tag{65}
\]

\[
[\%Mg] = P_{Mg} \cdot 10^{\frac{2180}{T} - 2.441} \quad P_{Mg} = [\text{Mpa}] \tag{66}
\]

The values calculated according to relation (65) are visually shown in Figure 49.

The amount magnesium in the solution decreases with increasing temperature and increases with increasing pressure over the level of the melt. These values apply for pure iron.

For a real melt of a cast iron, it is necessary to consider the content of carbon and silicon, or other elements, which have a considerable concentration for the thermodynamic calculation.
If we take these elements into consideration, we have to know the corresponding interaction coefficients $X_{Mg}^e$, which have the following values at the temperature of 1500 °C [25, 28, 56, 57]:

$$e_{Mg}^C = -3.33 \cdot 10^{-2} \quad e_{Mg}^{Al} = -9.2 \cdot 10^{-3}$$
$$e_{Mg}^{Si} = +8.9 \cdot 10^{-3} \quad e_{Mg}^{Ti} = +2.2 \cdot 10^{-3}$$
$$e_{Mg}^{Mn} = -5.9 \cdot 10^{-3} \quad e_{Mg}^{Cu} = -3.22 \cdot 10^{-2}$$
$$e_{Mg}^{Ni} = -1.7 \cdot 10^{-2} \quad e_{Mg}^{Mo} = 8.3 \cdot 10^{-3}$$

We may therefore write that

$$K = \frac{a_{Mg}}{P_{Mg}} = \frac{f_{Mg} \cdot [\%Mg]}{P_{Mg}} \quad (67)$$

The coefficient of activity $f_{Mg}$ is calculated based on the values $e_{Mg}^X$ as follows:

$$\log f_{Mg} = e_{Mg}^{Mg} \cdot [\%Mg] + e_{Mg}^{C} \cdot [\%C] + e_{Mg}^{Si} \cdot [\%Si] \quad (68)$$
where

\[ e_{Mg}^{\%Mg} = 1 \]

\[ [\%Mg] = \frac{K \cdot P_{Mg}}{f_{Mg}} \]

where

\[ K = 10^{\frac{970}{T-2804}} \text{ [bar]} \]

\[ K = 10^{\frac{2180}{T-2441}} \text{ [MPa]} \]

For 3.5 % C and 2.5 % Si and the pressure of 1 bar the concentration of Mg at the temperature of 1673 K according to formula (68) is \( f_{Mg} = 0.805 \)

\[ K = 10^{\frac{970}{1673-2804}} = 5.96 \cdot 10^{-3} \text{ [bar]} \]

\[ \frac{5.96 \cdot 10^{-3} \cdot 1}{0.805} = 7.4 \cdot 10^{-3} \% \]

\[ K = 10^{\frac{2180}{1673-2441}} = 7.27 \cdot 10^{-2} \text{ [MPa]} \]

\[ \frac{7.27 \cdot 10^{-2} \cdot 1}{0.805} = 9.04 \cdot 10^{-3} \% \]

On the next Figure 50 there is a nomographic chart that represents the relation between the pressure of saturated magnesium vapors (marked \( P_{Mg}^0 \)) and the temperature (marked T in Kelvin degrees) and the concentration of magnesium in the melt for the given temperature and the value of modification pressure (marked \( P_{Mg} \)), applicable for pure iron. The dashed connector indicated the orientation in the nomogram according to the selected example and expresses the present physical condition of the modification. In the mentioned case, the modification pressure was 8 bar and at the temperature 1773K (1500 °C) the concentration of Mg = 0.044 % in the solution in equilibrium, while at this temperature, the pressure of saturated vapors will be around 12 bars. There will be an evaporation of magnesium, the intensity of which is given by the difference of both monitored pressures. We may easily find out that the decrease of the value of modification pressure at the same temperature will lead to a higher intensity of evaporation of magnesium, to its higher losses and because of that, to its lower concentration in the solution. If the value of magnesium in the solution is lower than 0.03 %, then there is no formation of spheroidal graphite.

### 8.2 Definition of modification pressure

Figures 51a, b, c show the three basic examples of utility of the modification pressure. Figure 51a shows the case of the effect of atmospheric pressure (open ladle – pouring methods). Figure 51b shows the case of the effect of magnesium vapors (the course of the pressure is depicted on Figure 52 and reached the values of 3.5 bar). This case is typical for dipping methods with the ladle closed by a lid, there the Tundish methods and the methods of closed convertor pans but not closed hermetically.
Figure 51c shows the case of the modification pressure (modification by dipping in an autoclave with overpressure (system MŽ Olomouc).

However, in all the mentioned cases it is necessary to always add the metallostatic pressure, given by the liquid level in the ladle and calculated from the following formula:

\[ P_{\text{met}} = h \cdot \rho \]

(69)

where \( h \) – the height of the melt level in m
\( \rho \) – melt density in \( \text{kg/m}^3 \)

Figure 50 – Nomographic chart of the dependence between the temperature and the modification pressure (\( P_{Mg} \)), the amount of magnesium in the solution and the pressure of magnesium vapors (\( P_{Mg}^0 \)) at the given temperature (applicable for pure iron). Calculated according the formula 65.

Figure 50 shows the nomographic chart representing the physical condition of the modification. At the given temperature and modification pressure which is given by the method of modification (see Figure 51 a,b,c), we can read the corresponding concentration of Mg in the solution in %, which is in equilibrium with the temperature \( T = 1400 \, ^\circ\text{C} \). If we increase the modification temperature to \( T = 1500 \, ^\circ\text{C} \), there will be a magnesium boiling at the pressure of 12 bar, which is necessary for the formation of spheroidal graphite.
Figure 51 – The modification pressure during the production of cast iron with spheroidal graphite.

Figure 52 – Pressure of Mg vapors in a hermetic ladle (currently not used due to the safety reasons)

The maximum value of this pressure component of the modification is ensured by the “slimness” of the modification ladle, which is recommended to have a diameter of \( h = \min (1.5 \pm 2) \cdot d \), where \( d \) is the diameter of the ladle. The total value of the modification pressure can be calculated from the following formula:

\[
P_{Mg} = P_{a,b,c} + (h \cdot \rho) \cdot \frac{1.013}{10^{-3}} \quad \text{[bar]} \tag{70}
\]
where $P_{a,b,c}$ is the pressure over the level of the melt, the value of which depends on the method of modification (Figure 51).

During the above mentioned analysis of the physical condition of the modification, we find out that at the chosen modification temperature, its process can be influenced by pressure, which is, to some extent, decisive for the process and effectiveness of the modification.

As shown in the table 5 (the composition of the modifiers) some master alloys contain also calcium and that is why it is necessary to evaluate their effect from this point of view.

### 8.3 Physical properties of calcium

The basic physical properties of calcium are:

- Melting temperature 857 °C
- Evaporation temperature 1439 °C at the pressure of 1.073 bar

These values suggest that with regard to the temperature of the molten cast iron, a more important role will be played by the evaporation of magnesium (see the previous chapter). [28, 29, 55]

Thermodynamic conditions of the influence of calcium on the modification can be determined from the following relations:

$$ Ca_{pl} = \frac{[Ca]}{P_{Ca}} \quad \Delta G_T^0 = -5472 + 10.03 \cdot T $$

and then

$$ \log \frac{[Ca]}{P_{Ca}} = \frac{1196}{T} - 2.192 $$

and then

$$ [\% Ca] = P_{Ca} \cdot 10^{\frac{1196}{T} - 2.192} \quad \text{[bar]} \quad (71) $$

$$ [\% Ca] = P_{Ca} \cdot 10^{\frac{4912}{T} - 4.139} \quad \text{[MPa]} \quad (72a) $$

Valid for pure iron.

The following applies for the alloy of iron containing carbon and silicon:

$$ K = \frac{a_{Ca}}{P_{Ca}} = \frac{f_{Ca}}{P_{Ca}} \frac{[\% Ca]}{P_{Ca}} $$

and

$$ [\% Ca] = P_{Ca} \cdot 10^{\frac{4912}{T} - 4.139} \quad \text{[MPa]} \quad (72b) $$

The coefficient of activity $f_{Ca}$ can be calculated based on the values of $e_{Ca}^X$, as follows:
\[
\log f_{Ca} = e_{Ca}^{Ca} \cdot [%Ca] + e_{Ca}^{C} \cdot [%C] + e_{Ca}^{Si} \cdot [%Si]
\]  
(74)

where:

\[ \log e_{Ca}^{Ca} \cdot [%Ca] = 1 \]
\[ e_{Ca}^{C} = -34 \cdot 10^{-2} \]
\[ e_{Ca}^{Si} = -9.7 \cdot 10^{-2} \]

For the selected content of C=3.5 % a Si=2.5 % je \( f_{Ca} = 0.0369 \).

For the temperature of 1400 °C and the pressure of 1 bar, the concentration of calcium in the alloy is:

\[
K = 10^{1196} \cdot 2.192
\]

\[ [\%Ca] = \frac{K \cdot P_{Ca}}{f_{Ca}} = \frac{0.033 \cdot 1}{0.0369} = 0.902\% \]

\[ [\%Ca] = \frac{0.0626 \cdot 0.1}{0.0369} = 0.169\% \]

According to the formula (72b)

In comparison with magnesium, the concentration of calcium is far higher in the solution at the same conditions and in the real solution of the cast iron, calcium will be mostly in the solution, which will support its desulphurizing and deoxidizing effect during modification.

### 8.4 Chemical conditions of the modification

Elements present in the modifier come to chemical reactions according to the affinity in the following manner:

\[
2 \cdot Ca + O_2 = 2 \cdot CaO \quad - \Delta G = 1010 kJ \cdot mol^{-1}
\]
\[
2 \cdot Mg + O_2 = 2 \cdot MgO \quad - \Delta G = 1000 kJ \cdot mol^{-1}
\]
\[
\frac{3}{4} \cdot Al + O_2 = \frac{2}{3} \cdot Al_2O_3 \quad - \Delta G = 850 kJ \cdot mol^{-1}
\]
\[
2 \cdot Ca + S_2 = 2 \cdot CaS \quad - \Delta G = 840 kJ \cdot mol^{-1}
\]
\[
2 \cdot Mg + S_2 = 2 \cdot MgS \quad - \Delta G = 620 kJ \cdot mol^{-1}
\]

In the following text we are going to define the course of isotherms based on free energies and with regard to other conditions mentioned in the previous chapter. We will preferably state the reaction between magnesium and sulphur, because sulphur is listed as the most important condition of the modification. Sulphur is a very important element during the modification because it forms the MgS compound, which gets into the slag and that is why it does not influence the modification, in other words, the formation of spheroidal graphite.
8.5 Mg-S reaction

The relation between Mg and S is given by thermodynamic conditions in the following way:

\[ [\text{Mg}] + [S] = \text{MgS} \quad \Delta G^0_T = -543000 + 239.8 \cdot T \]

From that

\[
\ln K = \frac{\Delta G^0}{R \cdot T} = \frac{65311.5}{T} - 28.84
\]

\[ R = 8.314 \cdot J \cdot K^{-1} \cdot mol^{-1} \]

\[
\log K = -\frac{28359.3}{T} + 12.522
\]

The amount Mg in the solution \( \%\text{Mg} = f(\%S, T, P_{\text{Mg}}) \) is given by the formula:

\[
\log[\%\text{Mg}] = -\frac{28359.3}{T} + 12.522 - \left( e_S^C \cdot [%C] + e_M^S \cdot [%Si] \right) - \\
\left( e_S^S \cdot [%S] + e_C^S \cdot [%C] + e_S^{Si} \cdot [%Si] \right) - \log[\%S] + \log P_{\text{Mg}}
\]

The interaction coefficients of sulphur for the temperature of 1500 °C:

\[ e_S^S = -2.8 \cdot 10^{-2} \quad e_C^S = +11 \cdot 10^{-2} \quad e_S^{Si} = +6.3 \cdot 10^{-2} \]

Interaction coefficients of magnesium were listed before.

We calculate the corresponding isotherms for given temperatures and pressures from the equation (76). In general, these relations can be displayed on Figure 53, where we can see the isotherm of the reaction Mg-S as well as the concentration of magnesium depending on the temperature and the pressure for generally selected conditions (the perpendicular lines determine the concentration of magnesium).
Figure 53 – The influence of evaporation and desulphurization during the modification on the final value of residual magnesium.

Figure 53 also indicates the slope of the line determining the magnesium consumption to sulfur according to the stoichiometric ratio of the Mg-S reaction (Mg = 0.76S):

\[ \text{Mg} + \text{S} = \text{MgS} \quad \text{Mg} = 0.76 \cdot \text{S} \]

If we have a certain concentration of magnesium before the modification (according to Figure 53 0.04 %) and a certain concentration of sulphur (0.15 %) in the melt, there will be two processes ongoing from this initial point (marked A):

- Evaporation (horizontal vector) and
- Desulphurization (oblique vector)

By combining the two vectors, we obtain the amount of magnesium that will remain in the solution as the result of these two processes. This value is of interest, because it should reach the value of Mg\(_{\text{byt}}\) = 0.03 %. Based on this thought, other possible combination determining the process of modification are given.

Figure 54 shows the isotherms for various temperatures and contents of sulphur in the cast iron with the content of 3.5 % C and 2.5 % Si. On the picture, the concentration of magnesium in % for \( P_{\text{Mg}} = 1 \text{bar} \) is shown for at the given temperature. According to equation (76) it is possible to calculate the Mg-S isotherm for whatever chemical composition based on the above mentioned interaction coefficients \( e_{\text{Mg}} \).
Figure 54 – Isotherms for various temperatures and contents of sulphur at the pressure of 1 bar.

With the decreasing temperature, the desulphurizing ability of magnesium rises even for very low contents of sulphur. For example, at the modification temperature of 1300 °C and the content of S = 0.001 %, there is an equilibrium at the content of Mg = 0.0012 %, which practically means a total bond of magnesium to sulphur.

On the other hand, at 1500 °C and the content of S = 0.01 % it is in equilibrium with 0.012 % Mg and therefore the bond with sulphur might not occur, because part of the magnesium will evaporate to the value of 0.0072 % at the pressure of 1 bar.

Calculated isotherms (Figure 54) consider the pressure of 1 bar. The influence of pressure is shown on the Figure 55, where the isotherms are shown for the temperature of 1300 °C and the pressure of 1 and 5 bars.

Due to the influence of higher modification pressure, the isotherms move to the right and expand the area of mutual reaction of magnesium and sulphur, which decreases the desulphurizing ability of magnesium at the given ratio of magnesium and sulphur.

Let us analyze the Mg-S relation in detail for various cases based on the above mentioned thermodynamic relations.

Figure 56 shows the dependencies Mg-S at the temperature of 1400 °C and the modification pressure of P$_{Mg}$ = 1.5 bar for two types of cast irons (full and dashed lines). On the picture, there is also the dependency of magnesium content on the bond with sulphur at constant stoichiometric ratio of 0.76. There is also a vertical line determining the content of magnesium in %, which is in equilibrium in the solution at the given temperature and pressure (0.0113 %, or 0.0161 % depending on the type of cast iron).
Figure 55 – Isotherms for the temperature of 1300 °C and the pressure of 1 and 5 bars
Figure 56 – Isotherm Mg-S for a constant content of sulphur and a varying content of added magnesium, at the temperature of 1400 °C and pressure of 1.5 bar

For a non-alloyed cast iron ① (full lines, a comment for an alloyed cast iron is further in the text) the constant amount of sulphur of 0.02 % has been selected and the amount of added magnesium was changing. Assuming that the desulphurization and the evaporation of magnesium are occurring at the same time, its final value in the solution will be the result of combined vectors of desulphurization (vector of the same direction as the stoichiometric ration 0.75) and the vector of evaporation (horizontal direction until the amount of magnesium that is in equilibrium for given conditions (see Figure 53).

By combining these vectors, we obtain a resultant of these processes. By evaluating the resulting values of magnesium (Mg_{zbyt}) we will find out the basic parameters of these processes for Mg = 0.03 %, Mg = 0.04 % and Mg = 0.05 %. We will prepare the table 21 from the conversion of the data from Figure 56.

Table 21 – Converted from Figure 56

<table>
<thead>
<tr>
<th>%Mg [%]</th>
<th>Mg_{zbyt} [%]</th>
<th>Yield of Mg [%]</th>
<th>Desulphurization [%]</th>
<th>Evaporation of Mg [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>0.0046</td>
<td>15</td>
<td>47</td>
<td>38</td>
</tr>
<tr>
<td>0.04</td>
<td>0.0052</td>
<td>13</td>
<td>36</td>
<td>51</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0060</td>
<td>12</td>
<td>28</td>
<td>60</td>
</tr>
</tbody>
</table>

Low yield of magnesium is caused by high value of desulphurization and evaporation. For the given content of sulphur (0.02 %) the increasing content of magnesium is not
effective, because it increases the portion of evaporation (decreasing tendency of desulphurization against rising tendency of evaporation). Comparison of full and dashed lines.

Figure 57 shows the non-alloyed cast irons, but the reaction temperature was chosen for 1450 °C. The isotherm was moved to the right, which decreased the desulphurization ability of magnesium. This pictures shows the line of constant magnesium, necessary for modification, determined from the relation

\[ Mg = 0.025 + 0.76 \cdot S. \]

![Diagram showing Mg-S isotherm](image)

Figure 57 – Mg-S isotherm for a constant content of sulphur and variable amount of magnesium, temperature of 1450 °C and pressure of 1.5 bar

<table>
<thead>
<tr>
<th>Mg [%]</th>
<th>Mg$_{abs}$ [%]</th>
<th>Yield of Mg [%]</th>
<th>Desulphurization [%]</th>
<th>Evaporation of Mg [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>0.0078</td>
<td>26</td>
<td>42</td>
<td>32</td>
</tr>
<tr>
<td>0.04</td>
<td>0.0092</td>
<td>23</td>
<td>33</td>
<td>44</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0085</td>
<td>17</td>
<td>20</td>
<td>53</td>
</tr>
<tr>
<td>0.08</td>
<td>0.0120</td>
<td>15</td>
<td>15</td>
<td>70</td>
</tr>
</tbody>
</table>

The utilization of magnesium has increased a little, but it decreases quickly with the increasing amount of Mg coming to the reaction, even the value of 0.08 % is considered. It is
possible to say the same that was said in the first case: the higher the content of magnesium, the higher the value of its evaporation.

Figure 58 – The Mg-S isotherm for a constant amount of magnesium and varying amount of sulphur, temperature of 1450 °C and the pressure of 1.5 bar

Figure 58 shows the reverse method. At the constant amount of Mg = 0.05 %, the content of sulphur coming into the reaction with magnesium was changing in the range of 0.005-0.02 %.

Table 23 – Evaluation of Figure 58

<table>
<thead>
<tr>
<th>%S</th>
<th>Yield of Mg [%]</th>
<th>Desulphurization [%]</th>
<th>Evaporation of Mg [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>20</td>
<td>27</td>
<td>53</td>
</tr>
<tr>
<td>0.015</td>
<td>25</td>
<td>20</td>
<td>55</td>
</tr>
<tr>
<td>0.01</td>
<td>30</td>
<td>12</td>
<td>58</td>
</tr>
<tr>
<td>0.005</td>
<td>42</td>
<td>2</td>
<td>53</td>
</tr>
</tbody>
</table>

The yield of magnesium has increased considerably. It increases with the decrease of sulphur, and at the same time the desulphurizing ability of magnesium also decreases. The value of evaporation ranges between 50-60 %.

The case on the Figure 58 documents the importance of the initial amount of sulphur in the cast iron before the modification. At 0.05 % of added magnesium for the modification and the amount of S = 0.005 %, the residual magnesium is 0.022 % and the utility of magnesium reaches 42 %.
Figure 59 shows a model case where the temperature is chosen at 1400 °C and the pressure of modification is changing from 1.5 to 3 and 5 bars. The amount of sulphur in the cast iron is 0.008 %, in the second case 0.005 %. The value of magnesium content coming to the reaction is 0.025 % and 0.045 %.

![Mg-S isotherms for various modification pressures and the temperature of 1400 °C](image)

**Table 24 – Evaluation of Figure 59**

<table>
<thead>
<tr>
<th>Pressure [bar]</th>
<th>Mg yield [%]</th>
<th>Desulphurization [%]</th>
<th>Evaporation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>37</td>
<td>24</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>72</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>85</td>
<td>15</td>
<td>0</td>
</tr>
</tbody>
</table>

From the Figure 59 we can read the increasing yield of magnesium and a sharp decrease of the proportion of evaporation down to 0 at the pressure of 5 bar.

Figure 59 also shows the real case of a modification using the In Mold method (directly in the form), where the amount of magnesium coming into the reaction was 0.045 % (0.8 % modifier with 5.6 % Mg), the amount of Mg<sub>zbyt</sub> = 0.026 % and the amount of initial S = 0.005 %. With regard to the level of melt in the ladle during the pouring into the form...
(pouring from greater height increases the metallostatic pressure) it is possible to presume the modification pressure of 3 bars. According to Figure 59 the course of modification is the following:

Table 25 – Evaluation of Figure 59 – In Mold method

<table>
<thead>
<tr>
<th>%Mg</th>
<th>Yield of Mg [%]</th>
<th>Desulphurization [%]</th>
<th>Evaporation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.045</td>
<td>53.4</td>
<td>6.6</td>
<td>40</td>
</tr>
</tbody>
</table>

The final value of Mg = 0.024 %, which is almost identical to the real value (0.026 %).

The condition of low content of sulphur is justified, because by increasing the content of sulphur we will increase the component of desulphurization at the expense of added magnesium (the vector of evaporation is constant).

It is possible to mention other alternative changes of modification conditions, in particular changing the chemical composition:

\[ C = 3.8 \% \quad Mn = 0.6 \% \quad Mo = 0.5 \% \quad (\text{alloyed CISG- Figure 53}) \]

\[ Si = 2.2 \% \quad Cu = 2 \% \]

The temperature and the pressure are constant, as well as the initial amount of sulphur: 1400 °C, 1.5 bar a 0.02 % S.

Changing the chemical composition has led to a change of magnesium content in the solution, which is in equilibrium for the given temperature and pressure 0.0113 = to 0.0161 %. Figure 56 shows the change of shift of the correspondent isotherm calculated from the equation (76) – it is marked with a dashed line. The change of modification conditions is in the following table.

Table 26 – Change of modification during the change of chemical composition - Figure 56

<table>
<thead>
<tr>
<th>%Mg</th>
<th>Yield of Mg [%]</th>
<th>Desulphurization [%]</th>
<th>Evaporation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>32.6</td>
<td>40.6</td>
<td>26.8</td>
</tr>
<tr>
<td>0.05</td>
<td>23.6</td>
<td>24.4</td>
<td>52</td>
</tr>
</tbody>
</table>

The residual magnesium is low in both cases and does not warrant the formation of spheroidal graphite:

at 0.03 % Mg\(_v\) = 0.00978 % Mg\(_{zbyt}\), at 0.05 % Mg\(_v\) = 0.0118 % Mg\(_{zbyt}\)

To reach the required amount of residual magnesium warranting the formation of spheroidal graphite for the given case we have 3 possibilities:

1/ decreasing the amount of sulphur – metallurgical problem
2/ increasing the amount of magnesium added by the modifier – magnesium in excess
3/ increasing the modification pressure – the problem of choosing the modification method
1/ Decreasing the amount of sulphur

from 0.02 to 0.005 % the amount of magnesium consumption of desulphurization will
decrease, and the utility of magnesium will increase to 44 %. The value of \( \text{Mg}_{\text{res.}} = 0.022 \) %,
which can warrant the formation of spheroidal graphite.

2/ Increasing the amount of magnesium added by the modifier

We can proceed according to the formula:

\[
\text{Mg} = 0.035 + 0.75 \cdot \text{S} = 0.035 + 0.75 \cdot 0.02 = 0.050 \%
\]

where the value 0.035 is the value of \( \text{Mg}_{\text{res.}} \). This value will not suffice according to Figure 53, because as was mentioned above, the \( \text{Mg}_{\text{res.}} \) is 0.0118 %. Further adding of magnesium leads to an ineffective modification.

3/ Increasing the modification pressure

We increase it from 1.5 bar to 3 bars. The value of magnesium in equilibrium at the
given temperature and pressure is 0.0323 %. The changes of modification conditions lead in
this case to an increase of magnesium utility and therefore to an increase of residual magnesium, in this case to the value of 0.021 %. The effect is therefore the same as in decreasing the content of sulphur.

The result of effective modification relies on the option that we have in the foundry: either we choose the option of adding magnesium in considerable excess according to the relation:

\[
\text{Mg}=0.04+0.76 \text{ S} \quad \text{pro } \text{Mg}_{\text{res.}} = 0.04 \%
\]

Or through the method of decreasing the amount of sulphur in the initial cast iron while
increasing the modification pressure at the same time. In other words, metallurgical conditions of melting a cast iron and the method of modification.

8.6 The influence of calcium on the modification

Ca – S reaction

To calculate the corresponding Ca-S isotherms, we consider the following thermodynamic values.

\[
[Ca][S] = \text{CaS} \quad \Delta G_0 = 336710 + 9.44 \cdot T
\]

calculated

\[
\log K = \frac{17593.8}{\text{R} \cdot \text{T}} - 4.78 \quad R = 8.314 \cdot J \cdot K^{-1} \cdot \text{mol}^{-1} \quad K = 10^{\frac{175938}{T} - 4.78}
\]

And then the equation of the Ca-S isotherm depending on the temperature has the
following form:

\[
\log [\% \text{Ca}] = - \frac{17593.8}{T} + 4.78 - \left( e_{\text{Cu}}^c \cdot [\% C] + e_{\text{Cu}}^{si} \cdot [\% Si] \right) - \left( e_{\text{S}}^c \cdot [\% S] + e_{\text{S}}^{ci} \cdot [\% C] + e_{\text{S}}^{si} \cdot [\% Si] - \log [\% S] \right)
\]
Metallurgy of cast irons. Out-of-furnace processing of molten cast iron. 2014

**Note:** $P_{Ca}$ is not considered in this equation, because there is no evaporation of calcium at the given temperature (the temperature of the molten cast iron is low).

Figure 60 shows the calculated isotherm for the temperature of 1400 °C, 1450 °C and 1500 °C.

The constant proportion of $Ca/S = 1.25$, which derives from the stoichiometric ration of both components entering the reaction, is marked on this figure.

Example on Figure 60 initial content $S = 0.014 \%$ and the initial content of $Ca = 0.025 \%$. The equilibrium of desulphurization corresponds with the values of sulphur depending on the temperature. The higher the temperature, the lower the desulphurization ability of calcium.

The next Figure 61 visually shows the combination of Mg-S and Ca-S isotherms at the temperature of 1450 °C and with the chemical composition of iron containing 3.5 \% C and 2.5 \% Si.

Initial considered values: $S = 0.012 \%$
$Ca = 0.017 \%$
$Mg = 0.035 \%$

Due to the effect of calcium (the reaction occurs before the reaction with magnesium due to the affinity of calcium to sulphur) the amount of sulphur will decrease from 0.012 \% to 0.004 \%. This changes the modification conditions in such a way that for $Mg = 0.035 \%$ there is $Mg_{res.} = 0.0202 \%$.

![Figure 60 – Ca-S isotherms for various temperatures.](image-url)
Figure 61 – Simultaneous action of magnesium and calcium during modification.

If calcium was not present, then at Mg = 0.035 % the Mg_{sht} = 0.012 % (marked with a dashed line on Figure 61).

The thought about the effect of calcium as a desulphurizing agent is complicated because of the fact that the desulphurizing ability is dependent on temperature and pressure as well as on its concentration in the solution.

From the above mentioned example we assume the preferential reaction of calcium with sulphur at the same time in the case that the initial values of magnesium and calcium during the modification will be the same (in the mentioned example, the initial content of calcium is lower than the content of magnesium).

### 8.7 Deoxidation effect of magnesium, calcium and aluminum during the modification

The decrease of the content of oxygen during the modification is generally recognized, although literary and operating data are contradictory. Chemical reactions of the elements present in the modifiers are to be defined, so that we can calculate the magnesium losses during the modification. The analyses of slags after the modification unambiguously define the course of the processing of the molten cast iron by the modifier. We are presenting the chemical analysis of the modification slags.

The degree of oxidation of the melt is given by the \( \frac{SiO_2}{MnO + FeO} \) proportion. In case of using the pre-alloy it is 0.8, which is the optimal value expressing the quality of the modification.

If pure magnesium is used, this proportion is 1.02 – the degree of oxidation is higher and there is a risk of creation of bubbles and slags in the casting. Pure magnesium, as an
important deoxidizing and desulphurizing element at concentration of almost 100 % (99.8 %) behaves in this way, while the modifier in the form of a pre-alloy contains, apart from magnesium, other elements (calcium, aluminum, cerium, rare metal earths) with the same character as magnesium. These elements are, however, at lower concentrations than the concentration of magnesium. The modification has a chemically different course – with lower intensity compared to pure magnesium.

Table 27 – The composition of a slag after the modification by a pre-alloy FeSiMg5 and by pure Mg

<table>
<thead>
<tr>
<th></th>
<th>FeSiMg5</th>
<th>pure Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_{tvch}</td>
<td>0.015</td>
<td>0.08</td>
</tr>
<tr>
<td>S_{kon}</td>
<td>0.010</td>
<td>0.005</td>
</tr>
<tr>
<td>SiO₂</td>
<td>30.2</td>
<td>17.0</td>
</tr>
<tr>
<td>MgO</td>
<td>25.35</td>
<td>42.9</td>
</tr>
<tr>
<td>CaO</td>
<td>0.001</td>
<td>0.56</td>
</tr>
<tr>
<td>MnO</td>
<td>1.4</td>
<td>2.6</td>
</tr>
<tr>
<td>FeO + Fe₂O₃</td>
<td>36</td>
<td>14.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.8</td>
<td>5.94</td>
</tr>
<tr>
<td>S</td>
<td>0.06</td>
<td>17.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.17</td>
<td>-</td>
</tr>
<tr>
<td>Basicity of the slag</td>
<td>0.84</td>
<td>2.56</td>
</tr>
</tbody>
</table>

Reaction Mg - O

\[ [\text{Mg}] + [O] = MgO \]

\[ G^0_T = -143572 + 37.26 \cdot T \]

\[ \ln K = \frac{a_{Mg} \cdot a_{O}}{a_{MgO}} = - \frac{31375}{T} + 8.208 \]

Isotherms for the Mg-O reaction can be determined from the relation:

\[ \log [\%O] = K_{MgO} + \log a_{MgO} - \log [\%Mg] + 160 \cdot [\%Mg] + 243 \cdot [\%O] \]

where: \( \log a_{MgO} = 1 \)

\[ \log (243 \cdot [\%O]) = \frac{243 \cdot 2.3 \cdot K_{MgO}}{[\%Mg]^2} \]

\[ \log (160 \cdot [\%Mg]) = \log \left( -e_{O}^{Mg} \right) = \frac{10744}{T} - 3.549 \]
temperature and pressure, in our case for $T = 1400 \, ^\circ C$ the concentration of $\text{Mg} = 0.055 \%$. Figure 62 shows the examples of deoxidation at various initial content of magnesium during modification. Anyhow, the consumption of magnesium for deoxidation is not high. The higher the content of oxygen in the melt, the more probable the occurrence of deoxidation by magnesium.

The influence of calcium and aluminum is given by the following thermodynamic conditions of the corresponding reactions.

**Ca-O reaction**

$$[\text{Ca}]+[O] = \text{CaO}$$

$$G_T^0 = -156060 + 35.41 \cdot T$$

$$\ln K_{\text{CaO}} = \frac{a_{\text{Ca}} \cdot a_O}{a_{\text{CaO}}} = -\frac{31375}{T} + 8.208$$

The isotherms for the Ca-O reaction can be determined from the relation.

$$\log[\%O] = K_{\text{CaO}} + \log a_{\text{CaO}} - \log[\%\text{Ca}] + 416 \cdot [\%\text{Ca}] + 1040 \cdot [\%O]$$

where: $\log a_{\text{CaO}} = 1$

$$\log(1040 \cdot [\%O]) = \frac{1040 \cdot 2.3 \cdot K_{\text{CaO}}}{[\%\text{Ca}]^2}$$

$$\log(416 \cdot [\%\text{Ca}]) = \log\left(-e^{Ca}_O\right) = \frac{11949}{T} - 3.761$$

Figure 63 shows the corresponding isotherms for the temperatures of 1400 °C and 1500 °C. This figure also shows the concentration of calcium at the pressure of 1 bar and for the corresponding temperatures. Furthermore, it shows the decrease of oxygen depending on the content of initial calcium during modification. The reaction of deoxidation by calcium is very unlikely even at low contents of calcium, and may favorably influence the process of modification.
Figure 62 – Isotherms Mg - 0 for temperatures 1400 °C and 1500 °C and the consumption of magnesium by bonding with oxygen at the pressure of 1 bar and the temperature of 1500 °C and 1400 °C.

Figure 63 – Isotherm Ca - 0 for temperatures of 1400 °C and 1500 °C. The decrease of oxygen content at the Ca content of 0.01 % Ca.
Al-O reaction

\[ [2 \cdot Al] + [3 \cdot O] = Al_2O_3 \]

\[ G^0_r = -291830 + 94.18 \cdot T \]

\[ \ln K_{AlO} = -\frac{64900}{T} + 20.57 \]

The equation for the isotherms has the following form:

\[ \log[\%O] = \frac{1}{3} K_{Al,O} - \frac{2}{3} \log[\%Al] + 1.17 \cdot [\%Al] \]

Figure 64 shows the isotherms for the temperatures of 1400 °C and 1500 °C. The reaction also depends on the mutual concentration of aluminum and oxygen during modification. Figure 64 shows an example for the concentration of 0.1 % Al in the solution. At this concentration, there is deoxidation by forming Al_2O_3 while at the same time the content of oxygen decreases.

The presence of calcium and aluminum in the modifier is important with regard to the oxygen present in the molten cast iron, because the deoxidation through these elements favorably influences the course of modification.

Deoxidation increases the nodulation effect of Mg.

Figure 64 – Al-0 isotherm for temperature of 1400 °C and 1500 °C. The decrease of oxygen content due to the reaction with aluminum
8.8 Evaluation of the theoretical analysis

The presented theoretical analysis of thermodynamic conditions of the modification of the cast iron provides a good orientation in the evaluation of influence of the Mg based modifiers (and component modification additives Al and Ca, with different sulfur content in the melt, pressure modification, melt temperature and other conditions). The examples of using the theoretical dependencies indicate their practical use.

According to some authors [24, 25, 28, 56] the reactions between Ca, Mg, Ce, O and S can be evaluated according to the correspondent equilibrium constants as follows:

Reactions of Ca and the value of constants

\[
\log[\%Ca] \cdot [\%O] = \frac{30046}{T} + 6.0
\]  
(77)

\[
\log[\%Ca] \cdot [\%S] = \frac{28113}{T} + 6.95
\]  
(78)

While in cast iron it is possible to accept the reaction with C

\[
[Ca] + 2 \cdot [C] = CaC_2
\]  
(79)

At the value of

\[K_{CaC_2} = \frac{8642}{T} - 2.96\]  
(80)

In cast iron containing C = 3.3 % and Si = 2.5 % at the temperature of T = 1673 K there is the formation of CaC₂ already at the concentration of Ca = 2.10 % in the modifying additive.

Figure 65b compares the refining effect of calcium in the cast iron and in steel (Figure 65a). Steel has a 0.02 % content of O₂ and 0.032 % content of S, cast iron (Figure 65b) has a 0.008 % content of O₂ and 0.03 % content of S. The desulphurizing ability of Ca is high in the cast iron. The symbols S_K, S_N mark the contents of sulphur at the beginning (S_N) and at the end (S_K) of the reaction. The same applies for oxygen.
Figure 65 – The calculation of mutual effect of Ca, O a S – the initial values in the melt.

a) steel with 0.02 % O and 0.03 % S
b) cast iron with 0.008 % O and 0.03 % S

Figure 66 shows the influence of Mg on [O] and [S] according to the constants:

\[
\log[\%Mg][\%O] = -\frac{31384}{T} - 1.5 \cdot \log T + 16.5 \quad (81)
\]

\[
\log[\%Mg][\%S] = -\frac{234111}{T} + 8.5 \quad (82)
\]

Figure 66a applies for the content of S = 0.04 % and the Figure 66b applies for the content of S = 0.008 %. At the low content of S the proportion of Mg-S bond decreases considerably. Mg\(\alpha\) marks the final content of Mg after the modification.

The influence of Ce on the modification is displayed on Fig.67. Corresponding constants.

\[
\log[Ce^3][O] = -\frac{81100}{T} + 26.4 \quad (83)
\]

\[
\log[Ce^3][S] = -\frac{26940}{T} + 7.95 \quad (84)
\]

Figure 67 shows that the deoxidation occurs first and then comes the desulphurization, which creates more CeS.
Figure 66 – Calculation of mutual effect of Mg, O and S in the molten cast iron – the initial values in the melt. Full line – oxygen, dashed line – sulphur.

a) with 0.04 % S
b) with 0.008 % S

Figure 67 – Calculation of mutual effect of Ce, O and S in the molten cast iron.
The following conclusions can be made from the above mentioned facts:

1/ Magnesium is a strong desulphurization agent due to its high affinity to sulphur. The correspondent isotherms show that desulphurization occurs even at very low concentrations of magnesium in the solution. This means that the Mg-S reaction cannot be prevented, we can only define the mutual proportion of $\text{Mg : S = 3 : 1}$, which is given as authoritative for this reaction.

Figure 68 shows the relation between the content of sulphur in the cast iron before modification ($S_v$) and the necessary amount of magnesium for modification ($M_{g,v3}$) at the given utility of Mg during modification.

2/ The assessment of the influence of temperature and pressure shows that the most important factor is the pressure and its importance clearly dominates.

3/ The presence of calcium in the modifiers favorable influence the process of modification, because it helps the spheroidizing effect of magnesium with its desulphurization effect. Its content in the modifiers varies depending on the method that we use to manufacture CISG. The similar principle applies for Ce.

4/ The deoxidizing effect of calcium and aluminum favorably influences the process of modification by decreasing the content of oxygen in the molten cast iron. It decreases the deoxidizing effect of magnesium and supports its spheroidal effect.
Terms summary

- Mentioned in the “contents of the chapter” part

Questions

- How can we define the physical conditions of the modification?
- How can we practically use the definition of the modification pressure?
- What are the chemical conditions of modification?
- What is the process of the deoxidation of the melt by magnesium, calcium and aluminum during the modification?
9 PRACTICAL ASPECTS OF THE CAST IRON MODIFICATION

Contents of the chapter

✓ “Clean” process option
✓ Chemical process option
✓ Conclusion

Time to study: individual

Aim After studying this chapter you will be able to:

• Describe the “clean” process option
• Describe the chemical process option

Presentation

Thermodynamic analysis of the modification suggest that its principle is given by the physical and chemical processes, which gain importance according to chosen method.

The scheme on Figure 69 depicts the various options of modification. There are three options listed, one of which, representing the physical conditions of the modification (temperature and pressure of the modification), is common for the other two options and is determining the meaning (see the theoretical analysis).

9.1 “Clean” process option

The condition of modification in this option are very demanding on the metallurgical process of melting. At these conditions, we are trying to reduce the chemical processes to a minimum, so that Mg contained in the modifier serves as a spheroidizer during the crystallization of graphite, in other words meaning that the molten cast iron has to contain minimum amount sulphur, oxygen and disturbing elements. Therefore, this melt has a minimum amount of inclusions and that is why the CISG produced in this way is suitable for very demanding castings, e.g. hydraulic elements or castings replacing castings from cast steel.

These conditions are met by the synthetic method of melting (the cast iron is melted from the steel scrap by carburization and other modification of the chemical composition). Electric arc furnace is a suitable melting aggregate. In such a furnace, it is possible to
correspondingly change the contents of P and S. The metallurgical process is well controllable from the point of view of chemical composition.

The melting process is carried out in the oxidation and reduction period with carburization and final change of the chemical composition. This method is energy intensive. The semi-synthetic method of melting allows the use of electric induction furnace crucible as well as arc furnace by selecting the suitable composition of the batch (certain proportion of quality pig iron in the batch). This case is more or less a method of re-melting with the final chemical change of the melt. It is less energy intensive, but more demanding on the quality of batch material.

The cast iron melted in this way has a low content of S (under 0.01 %) and a low content of O₂. It allows to use Mg with minimal excess and production of CISG with Mg_{res.}= 0.03 % it is possible to achieve the spheroidal graphite in the structure with the content even lower than Mg_{res.}< 0.03 %.

The choice of “clean” process of modification is therefor given not only by technical conditions but also by solid economic reasons.

We compare the costs of melting and preparation of initial cast iron with the savings on modifier and the operational certainty of the modification.

There are very specific conditions in the production of ductile cast iron CISG for the casting of higher weight category (> 5 t), where the cooling of the casting lasts longer and the modifier has to be applied for a longer period to cause the spheroidization of graphite. If we accept the desulphurization by magnesium in these conditions, then if the reaction of desulphurization proceeds until the solidification of the casting, then there is a great danger of formation of imperfect spheroidal graphite in the thermal axes of the casting.

As seen above, the choice of a suitable method of production of a cast iron with spheroidal graphite is given by a broad spectrum of knowledge of the initial inputs, which determine the optimal methods for the production of CISG.

9.2 Chemical process option

In this modification method, we do not place high demands on the preparation of melting of the initial cast iron. That is why we accept the possibility of chemical reactions between the modifier and the elements present in the melt. During the modification, deoxidation, desulphurization and refining of the melt take place as well. The modifier, magnesium, is added in a certain excess, so that we achieve the necessary amount of Mg_{res.} after the modification. The methods of modification allow up to 0.1 % S in the initial cast iron.

That is why the cast iron can be melted in cupolas with the possibility of duplex processes of melting. In the table, the process of melting is marked with the word “unlimited”. It is obvious that any decrease of the content of initial sulphur in the cast iron lead to a higher operational certainty of the production of CISG.

9.3 Conclusion

The diagram on Figure 69 includes all the possible methods of production of CISG, also taking into account the economic point of view. During the CISG production, it is not possible to clearly recommend one method or the other, because the decisive factor is the state
and possibilities of melting of the initial cast iron including the control over the melting process. Another decisive factor is the range of produced castings. Especially in CISG, this point of view is important for the choice of production method.

The range of castings is determined from these points of view:

a) the weight of the casting
b) requirements on the casting function, in other words its functionality and durability
c) series production

All the three mentioned criteria have their relevance, and their mutual importance is used in particular conditions, expressed in the order and closed contract.

![Diagram of the process of cast iron modification]

**Figure 69 – The scheme of the process of cast iron modification**

### Terms summary

- Mentioned in the „Contents of the chapter“

### Questions

- What is the principle of the “clean“ process option?
- What is the principle of the chemical process option?
10 MODIFICATION TECHNOLOGY

Chapter division

✓ Pouring methods
✓ Converter method
✓ Immersion methods
✓ Method of filled profiles

Time to study: individual

Target After studying this chapter, you will be able to

- Characterize basic methods of modification:
- Pouring methods
- Converter method
- Immersion methods
- Continuous modifications
- Method of core wire

Presentation

Currently, there are around 200 patented methods of adding modifiers into a melted cast iron, the use in practice represents around 40 to 50 ways to produce CISG. Requirements that condition a certain certainty of modification can be summarized into these points:

1/ reliability
2/ economy
3/ low costs
4/ ecological conditions

Later on we will give the main representatives of the individual groups of the modification methods. They are:

- Pouring (“Sandwich”)
- immersion
- converter
- continuous
- filled profiles
In Table 28, these methods are stated. With each method of modification in a ladle it is necessary to maintain a certain measure of its thinness, as resulted from physical conditions of the modification. The thinness is given, i.e. the height of the ladle \( h = 1,5 \cdot d \) of the diameter as the minimum thinness.

From the stated, different opinions arise on evaluation of the individual methods of CISG. These differences affirm that it is not possible to straightforwardly prefer this or that method but rather that every method is specific for certain conditions, which exist in a foundry from the king of melting aggregate to the type of produced castings.

Table 28 – Operating conditions of modification methods

<table>
<thead>
<tr>
<th>Method</th>
<th>pouring</th>
<th>immersion</th>
<th>converter</th>
<th>In-Mold</th>
<th>Core wire</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg Pre-alloy% Mg</td>
<td>FeSiMg 3-10</td>
<td>pure Mg FeSiMg 5-35</td>
<td>pure Mg FeSiMg 5-10</td>
<td>pure Mg + + other elements</td>
<td></td>
</tr>
<tr>
<td>yield of Mg in %</td>
<td>35-60</td>
<td>40-50</td>
<td>45-60</td>
<td>70-80</td>
<td>35-70</td>
</tr>
<tr>
<td>equipment costs</td>
<td>-</td>
<td>low</td>
<td>high</td>
<td>-</td>
<td>low</td>
</tr>
<tr>
<td>limitations of %S</td>
<td>0.040</td>
<td>0.080</td>
<td>0.15</td>
<td>0.010</td>
<td>any</td>
</tr>
<tr>
<td>necessity of operator</td>
<td>any, no device</td>
<td>immersion device, necessary of processing place</td>
<td>necessary device, processing place</td>
<td>simple for mass production</td>
<td>simple, automatic adjustment</td>
</tr>
<tr>
<td>max. processing</td>
<td>unboundary</td>
<td>unboundary</td>
<td>5t</td>
<td>unboundary</td>
<td>unboundary</td>
</tr>
<tr>
<td>disadvantages</td>
<td>dosage, accurate content of Mg</td>
<td>dosage, accurate content of Mg, immersion bell</td>
<td>regulation of the processing procedure, the high cost</td>
<td>danger of dosing, accurate content of Mg</td>
<td>costs of Mg in fulfilling profile</td>
</tr>
</tbody>
</table>

Inoculation by graphite can be done consequently with the modification (as one-step inoculation) or inoculation can be done during pouring from modification ladle into the casting ladle or inoculate in the form or a combination of these options.

10.1 Pouring methods

These methods are very simple, they do not require high investment costs, but they are uneconomical from the viewpoint of the modifier use. The principle of this method is in placing the modifier on the bottom of the ladle, which is either modified with a small chamber or divided by a partition. Before the pouring, it is necessary to cover the modifier by steel turnings or plates to delay the melting and thus keep the modifier near the bottom of the pan. This method allows for the production in high amounts (in up to 60-ton pans). Certain improvement in the economy is represented by the Tundish-Cover method (ladle with a cover), where the ladle is covered during the pouring by a lined cover, which also serves as the funnel and thus prohibits the oxidation of Mg and creates a high modification pressure due to the Mg vapor. The ladle is not hermetically sealed by the lid. Figure 70 shows a
construction of the modification ladle for the Sandwich method and figure 71 shows it for the Tundish-Cover method. The liquid metal is poured into the ladle on the opposite side from where the modifier is placed.

Figure 70 shows that the pouring hole’s volume corresponds with the amount of modified melt. Before the modification, we cover the releasing opening by a plug. This method is suitable for a smaller amount of metal from 300 to 500 kg and is reliable.

Figure 70 – Pouring method – modifier covered by steel turnings.  
Figure 71 – Pouring method by Tundish-Cover system

The use of Mg in the pouring method of CISG production is:
- 10 – 30 % in an open ladle
- 35 – 55 % in a lid-enclosed ladle

Lower use is caused by premature rising and subsequent burning out of the modifier on the surface of the melt.

10.2 Converter method

Another alternative to the pouring method is the method of a converter ladle.

In a specially shaped modified ladle in form of a converter, it is possible to modify by pure Mg. The producer of this ladle and the whole modification apparatur fa +GF+ Georg Fischer analysed the conditions of modification in great detail and recommends it even for higher amounts of initial sulphur (it is also possible to use it for cupola melt.) The principle of this method is shown on figure 72.
In a horizontal position of the ladle, the filling by the liquid metal occurs. The modifier is placed in a specially adjusted space which prevents rise of the modifier to the surface. This meets the condition of the effect of metalostatic pressure of the column height of the melted cast iron. The modification occurs by rotating the ladle into a vertical position. The ladle can be enclosed by a cover which limits the Mg oxidation during the modification and it is controlled remotely so that the staff is not endangered during the modification by any splashing of the liquid metal.

Modification in a converter ladle is a reliable method; the use of Mg is given in relation with the content of sulphur \( S = 45 - 60\% \). Up to 0.15\% of initial sulphur in the cast iron is acceptable. Graphite inoculation is recommended, but not during the modification. The amount of modified cast iron is up to 5 t. The use of this method requires high acquisition costs and special treatment of the workplace within the foundry.

![Figure 72 – Modification in a converter by pure Mg](image)

Based on the foundry’s disposition, it is possible to place the convertor on a moveable cart or a crane and therefore to produce CISG directly on the pouring field, which shortens the manipulation time and also the time of the modifier effectiveness.

### 10.3 Immersion methods

**Immersion atmospheric methods**

An advantage of this method of CISG production is basically adding the modifier into the melted cast iron placed in the bell and submerging to the bottom of the modification ladle. Thus possible rising of the modifier to the surface is avoided. During submerging, the ladle is closed by a cover, which increases the effectiveness of the modification. Figure 73 states the basic parameters which are necessary to uphold while submerging the modifier into the melt. This method of modification allows for use of modifier in form of a pre-alloy with Mg concentration of up to 35\% which is in compact state.
Immersion overpressure method

This method allows to modify under artificial overpressure. This means it enables modification in an autoclave or in an autoclave ladle and therefore the use of pure Mg as a modifier. Overall arrangement of this immersion method of modification is on figure 74. It is necessary to point out that this form of modification does not necessitate an extremely low amount of sulphur in the initial cast iron.
Figure 75 shows a schematic method of modification in a pressure vessel (autoclave). Modification under pressure requires periodic checks of the ladle, because it is a pressure vessel, which is subject to strict operating regulations. A check of the pressure during modification is problematic, because the control manometer can fail and when the ladle opens, an ejection of the melt can occur which can cause an injury. Despite that, from the theoretical standpoint, this method is ideal because it ensures regulation of the modification by pressure and temperature. Usually, the modifier - pure magnesium - is used in compact state.

Due to the fact that we can regulate the partial pressure over the metal surface, this method allows for low consumption of Mg. Currently, autoclave is used instead of autoclave pan, where the ladle can be used without a lid; we created an overpressure over the surface and then immerse the modifier, which amounts to about 0.12 ÷ 0.15 % of the mass of liquid metal. This method is patented in the Czech Republic. Autoclave under the name Sphäre guss is produced and supplied in 1 t or 2 t version by Moravské železářny in Olomouc.

This method has high consumption of magnesium and it can modify up to 5 tons in a ladle. The value of overpressure is controlled by the temperature of the molten cast iron. The higher the temperature of the metal in the pan, the higher the overpressure must be. For example during the melting in cupolas, where temperatures rise to 1480-1500 °C, the overpressure must be 6 atm and during melting in induction furnaces, where temperatures are 1520-1560 °C, the value of overpressure is 8 atm.
10.4 Continuous modifications

In this method of CISG production, the modification occurs during casting of liquid metal from the melting aggregate and we modify either directly in the gating system of the casting mold (i.e. In Mold method) or by pouring into a specially prepared reaction chamber, where the modifier is placed and then into the casting ladle (i.e. Flotret method).

Continuous method of modification is very effective, because apart from the aforementioned conditions, dynamic effect of the metal flow is also used, which ensures good dissolution of the modifier and high effect of graphite inoculation. On the other hand it requires a low amount of S in the cast iron (under 0.01 % of S), because desulphurization during the modification is not possible.

The acquiring costs are low to minimal, with a reaction chamber, the only cost is on its treatment.

We can clearly see on figure 76 the arrangement of the gating system for direct modification in mold cavity, i.e. the In Mold Method. In the gating system, a reaction chamber is placed in the parting plane, where granular modifier in form of a master alloy is placed before closing the mold, this contains up to 5 % of Mg and an increased amount of Ca (max. 2 %). The dimension of the chamber are determined based on this relation:

\[
K_d = \frac{m_o}{S} = 0.04 \div 0.06 \text{ kg.cm}^{-2}\text{.sec}
\]

where \(K_d\) - coefficient of dissolution
\(m_o/sec\) - mass speed of casting in kg/sec
\(S\) - floor surface of the chamber in cm²

![Diagram of gating system with reaction chamber](image)

Figure 76 – Method of ductile cast iron production in casting mold

The volume of the chamber is calculated from the amount of modifier used. Due to a low amount of S in the cast iron, 0.8 - 1.1 % of the total mass of liquid metal is the amount of
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modifier used. It is important to set the period of pouring, which can be determined based on commonly used formulas; however, it is better to use practical measurement, because the casting period = the time in which the modifier dissolves. We keep around 30% of the overall chamber volume in the chamber for the so called free space necessary for the mixing of the modifier.

If complete purity of the casting is required, it is necessary to use ceramic sieves and filters placed behind the reaction chamber. These will hold possible products of the modification. The disadvantage of this method is the necessary control of nodulation of each casting.

An example of reaction chamber calculation:

<table>
<thead>
<tr>
<th>Chamber volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Floor surface = S_{RK} = \frac{m_{p} \cdot s}{K_{d}} \text{ [cm}^2\text{]}</td>
</tr>
</tbody>
</table>

Minimum volume of the modifier = \( V_{M} = \frac{m_{M}}{\rho_{M}} = \frac{\text{mass in kg}}{\text{bulk density vkg/cm}^3} \)

\( \rho_{M} = 2.03 \text{ kg/dm}^3 \) - bulk density of the modifier

\( V_{M} \) - volume of the modifier

Height of the chamber \( H_{RK} \):

\( H_{RK} = \frac{V_{M}}{S_{RK}} + 1.5 + v \)

\( v \) - height of the channel leading into the chamber

Overall chamber volume:

\( V_{RK} = S_{RK} \cdot \left( \frac{V_{M}}{S_{RK}} + 1.5 + v \right) \)

Dimensions of the gating system:

- surface of the ingates: \( \sum x \)
- surface of the slag trap: \( x + 10\% \)
- surface of the outflow cross section: \( x + 12\% + 15\% \)
- surface of the inflow cross section: \( x + 30\% \)
- surface of the sprue pin: \( x + 30\% \)

This method is shown as an example, there are similar procedures according to various authors differentiating in only minor details, such as the chosen value of the dissolution coefficient \( K_{r} \). Detailed description of the calculation is stated in the literature. [63]

This problem is solved by the second alternative to continuous modification, the so called modification in the reaction chamber (Flotret method). In this method, the modified cast iron in the casting ladle can be controlled in terms of the effectiveness of the modification.

Figures 76, 77 and 78 show schematics of various alternatives to this method of continuous modification. Figure 77 is the Flotret method. The treatment chamber, where the modification occurs has the character of a tundish.
The bottom outlet flows away the cast iron into the pouring ladle.

Figure 78 is yet another construction of a tundish called Incomod. The function of treatment chamber is evident from figure 78. Figure 79 shows another alternative where the liquid metal can be input in three ways, labeled A, B and C on figure 79.

The modified cast iron flows out into the maintenance tundish with a drain stopper. This arrangement allows for rising of modification slag to the surface.

![Modification in a tundish](image1)

**Fig.77 – Modification in a tundish**

![Modification in a tundish](image2)

**Fig.78 – Modification in a tundish**
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Fig. 79 – Modification in a tundish with various arrangements A, B and C

By using this method, we can modify immediately and cast, because this ladle can also serve as the pouring ladle.

Modification by this method can be controlled by calculation (see chapter 7.1).

10.5 Core wire method (CW)

This method has been gathering some importance recently. It is relatively simple and reliable.

The principle of this method consists of injecting the molten cast iron with a core wire at certain speed so that the profile is melted away at the bottom of the ladle.

The method is characteristic for its high investment costs to acquire the ladle of certain thinness with a cover and also a dosing device which ensures the movement with the possibility of regulating the speed of the filled profile. The method ensures control of the amount of core wire and all types of CISG can be produced using this method. A problem of this method is graphitizing inoculation, which is necessary to perform after the modification is finished when it is cast into the pouring ladle. Graphitizing inoculation done during the modification is only possible with another core wire containing the graphitizing inoculant.

The ladle is covered by a lid during the modification. The utilization of Mg is given based on the amount of S from 35 % to 70 %. The initial amount of S is not limited.

Core wire is a hollow wire with the steel cover of 0.2 - 0.5 mm thick filled with its own modifier and other accompanying elements. Examples are shown in the table.
Table 29. Contents of the modifier in filled profiles.

<table>
<thead>
<tr>
<th>Marking</th>
<th>% Mg</th>
<th>% CaC₂</th>
<th>Content [g/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg 78</td>
<td>78</td>
<td>22</td>
<td>70 75 180</td>
</tr>
<tr>
<td>Mg 60</td>
<td>60</td>
<td>40</td>
<td>75 180</td>
</tr>
<tr>
<td>Mg 40</td>
<td>40</td>
<td>60</td>
<td>75 180</td>
</tr>
<tr>
<td>Mg 60 Si</td>
<td>60</td>
<td>40 FeSi 75</td>
<td>80 190</td>
</tr>
<tr>
<td>Mg 40 Si</td>
<td>40</td>
<td>60 FeSi 75</td>
<td>95 190</td>
</tr>
<tr>
<td>Mg 60 SiCe</td>
<td>60</td>
<td>30 FeSi 75 10 CeMMSi</td>
<td>80 190</td>
</tr>
<tr>
<td>Mg 40 SiCe</td>
<td>40</td>
<td>50 FeSi 75 10 CeMMSi</td>
<td>100 200</td>
</tr>
</tbody>
</table>

Core wire is injected by the dosing device which allows for a change of speed in feeding the profile and registers its use in metres. Profiles are made in various diameters: 3, 5, 8, 12 and 18 mm. Construction of the dosing device is such that 2 or 3 profiles can be fed at once. This allows for consequent graphitizing inoculation.

An example of the modification balance is shown in table 30.

Table 30 – Balance of modification

<table>
<thead>
<tr>
<th>Balance</th>
<th>1.</th>
<th>2.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight kg</td>
<td>1000</td>
<td>1425</td>
</tr>
<tr>
<td>Temperature before °C</td>
<td>1489</td>
<td>1490</td>
</tr>
<tr>
<td>Temperature after °C</td>
<td>1439</td>
<td>1401</td>
</tr>
<tr>
<td>Content of S before %</td>
<td>0.097</td>
<td>0.015</td>
</tr>
<tr>
<td>Content of S after %</td>
<td>0.010</td>
<td>0.008</td>
</tr>
<tr>
<td>The need of wire m</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>Speed m/min</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Consumption of Mg kg/t Fe</td>
<td>2.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Mg res. %</td>
<td>0.034</td>
<td>0.046</td>
</tr>
<tr>
<td>Mg yield %</td>
<td>42</td>
<td>43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Modifier</th>
<th>Mg 40 Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filled profile</td>
<td>85 g/m</td>
</tr>
<tr>
<td>Ø profile</td>
<td>9 mm</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.4 mm</td>
</tr>
<tr>
<td>Filled Mg</td>
<td>34 g/m</td>
</tr>
</tbody>
</table>

The consumption of a filled profile, as is evident from the table, and the related consumption of Mg (or the profile) depends on the amount of S, temperature and speed of the profile injection. Figure 80 shows the principle of the method. The use of core wire requires some adjustment of the workplace so that the safety requirements and workplace hygiene are met.
The arrangement of the workplace based on the aforementioned is shown on figure 81. It consists of the day storage of filled profile, dosing device and foundry and casting workplace.

The advantage of this method of modification is the ability to choose various composition of the modifier for given conditions and also this method offers other use in out-of-furnace processing of cast iron, as shown in figure 82.

Fig.80 – The principle of ductile cast iron production by injection of filled profile.

Fig.81 – Schematic arrangement of the injection when using multiple core wire.
Summary of the chapter terminology

- Is given in the section „Division of the chapter“

Questions for the material studied

- What are the advantages and disadvantages of the basic modification methods:
  - Pouring methods
  - Converter method
  - Immersion method
  - How do we determine the size of the reaction space for the method of continuous modification
  - Method of core wire
11. CISG PRODUCTION ORGANIZATION

Time to study: individual

Target After studying this chapter, you will have learnt about:

- The overview of workplace organization
- Cupola foundries with out-of-furnace desulphurization.
- Cupola furnace-GF converter combination
- CISG production using pre-alloys with the use of electrical induction furnace.
- Production of ductile cast iron CISG by the GF converter method with the use of electrical induction furnace.

Presentation

From the aforementioned stems the importance of knowing the problems of out-of-furnace processing of cast irons as an option for influencing the crystallization of cast iron and at the same time influencing the utility properties of this material. Out-of-furnace desulphurization, inoculation and modification and alloying of the melting cast iron are an inseparable part of the melt processing, which are included in the metallurgy of cast-iron.

A schematic arrangement of production of cast-iron with spheroidal, lamellar and tempered graphite is shown on Figure 82. The possibilities of overall arrangement of the processed liquid metal during the production of cast-iron with spheroidal graphite is shown on Figures 83 to 86.
Metallurgy of cast irons. Out-of-furnace processing of molten cast iron. 2014

Figure 82 – Overview of the workplace arrangement

CILG - cast iron with lamellar graphite
CISG - cast iron with spheroidal graphite
CGI - compacted graphite cast iron
Cupola furnace with out-of-furnace desulphurization

In CISG production in a cupola furnace (figure 83), out-of-furnace desulphurization can be used, when the melting cast-iron is desulphurized using CaC$_2$ with an inert gas being blown through (N, Ar). From the maintenance forehearth, the cast-iron is poured into the electrical induction furnace, pre-heated to the required temperature of modification. The pouring method produces a ductile cast-iron CIAG and the casting stage follows. The temperature regime is shown on the diagram.

![Diagram of cupola furnace with out-of-furnace desulphurization](image.png)

Figure 83 – Cupola furnace with out-of-furnace desulphurization
Figure 84 – Cupola furnace–GF converter combination

Figure 85 – CISG production with master-alloys when using electrical induction furnace
Rotation gas furnaces can also be used to produce CISG.

The whole production process can be simplified by using a converter, in which desulphurization and modification can be done with lower temperature losses, as is shown on Figure 84.

During the melting in electric crucible furnace using the overmelting system, we can produce CISG using the pouring method. The initial amount of sulphur is given by the composition of the charge. The temperature regime is shown on Figure 85; on Figure 86 is the same combination used with the converter. This combination is again independent on the initial amounts of sulphur.

In table 7, the different options for CISG production are stated, which are also given in the chapter on thermodynamic modification.

This study material presents the basic knowledge in out-of-furnace cast-iron processing and serves for a very general orientation of the reader.
Metallurgy of cast irons. Out-of-furnace processing of molten cast iron. 2014

Summary of the chapter terminology

- Is given in the section „Chapter division“

Questions on the material studied

- The overview of workplace organization
- Cupola melting with out-of-furnace desulphurization.
- Cupola furnace-GF converter combination
- CISG production using master alloys with the use of electrical induction furnace.
- Production of ductile cast iron CISG by the GF converter method with the use of electrical induction furnace.

- The phrasing of the questions corresponds to the names of the chapters in the section „Chapter division“
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