VŠB - Technical University of Ostrava

Faculty of Metallurgy and Materials Engineering

# Secondary Metallurgy

(Lecture notes)

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# STUDY REGULATIONS

**Secondary Metallurgy**

For the subject Secondary Metallurgy in the 3rd semester of the field of study Modern Metallurgical Technologies you have obtained an educational packet including integrated lecture notes for the combined study comprising also study regulations.

**The objectives of the subject and outputs from the education**

The aim of the subject is to give students basic theoretical and practical knowledge of secondary metallurgy procedures, i.e. ladle processing of liquid steel.

After studying the subject, a student should be able to:

Acquired knowledge:

- o *A student will be able to characterize secondary metallurgy technologies and their theoretical principles*

Acquired skills:

- o *A student will be able to use own knowledge to describe basics of theory and practice in steel secondary processing and steel casting*
- o *A student will be able to develop own theoretical and practical knowledge through following studies*

**For whom the subject is intended**

The subject falls within the follow-up Master's study of the field of study Modern Metallurgical Technologies of the study programme Metallurgical Engineering, but it can also be studied by applicants from any other branch, on condition of having met the demanded prerequisites.

The lecture notes are divided to parts – chapters, which correspond to the logical dividing of the studied subject matter, but they are not of the same volume. The assumed time for the study of the chapter may differ significantly, therefore large chapters are further divided to numbered subchapters and these correspond to the structure of the lecture notes described below.

**Recommended procedure for studying each chapter**

The lecture notes divided to chapters need to be read-through as a whole at first. Only after that it is advisable to begin to study the particular chapters. After having finished, answer the questions for each chapter.

**A way to communicate with lecturers**

Within this subject, elaboration of a semester project on a given topic will be a task for students:

- o *About ladle refining of steel*

The semester project will be checked by the teacher within 14 days from the submission and results will be sent to students by means of the information system. A student will pass a credit test, the results of which will be communicated to students afterwards.

Individual topics of the semester project will be given to students at the beginning of the semester. Students will obtain more detailed instructions at the beginning of teaching. Questions for the given topic can be consulted with the teacher-tutor (prof. Zdeněk ADOLF, CSc. or doc. Ing. Ladislav SOCHA, Ph.D.):

- o *Within consultation hours*
- o *On the telephone number 597 325 135; 597 323 534*
- o *Through e-mail: zdenek.adolf@vsb.cz; ladislav.socha@vsb.cz*

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# 1. SECONDARY METALLURGY METHODS

**Subchapters:**

- ✓ Causes of the secondary metallurgy development
- ✓ Main causes of development of the secondary metallurgy methods and equipment
- ✓ Advantages and benefits of ladle refining of steel
- ✓ Basic processes of steel secondary metallurgy and their effects

**Time needed for the study:** individual

**Objective:** After studying this chapter a student will be able to:

- *Define causes of the secondary metallurgy development*
- *Characterize advantages and benefits of steel processing through secondary metallurgy methods*
- *Define basic methods and equipment in the secondary metallurgy*

**Lecture**

## 1.1 Causes of the secondary metallurgy development

The second half of the 20th century in steelmaking is characterized by noticeable effort to reduce material and energy demandingness. At the same time, users' demands for steel quality representing enhancement of usable properties of products increase. This resulted in origination of new steelmaking technologies called secondary metallurgy. Metallurgy of iron and steel covers a system of operations and equipment, which can be divided to two groups depicted in **Fig.1**.

| Secondary metallurgy contains: | | |
|---|---|---|
| **I.** Refining of liquid raw iron, mostly desulphurization or dephosphorization | **II.** Modification of liquid steel in ladle. This system is often called ladle metallurgy or secondary metallurgy | **III.** Remelting processes (e.g. electro-slag remelting of steel) and production of homogenous ingots |
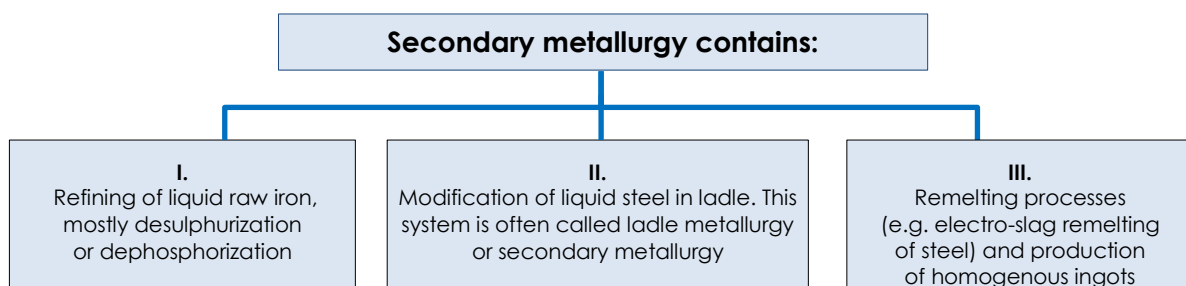
**Fig. 1** Characteristics of secondary metallurgy

## 1.2 Main causes of development of the secondary metallurgy methods and equipment

Moving refining operations from the production reactor into a ladle enables:

o *To reduce production costs per one ton of manufactured steel*

o *To enhance the manufactured steel quality to a level unreachable in a furnace aggregate*

o *To prepare liquid steel for continuous casting in CCM with accurate casting temperature and controlled chemical and metallographic cleanliness*

## 1.3 Advantages and benefits of ladle refining of steel

The purpose of a furnace aggregate is to decarburize and dephosphorize a metal charge and to heat steel to a tapping temperature. Benefits of steel refining in ladle can be summarized as follows:

o *The production cost reduction consists in shortening of melting time in the furnace aggregate and this results in:*

- *Enhancement of production of the furnace aggregate*

- *Reduction of lining wear*

- *Decrease in heat losses*

- *Possibility of automatization of the simplified production technology*

o *Steel quality enhancement is possible due to:*

- *Higher temperature and chemical homogeneity of the metal bath*

- *Reduction of the content of dissolved gases ([H], [N])*

- *Decrease in a content of inclusions in molten steel and a possibility to modify their shapes and sizes*

- *Deep desulphurization or, on the contrary, control of the sulphur content in steel*

- *Accurate alloying even on the lower limit of the range*

o *An accurate casting temperature in a low range between 3 – 5 °C can be ensured in a ladle with steel temperature raising – a ladle furnace*

Managing the above mentioned refining methods allows implementation of new steel grades.

## 1.4 Basic processes of steel secondary metallurgy and their effects

Basic processes of steel ladle processing (secondary metallurgy) and their effects can be summarized as follows

o *Inert gas blowing*

- *Only blowing (floatation of inclusions, temperature and chemical homogenization of steel)*

- *Blowing under the active slag (a reaction between the slag and metal; steel desulphurization)*

- o *Injection of additives*
  - - *Blowing of pulverized substances using an inert gas (steel desulphurization, inclusion modification + steel deoxidation, steel alloying, steel carburization)*
  - - *Inputting additives in a form of cored steel wires (accurate and economy alloying of steel, inclusion modification)*
  - - *Aluminium wire feeding (controlled deep deoxidation of steel)*
- o *Steel refining by synthetic slags (steel deoxidation, controlled desulphurization, absorption of non-metallic inclusions)*
- o *Vacuum steel refining:*
  - - *Ladle degassing*
  - - *Stream degassing*
  - - *Chamber degassing (recirculating RH, lift DH)*
  - - *($H_2$ and $N_2$ content reduction, vacuum carbon deoxidation, steel additional alloying)*
  - - *Vacuum oxygen decarburization – VOD (stainless steel production - deep decarburization by chromium of high alloyed steels)*
- o *Steel refining by gas mixture $O_2$ – Ar, or $O_2$ - $H_2O$ in a converter AOD, CLU, K-OBM-S (stainless steel production – deep decarburization under the atmospheric pressure)*
- o *Steel temperature raising in ladle:*
  - - *Electric arc under the atmospheric pressure*
  - - *Electric arc with a possibility of steel vacuum degassing – ASEA, VAD*
  - - *Chemical temperature raising – by Al or FeSi oxidation under the atmospheric pressure – IR-UT, CAS-OB*
  - - *Chemical temperature raising – by Al or FeSi oxidation in vacuum - ISSM*

## ∑  Summary of terms of this chapter (subchapters)

- o Mentioned in the part "Subchapters"

## ?  Questions to the topic

- o Questions to this topic correspond to titles of the subchapters in the part "Subchapters"

## 2. STEEL REFINING BY INERT GASES

**Subchapters:**

✓ Steel refining by inert gases

✓ Stirring and homogenization of the molten metal

✓ Inclusions flotation at inert gas blowing and their absorption by slag

✓ Reduction of a content of gases dissolved in steel – hydrogen and nitrogen in molten iron and steel

✓ Simultaneous solubility of hydrogen and oxygen in molten steel

✓ Oxygen in molten iron and steel

✓ Thermodynamic conditions of steel degassing

✓ Kinetics of steel degassing

✓ Methods of feeding argon into steel in a ladle

✓ Requirements for blowing elements


**Time needed for the study:** individual


**Objective:** After studying this chapter a student will be able to:

- *Describe a principle of steel refining by inert gases, stirring and homogenization of the molten metal*
- *Characterize flotation of inclusions at inert gas blowing*
- *Define reduction of gas contents, gas solubility in the molten steel*
- *Describe thermodynamic and kinetic conditions for steel degassing*
- *Define methods of an inert gas feeding into steel in a ladle*
- *Characterize requirements for blowing elements*


**Lecture**


### 2.1 Steel refining by inert gases

Argon is the most frequently used gas for steel refining. However, carbon dioxide bubbles at occurring reaction of carbon with oxygen fulfil the same function. This is a simple refining method with low investment costs for installation and a high economic return. Achieved effects are mentioned below:

- o *Steel homogenization – temperature as well as concentration*
- o *Inclusions floating-out both by a directed flow of steel and by forced flotation*
- o *Reduction of a content of hydrogen, in vacuum also of nitrogen*
- o *Support of the carbon reaction process (reduction of a content of carbon and oxygen)*

o *Ensuring the run of reactions between the slag and metal by renewing the reaction surface (above all steel desulphurization)*

This is necessary part of all other methods of steel ladle refining. This is a minimal condition for successful casting at CCM.

## 2.2 Stirring and homogenization of the molten metal

Buoyant energy of floating-out gas bubbles is used for stirring and homogenization of the molten metal.

$$\varepsilon = 14{,}23 \left( \frac{V \cdot T}{M} \right) \cdot log \left( \frac{1+H}{1{,}48 \, P_0} \right) \tag{1}$$

where  $\varepsilon$  is  stirring energy, W.t$^{-1}$
   $V$  -  gas blowing intensity, Nm$^3$.min$^{-1}$
   $T$  -  melt temperature, K
   $M$  -  melt weight, t
   $H$  -  injection depth, m
   $P_0$  -  pressure on the melt surface, atm

Time needed for achieving 95% of melt homogenization with regard to a ladle diameter and injection depth was derived by Mazumdar and Guthrie:

$$\tau = 116 \cdot \varepsilon^{-1/3} \cdot \left( D^{5/3} \cdot H^{-1} \right) \tag{2}$$

where  $\tau$  is  time for 95% of melt homogenization, s
   $D$  -  ladle diameter, m

**Fig. 2** below shows a calculated homogenization time for a melt of 100, 200 and 300 tons.



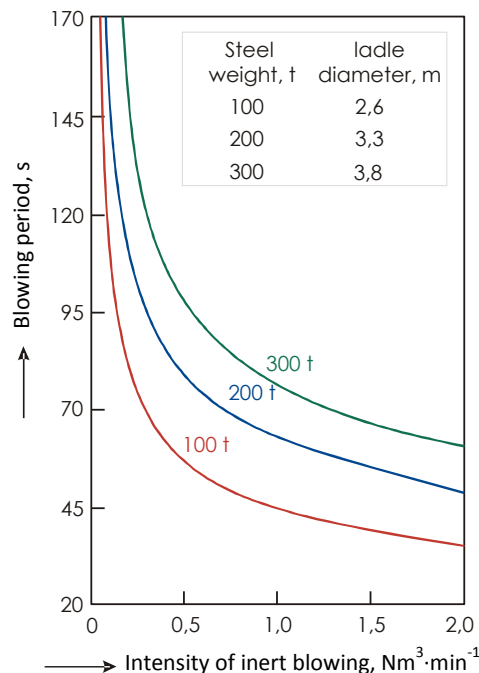| Steel weight, t | ladle diameter, m |
|---|---|
| 100 | 2,6 |
| 200 | 3,3 |
| 300 | 3,8 |

**Fig. 2**   Calculated homogenization tim for a melt of 100, 200 and 300 tons depending on gas blowing intensity

## 2.3 Inclusions flotation at inert gas blowing and their absorption by slag

Non-metallic inclusions are floated-out from liquid steel by a steel flow towards the phase interface with slag, where they are caught and subsequently absorbed by the liquid slag. This process requires laminar flow of the melt, which does not cause entrainment of particles of the slag into the steel, and a negative value of the Gibbs energy in the process of inclusion absorption by slag. For the inclusion absorption by slag a relation can be derived:

$$\Delta G = \sigma_{v-s} \cdot S_{v-s} - \sigma_{v-l} \cdot S_{v-l} \tag{3}$$

where $\Delta G$   is   Gibbs energy of the inclusion absorption by slag, J
     $\sigma_{v-s}$   -   inclusion-slag interphase tension, N.m$^{-1}$
     $\sigma_{v-l}$   -   inclusion-metal interphase tension, N.m$^{-1}$
     $S_{v-s}$   -   area of the inclusion-slag interphase surface, m$^2$
     $S_{v-l}$   -   area of the inclusion-metal interphase surface, m$^2$

The process runs spontaneously, if $\Delta G < 0$. This condition is met, if $\sigma_{v-s}$ is minimum and $\sigma_{v-l}$ is maximum. If chemical composition of an inclusion and slag is similar, then $\sigma_{v-s} \to 0$ and the inclusion is not wetted by metal. On these conditions $\Delta G < 0$ and inclusion absorption by slag runs successfully. Flotation of inclusions consists in adhesion of an inclusion to a surface of a blown inert gas bubble and following floating-out to slag, as shown in **Fig. 3**.
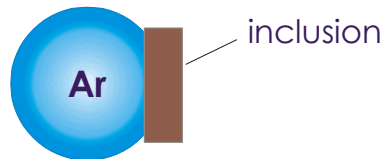


**Fig. 3**   Schematic depiction of an inclusion after joining Ar bubble

Firmness of a connection of an inclusion with a bubble can be described through the work of adhesion needed for separation of an inclusion from the bubble.

$$W_A = S_{v-g} \cdot \sigma_{l-g} \left( 1 - \cos\theta \right) \tag{4}$$

where $W_A$   is   adhesion work – firmness of a connection of the Ar bubble-inclusion
          system, J
     $S_{v-g}$   -   area of a connection of the Ar bubble-inclusion, m$^2$
     $\sigma_{l-g}$   -   surface tension of steel, N.m$^{-1}$
     $\theta$   -   wetting angle of the inclusion material wetting by steel

Firmness of the connection of an inclusion with a bubble, hence a probability of inclusion flotation, is dependent on wetting of an inclusion by steel, steel surface tension and an area of the inclusion-bubble connection, as shown in **Table 1**.

**Tab. 1**   Calculation of the work of adhesion according to the equation

| If | | | |
|---|---|---|---|
| | $\theta \to 0$ | $cos\ \theta \to 1$ | $W_A \to 0$ |
| | $\theta = 90°$ | $cos\ \theta \to 0$ | $W_A \to S_{v-g}.\ \sigma_{l-g}$ |
| | $\theta = 180°$ | $cos\ \theta \to -1$ | $W_A \to 2\ S_{v-g}.\ \sigma_{l-g} = (W_A)_{max}$ |

The metal surface tension $\sigma_{l-g}$ is maximal, if steel has a content of surface active substances minimized (particularly *[S]* and *[O]*). A significance of the area of the connection of an inclusion $S_{v-g}$ with a bubble increases, if the bubble size "gets near" the inclusion size. This means that flotation of inclusions requires a bubble mode of inert blowing – refining of steel.

This implies that argon blowing into steel can reduce above all a content of inclusions with high interphase tension towards steel. Particularly, these are stable inclusions formed by aluminium oxide. Steel should be deeply deoxidized and desulphurized and only refined by argon.

## 2.4 Reduction of a content of gases dissolved in steel – hydrogen and nitrogen in molten iron and steel

### 2.4.1 Hydrogen and nitrogen in molten iron and steel

Dissolution of gases in molten metals and their separation from metals are inverse processes. Atomic dissolution of gases in metals, as well as their removal from metals, can be described by a general equation

$$1/2\,X_{2(g)} \Leftrightarrow [X] \tag{5}$$

The absorption process mechanism of gas atomically dissolved in molten metal can be expressed using several following processes:

- o *Diffusion of gas molecules from atmosphere to the metal surface*
- o *Adsorption of gas molecules on the metal surface and their dissociation to atoms*
- o *Desorption and diffusion of gas atoms from the surface into the metal volume*

On the other side, removal of gas from the molten metal is related to molecularization of gas atoms in the metal surface prior to diffusion of such originated molecules to atmosphere.

The equilibrium of the molten metal-gas phase system is dependent on the gas content in metal */X/*, its partial pressure $p_{x_2}$ and temperature *T*. Regarding equation (5), for the atomic solution of gas in molten metal at constant temperature applies:

$$[X] = \frac{K_x}{f_x}\sqrt{(p_{X_2})_r} \tag{6}$$

whereas

$$\left(p_{x_2}\right)_r = \frac{p_{x_2}}{p_{x_2}^0} \tag{7}$$

where  $K_x$   is   equilibrium constant of Sieverts' law, wt. %, ppm

$p_{x_2}$   -   relative partial pressure of gas above metal, 1

$p_{x_2}$   -   partial pressure of gas above metal, Pa

$p_{x_2}^0$   -   101 325 Pa partial pressure of gas in a standard state, Pa

*[X]*   -   equilibrium content of gas atomically dissolved in metal, wt. %, ppm

Equation (6) is a mathematical expression of the Sieverts' law. The Sieverts' law is a limit case of a more general Henry's law, which describes molecular dissolution of gases in solutions. If dissolution of gases in metals is not completely of the atomic character, then the exponent of pressure in equation (6) reaches a value from 0.5 to 1.0.

Providing that $p_{x_2r} = 1$ and $f_x = 1$, then $[X]_{max.} = K_x$. Value $K_x$ then corresponds to the gas solubility in molten iron or low-alloyed steel ($f_x \rightarrow 1$).

Equilibrium concentrations of gas dissolved in metal at the specified values $p$ and $T$ characterize the absorption ability of the given gas and thus the gas solubility at the chosen thermodynamic conditions. Solubility is expressed in weight percentage, ppm or cubic centimeters of gas in 100 g of metal.

Temperature dependence of a content of gas atomically dissolved in molten metal can be, under the constant pressure, expressed by the equation:

$$ln[X] = -\frac{\Delta H}{2RT} + ln\ C \qquad (8)$$

where   $\Delta H$   is   dissolving heat of 1 mol of gas, $J.mol^{-1}$
$\qquad$ C   -   constant dependent on a type of gas and metal, wt. %
$\qquad\qquad$ -   coefficient 2 in the denominator shows, that the gas dissolves even in the dissociated condition.

Dissolving heat comprises adsorption heat $\Delta H_A$, dissociation heat $\Delta H_D$ and, in case that gas reacts chemically with metal, also reaction heat $\Delta H_R$.

$$\Delta H = \Delta H_A + \Delta H_D + \Delta H_R \qquad (9)$$

While dissociation of gas molecules to atoms is always an endothermic process $\Delta H_D > 0$, gas adsorption in the metal surface and its chemical reaction with metal are usually exothermic processes $\Delta H_A < 0$ and $\Delta H_R < 0$. In gases exhibiting low solubility in metals the resulting thermal effect of dissolving is endothermic $\Delta H > 0$, as heat consumed for dissociation of gas molecules exceeds the adsorption heat value, whereas $\Delta H_R = 0$. Therefore, for example, hydrogen solubility in $\alpha$, $\gamma$, $\delta$ and molten iron increases along with the increasing temperature, while nitrogen solubility in $\gamma$ iron decreases with temperature owing to the exothermic effect of the reaction of $\gamma$ iron with nitrogen at formation of nitrides $/\Delta H_R/ + /\Delta H_A/ > /\Delta H_D/$.

Dissolving of hydrogen and nitrogen in pure molten iron is governed by the Sieverts' law. Both the gases dissolve atomically in the molten iron and with regard to the mostly endothermic character of the dissolution process their solubility increases along with the increasing temperature.

The calculated values of hydrogen and nitrogen solubility in $\alpha$, $\gamma$, $\delta$ and molten iron are depicted in **Fig. 4** and **Fig. 5**.

The defined solubility of hydrogen and nitrogen in **Fig. 4** and **Fig. 5** correspond to the equilibrium of pure iron with a gaseous phase containing only hydrogen or nitrogen at pressure of 0.1 MPa. In operational conditions of ladle refining, steel containing many dissolved elements is degassed, and the atmosphere above the metal, or more precisely the gas bubble floating-out off the metal, contains also other kinds of gases.
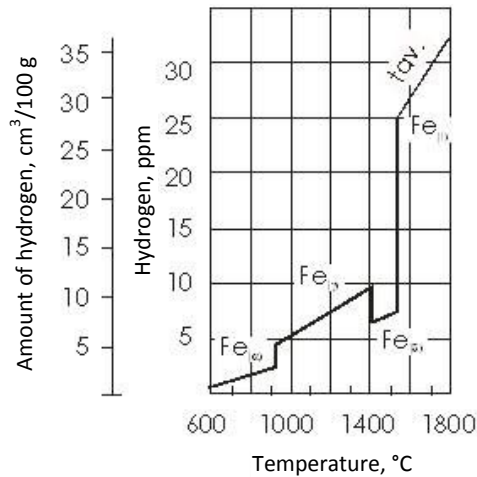
**Fig. 4** Influence of temperature on solubility of hydrogen in iron at 0.1 MPa pressure
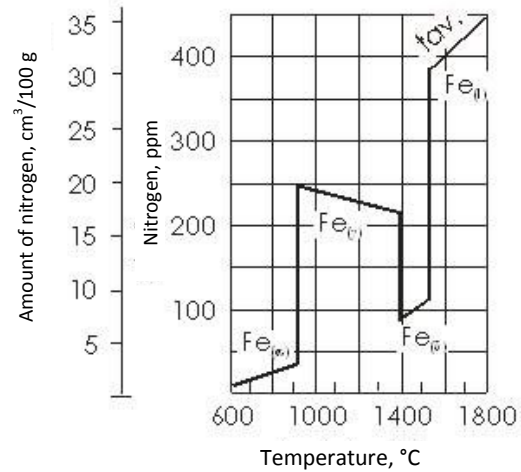


**Fig. 5** Influence of temperature on solubility of nitrogen in iron at 0.1 MPa pressure

Solubility of hydrogen and nitrogen in iron melt containing a third element is determined by interaction forces between a solvent (iron) and a dissolved substance (hydrogen or nitrogen) and an alloying element.

Active factors $f_{[H]}$ and $f_{[N]}$ in equation (6) can be calculated from interaction coefficients using equations (10) and (11).

$$log\ f_{|H|} = \sum e_H^i \, [i] \cdot \left( \frac{6945}{T} - 2,71 \right) \tag{10}$$

$$log\ f_{|N|} = \sum e_N^i \, [i] \cdot \left( \frac{3\,280}{T} - 0,75 \right) \tag{11}$$

where $e_H^i$ is    interaction coefficient expressing an element influence also on hydrogen activity in steel at t = 1 600 °C, 1

    $e_N^i$ -    interaction coefficient expressing an element influence also on hydrogen activity in steel at t = 1600 °C, 1

    *[i]* -    content of an element in steel, wt. %

### 2.4.2   Simultaneous solubility of hydrogen and oxygen in molten steel

During manufacturing and casting, steel gets into a contact with atmosphere, which contains hydrogen mostly in a form of water vapour. Water vapour in a contact with molten iron dissociates into hydrogen and oxygen, which reacts with iron to FeO (12). Oxygen dissolves in the molten iron according to reaction (13) and hydrogen transfers into iron in accordance with the Sieverts' law (6). The resulting reaction (15) is a sum of these three reactions:

$$H_2O_{(g)} + Fe_{(l)} = H_{2\,(g)} + (FeO) \tag{12}$$

$$(FeO) = Fe_{(l)} + [O] \tag{13}$$

$$\underline{H_{2\,(g)} = 2\,[H]} \tag{14}$$

$$H_2O_{(g)} = 2\,[H] + [O] \tag{15}$$

The temperature dependence of the equilibrium constant of reaction (15) is expressed by the equation

$$log \frac{[ppm\,H]^2 \quad [wt.\%O]}{p_{H_2O}\,(atm.)} = -\frac{5\,385}{T} + 5,123 \tag{16}$$

The relation of the hydrogen content in steel to the oxygen content and partial pressure of water vapour for t=1600 °C is depicted in **Fig. 6**.
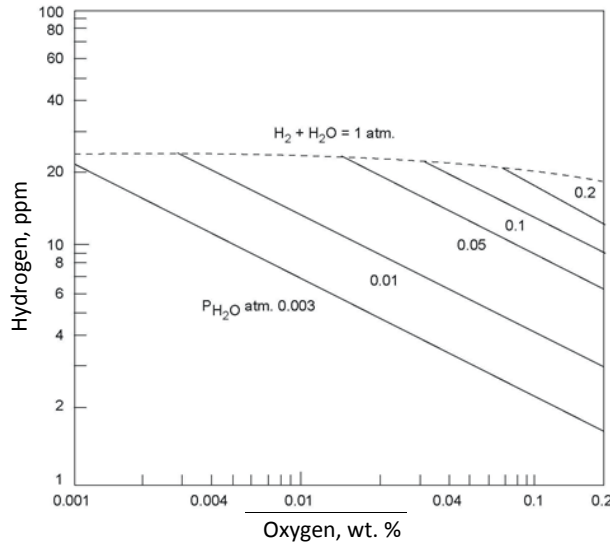


**Fig. 6**    Relation of hydrogen content in steel to the oxygen content and $p_{H_2O}$

The Figure implies that hydrogen from moist materials or from the atmosphere is well soluble above all in deoxidized steel.

### 2.4.3   Oxygen in molten iron and steel

The mechanism of dissolution of gaseous oxygen in liquid steel is different from dissolution of hydrogen and nitrogen. Regarding its high affinity for iron, oxygen reacts chemically to FeO at a contact with molten steel (or even to higher oxides $Fe_3O_4$, $Fe_2O_3$) and only after that FeO dissolves in steel. This process mechanism can be expressed as follows

$$Fe_{(l)} + \tfrac{1}{2}\,O_2\,(g) = (FeO),\,(Fe_3O_4),(Fe_2O_3) \tag{17}$$

$$\underline{(FeO) = Fe_{(l)} + [O]} \tag{18}$$

$$\tfrac{1}{2}\,O_2\,(g) = [O] \tag{19}$$

The resulting summary reaction (19) does not express the actual process of oxygen dissolution in steel. A proof of this mechanism is also a fact that oxygen cannot be removed from steel by mere vacuuming, because member (18) of the mechanism does not contain a gaseous phase, therefore the reduced pressure has no influence on the equilibrium of reaction (18).

Equilibrium pressures of oxygen in the atmosphere, which relate to the achieved contents of oxygen in steel, can be calculated from the temperature dependence of the equilibrium constant of reaction (19).

$$log \frac{[ppmO]}{p_{O_2}^{1/2}(atm.)} = \frac{6\,046}{T} + 4{,}242 \tag{20}$$

Equation (20) implies that even negligible contents of oxygen in atmosphere in order of magnitude $10^{-4}$ Pa can ensure high contents of this element in steel.

### 2.4.4 Thermodynamic conditions of steel degassing

The basic thermodynamic condition for steel degassing is a lower partial pressure of hydrogen and nitrogen in the gaseous phase (in the atmosphere above the bath or in a gas bubble in the metal bath) than the equilibrium pressure of these gases appropriate to their contents in steel.

$$p_{X_2} < p_{X_2,r} \tag{21}$$

where $p_{X_2}$ is partial pressure of hydrogen or nitrogen in the gaseous phase, Pa

$p_{X_2,r}$ - equilibrium partial pressure of hydrogen or nitrogen in steel according to the Sieverts' law, Pa

For metal degassing through a bath surface not covered with slag applies that the partial pressure of hydrogen or nitrogen in the atmosphere depends on the external pressure and the content of the given gas in the atmosphere above the bath

$$p_{X_2} = p_v \frac{\{X_2\}}{100} \tag{22}$$

At metal degassing through diffusion of hydrogen or nitrogen into bubbles of inert gas or CO in the bath volume, the partial pressure of these gases in the argon bubble depends on a total pressure in the bubble

$$p_{X_2} = P \frac{\{X_2\}}{100} \tag{23}$$

whereas the total pressure in the bubble is given by a sum of atmospheric, ferrostatic and capillary pressures

$$P = p_v + p_f + p_\sigma \tag{24}$$

where $P$ is total gas pressure in a bubble, Pa

$p_v$ - gas pressure above the bath, Pa

$p_f$ - ferrostatic pressure of a metal column above a bubble, Pa

$p_\sigma$ - capillary pressure, Pa

$[X_2]$ - hydrogen or nitrogen content above the bath or in the bubble, mass %

The respective contents of hydrogen or nitrogen in metal can be expressed from the Sieverts' law

$$[X] = \frac{K_X}{f_X} \sqrt{p_v \frac{\{X_2\}}{100}} \tag{25}$$

$$[X] = \frac{K_X}{f_X} \sqrt{P \frac{\{X_2\}}{100}} \tag{26}$$

Equations (25) and (26) imply that the achievable hydrogen content in metal is the lower, the lower the total pressure above the bath, or in a gas bubble. As especially at vacuum processes the ferrostatic and capillary pressure take a significant part in the total pressure in a gas bubble (if $p_v \rightarrow 0$, then $P = p_f + p_\sigma$), the achievable hydrogen content in metal calculated according to equation (25) is lower than according to equation (26). The same applies for nitrogen. For this reason, during steel vacuum processing the major part of hydrogen and nitrogen is removed through the metal bath surface and if these gases transfer into bubbles, then this occurs mostly near the metal bath surface.

### 2.4.5  Kinetics of steel degassing

After the performed degassing, the content of hydrogen and especially of nitrogen in liquid steel usually exceeds the values calculated from the thermodynamic equilibrium conditions. This is caused by incompleteness of degassing owing to limited velocities of the particular stages in the steel degassing process.

Removal of hydrogen and nitrogen from steel occurs through an interphase interface of metal with a gaseous phase. A phase interface can be a metal bath surface not covered with slag, a metal strand surface during casting or a surface of bubbles of blown argon or carbon monoxide during carbon boil.

Then, metal degassing is a heterogeneous process, the mechanism of which comprises several following stages:

- o  *Transfer of gas atoms from the metal volume to the interphase boundary metal – gas typically by turbulent diffusion and their adsorption on this interphase boundary*

  $[X] \rightarrow [X]_p$
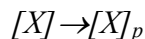
- o  *Association of the adsorbed gas atoms to molecules followed by desorption of gas molecules from the interphase boundary*

  $2\,[X]_p \rightarrow [X]_{2(g)}$
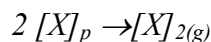
- o  *Diffusion of gas molecules from the interphase boundary into the gas volume*

Under laboratory as well as under industrial conditions it was found out that the first stage is the slowest stage of the overall degassing process. Velocity of diffusion of gas atoms from the metal volume to its surface can be expressed by a first-order kinetic equation

$$-\frac{d[X]}{d\tau} = \beta\,\frac{F}{V}\left([X] - [X]_p\right) \tag{27}$$

where  $-\dfrac{d[X]}{d\tau}$  is  decrease in a concentration of gas dissolved in metal in time $d\tau$, wt. %.s$^{-1}$

$\beta\,\dfrac{D}{\delta}$  -  mass transfer coefficient, m.s$^{-1}$

$D$  -  diffusion coefficient of gas in metal, m$^2$.s$^{-1}$

$\delta$  -  diffusion layer thickness, m

$F$  -  surface area of the metal - gas interphase interface, m$^2$

$V$  -  metal volume, m$^3$

$[X]-[X]_p$  -  concentration gradient of dissolved gas in a volume and on a surface of metal, wt. %

### 2.4.6 Conditions for achieving equilibrium in [C]-[O]-CO$_{(g)}$ system at argon blowing into steel in vacuum

Oxygen is contained in steel both as atomically dissolved gas and in a form of oxide inclusions. This implies two methods to reduce its content in steel during inert gas blowing. The first method consists in creation of conditions for a carbon reaction process, while a content of oxide inclusions can be reduced by improvement of conditions for their floating-out both by a directed steel flow and by flotation.

The carbon reaction is dramatically dependent on pressure and its reduction at vacuum and argon treatment of steel (in the argon bubble $p_{CO} \rightarrow O$) can be used for successful deoxidation of steel without occurrence of solid or liquid oxide inclusions.

Losses in carbon and oxygen contents during reaction (28)

$$[C] + [O] \rightarrow CO_{(g)} \tag{28}$$

can be expressed in molar units

$$- dn_c = -dn_o \tag{29}$$

or in weight percent ($M_C = 12$, $M_O = 16$)

$$- d[C\ wt.\%] = -\frac{12}{16} d[O\ wt.\%] = -\frac{3}{4} d[O\ wt.\%] \tag{30}$$

Equation (30) can be integrated and adapted to a form

$$[C] - [C]_r = \frac{3}{4}([O] - [O]_r) \tag{31}$$

where $[C]$, $[O]$     is initial content of carbon and oxygen in steel, wt. %
       $[C]_r$, $[O]_r$  -  equilibrium content of carbon and oxygen in steel, wt. % (at steel temperature t and external pressure $p_V$, or pressure in the argon bubble P)

The equilibrium between the carbon and oxygen contents can be described using an equilibrium constant of reaction (28) $K_C$ and partial pressure CO above the bath surface or in CO bubble, $p_{co}$. For $f_C = 1$ and $f_O = 1$, the following applies

$$[C]_r = \frac{(p_{CO})_r}{K_C\ [O]_r} \tag{32}$$

$K_C$ values can be calculated from the temperature dependence

$$log\ K_C = \frac{1\ 160}{T} + 2,07 \tag{33}$$

For temperature 1600 °C, $K_C = 494$.

By submitting equation (32) into (33), quadratic equation (34) can be obtained after adaptation. A positive solution of this equation is a relation of the equilibrium oxygen content in steel and partial CO pressure for the given initial contents of carbon and oxygen in steel

$$[O]_r^2 + \frac{4}{3}[O]_r\left([C] - \frac{3}{4}[O]\right) - \frac{4}{3}\frac{(p_{co})_r}{K_c} = 0 \tag{34}$$

$$[O]_r = -\frac{2}{3}\left([C]-\frac{3}{4}[O]\right) \pm \sqrt{\frac{4}{9}\left([C]-\frac{3}{4}[O]\right)^2 + \frac{4}{3}\frac{(p_{co})_r}{K_c}} \qquad (35)$$

Equation (32) can be also adapted to form (36)

$$[O]_r = \frac{p_{CO}}{494 \cdot [C]_r} \qquad (36)$$

By submitting equation (36) into (38), quadratic equation (37) can be obtained after adaptation

$$[C]_r^2 - [C]_r\left([C]-\frac{3}{4}[O]\right) - \frac{3}{4}\frac{(p_{co})_r}{K_c} = 0 \qquad (37)$$

A positive solution of this equation is a relation of the equilibrium carbon content in steel and partial CO pressure for the given initial contents of carbon and oxygen in steel

$$[C]_r = \frac{1}{2}\left([C]-\frac{3}{4}[O]\right) \pm \sqrt{\frac{1}{4}\left([C]-\frac{3}{4}[O]\right)^2 + \frac{3}{4}\cdot\frac{(p_{co})_r}{K_c}} \qquad (38)$$

**Fig. 7** shows:

- *A process of the carbon reaction from the initial content [C]init. = 0.1 wt. % and [O]init. = 0.05 wt. % to the equilibrium content of carbon and oxygen both at pCO = 1 and at pCO = 0.1 for vacuum carbon deoxidation of steel - VCD*

- *A process of the carbon reaction from the initial content [C]init. = 0.05 wt. % and [O]init. = 0.1 wt. % to the equilibrium content of carbon and oxygen both at pCO = 1 and at pCO = 0.1 for vacuum oxygen decarburization of steel - VOD*
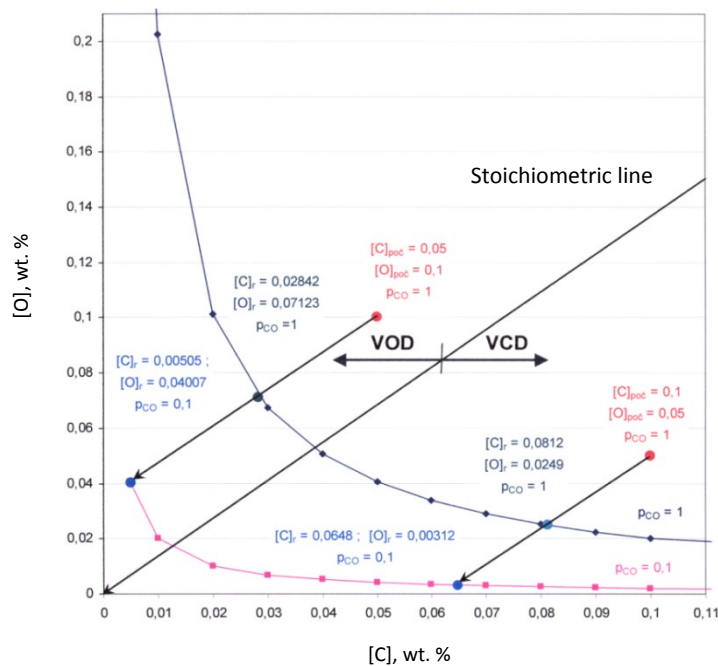


**Fig. 7** Equilibrium between the contents of carbon and oxygen in the steel melt at temperature t = 1600 °C and relative pressure $p_{CO}$ = 1 and $p_{CO}$ = 0.1 ($K_C$ = *494*)

Equation (35) applies for initial contents *[C] – 3/4[O] > 0, or [C] > 3/4 [O]*, this means for all points on the right-hand side from the stoichiometric line. This is a condition for the Vacuum Carbon Deoxidation process – VCD.

Equation (37) applies for initial contents *[C] -3/4[O] < 0, or [C] < 3/4 [O]*, this means for all points on the left-hand side from the stoichiometric line. This is a condition for the vacuum oxygen decarburization (VOD) process with the aim of deep decarburization of steel. This process is in operation used for deep decarburization of stainless steels high alloyed with chromium.

If $[C] = 3/4 [O]$, then the initial point is located on the stoichiometric line, where the contents of carbon and oxygen are in the stoichiometric ratio. Equation (35) can be simplified to form (39).

$$[O]_r = \sqrt{\frac{4 (p_{CO})_r}{3K_C}} = 1{,}1547 \sqrt{\frac{(p_{CO})_r}{K_C}} \tag{39}$$

This is a relation of oxygen content in steel to the partial CO pressure for temperature that is contained in $K_C$ value according to equation (33).

## 2.5 Methods of feeding argon into steel in a ladle

Inert gas blowing into the bath can be divided to the following kinds:
- *Lance (steel tube protected by a ceramic sheath)*
- *Steel tube ended with a porous ceramic plug (block)*
- *Porous refractory block located in the bottom of the ladle*

A schematic depiction of inert gas blowing through a submerged nozzle is shown in **Fig. 8** and **Fig. 9**.
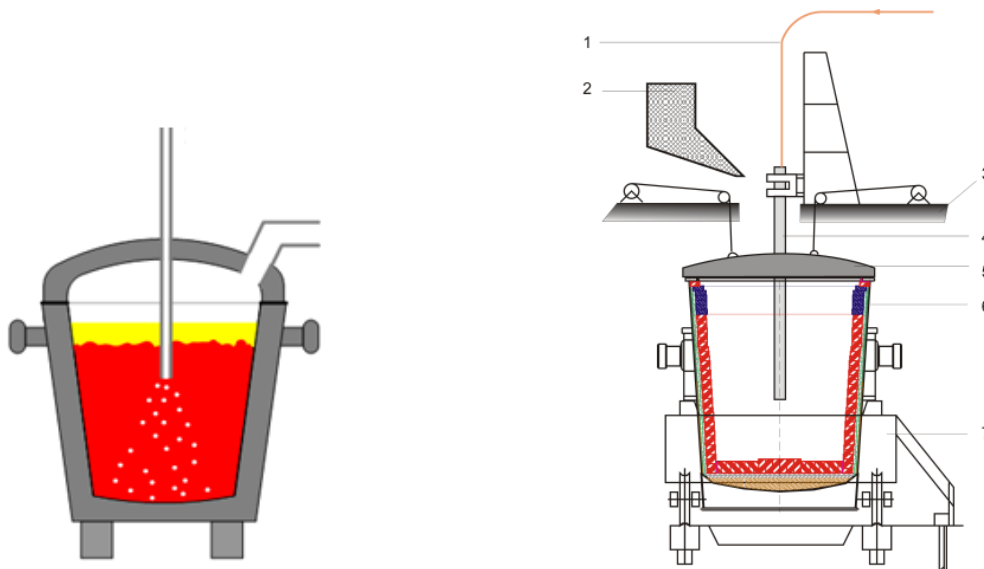




*Legend: 1 – Argon inlet, 2 – Funnel (slag-making and alloying additives), 3 – Working platform, 4 – Argon nozzles, 5 – Nozzle lid, 6 – Ladle, 7 – Traverse carriage*

**Fig. 8**   Inert gas blowing into a ladle      **Fig. 9**   Steel refining by inert gas

Attachment of a ceramic plug to a carrier steel tube is evident in **Fig. 10**.

Legend: 1 – Argon inlet
2 – Firming metal circle
3 – Hole in the circle for argon outlet
4 – Hollow filled with refractory material
5 – Matrix fixing a ceramic block
6 – Ceramic porous block
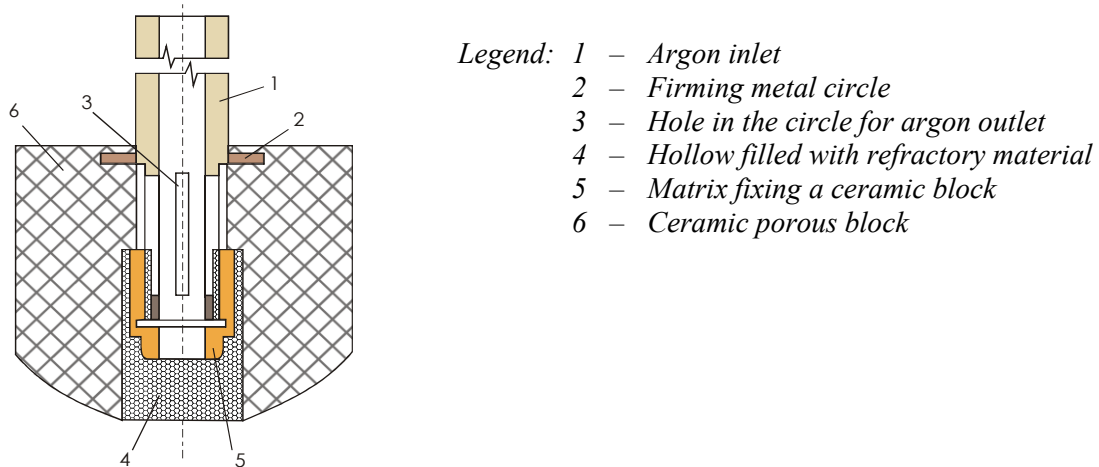
**Fig. 10**    Scheme of attachment of a ceramic block to a carrier metal tube

Advantages of inert gas blowing through a submerged lance:

o   *Simplicity of the design*
o   *Good contact of slag with metal, good desulphurization of steel*
o   *Lower investment and operation costs in comparison with electromagnetic stirring of steel*

Disadvantages of inert gas blowing through a submerged lance:

o   *Limited possibility to control the intensity of blowing*
o   *Steel cannot be degassed at the atmospheric pressure*
o   *Higher losses of alloying elements by their oxidation on the bath surface*
o   *Limited possibility to enhance metallographic cleanliness of steel – to remove inclusions by flotation*
o   *Steel is not stirred throughout the entire volume of the ladle (there are significant "dead" zones)*

Inert gas blowing through a porous block on the ladle bottom can be seen in the following **Fig. 11.**
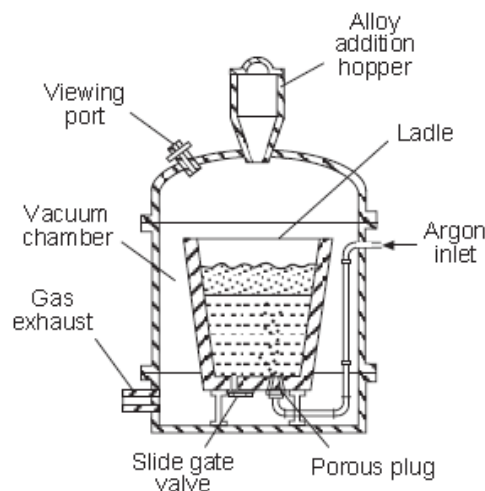


**Fig. 11**    Permeable porous block for argon bubbling into a ladle in a vacuum caisson

Advantages of inert gas blowing through a porous block on the ladle bottom:

- o *Uniform stirring of the bath*
- o *Minimum of areas without circulation*
- o *Possibility of argon blowing control from a "bubble" mode up to high intensity blowing*
- o *Excellent contact of slag with metal (steel desulphurization) and lower temperature gradient between metal and slag*
- o *Possibility of slight degassing and decarburization of steel*
- o *Lower investment and operation costs in comparison with electromagnetic stirring of steel*

Disadvantages of inert gas blowing through a porous block on the ladle bottom:

- o *Increased wear of ladle lining*
- o *Increased danger of outburst*

Induction stirring of steel is depicted in **Fig. 12**.
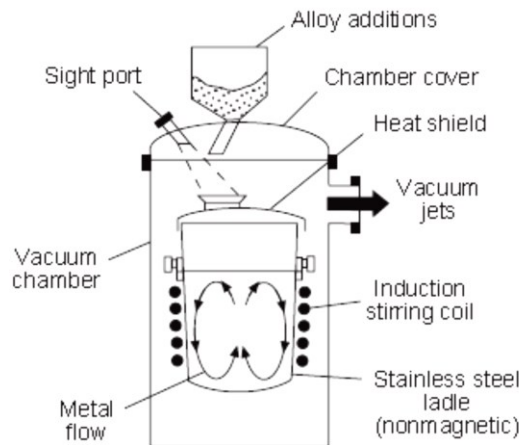


**Fig. 12**    Induction stirring of steel using a coil

Advantages of induction stirring:

- o *Steel flow direction control*
  - *Countercurrent stirring drawing-in slag into the steel volume during desulphurization*
  - *Concurrent stirring separating the steel surface from slag during degassing*
- o *Uniform stirring of the entire steel volume*

Disadvantages of induction stirring:

- o *High investment costs related to material of the non-magnetic ladle*

## 2.6   Requirements for blowing elements

Requirements for blowing elements can be summarized in the following items:

- o *Resistance to penetration of metal and slag to channels*
- o *Possibility to control the blowing intensity within a wide range*
- o *Long operating life*

- *Easy installation and replacement*
- *Resistance to break-through, equipment with a wear indication system*

Porous refractory materials have to be:

- *adequately porous*
- *at the same time solid and resistant to mechanical action of metal*
- *thermally stable at temperatures 1550 to 1650 °C*
- *chemically resistant to molten steel and slag*

Materials meeting the above mentioned requirements include corundum, spinet, corundum mullite, magnesite and zirconium-silicate.

## Σ Summary of terms of this chapter (subchapters)

- Mentioned in the part "Subchapters"

## ? Questions to the topic

Questions to this topic correspond to titles of the subchapters in the part "Subchapters"

# 3. VACUUM REFINING OF STEEL

**Subchapters:**

✓ Physical-chemical basics of processes occurring during steel vacuum processing

✓ Thermodynamic conditions of nucleation of gas bubbles in vacuum

✓ Technology of steel refining in vacuum

✓ Vacuum degassing of steel in a ladle

✓ Vacuum degassing of steel in a stream

✓ Vacuum degassing of steel in a lift method

✓ Vacuum degassing of steel in a recirculating method

**Time needed for the study:** individual

**Objective:** After studying this chapter a student will be able to:

- *Describe theoretical foundations of processes occurring in steel vacuum processing*
- *Characterize the technology of steel refining in vacuum*
- *Define basic methods and equipment for vacuum degassing of steel*

**Lecture**

## 3.1 Principle of vacuum processing of steel

At present, ladle vacuum refining of steel is the most significant way to enhance quality of manufactured steels. Ladle vacuum processing of steel enables to perform a substantial part of melt completing outside a production furnace. Particularly for liquid steel, it allows

- o *Reduction of contents of hydrogen and nitrogen*
- o *Deep decarburization of steel*
- o *Deoxidation of steel using VCD*
- o *Additional alloying of steel to a required grade*
- o *Modification of non-metallic inclusions in steel*

## 3.2 Physical-chemical basics of processes occurring during steel vacuum processing

Favourable effects of steel vacuum processing consist above all in reduction of contents of gases dissolved in steel and in affecting the carbon reaction process, the product of which is a gaseous phase - carbon monoxide. The process of steel vacuum degassing occurs through two mechanisms:

o *Formation of gaseous bubbles in molten metal, their growth and precipitation from the melt volume. In a case of casting stream degassing, the steel stream disintegrates to individual droplets; in a case of ladle degassing, vacuum chamber etc., this process results in boil of the bath. For this steel degassing method, the carbon reaction has a decisive importance.*

o *Metal degassing through diffusion of dissolved gas atoms to the melt surface and their transfer into the outer atmosphere. In a case of casting stream degassing, there is a diffusion to the surface of droplets of the disintegrated casting stream; in a case of degassing through the bath surface, there is a diffusion of gases to this surface, or to the surface of CO bubbles originated as a result of the carbon reaction occurring simultaneously or to the surface of bubbles of argon blown into the melt. This form of degassing is typical for reduction of contents of hydrogen and nitrogen in molten metal.*

Possibilities of reducing the contents of hydrogen, oxygen and carbon in steel in a ladle are depicted schematically in **Fig. 13**.
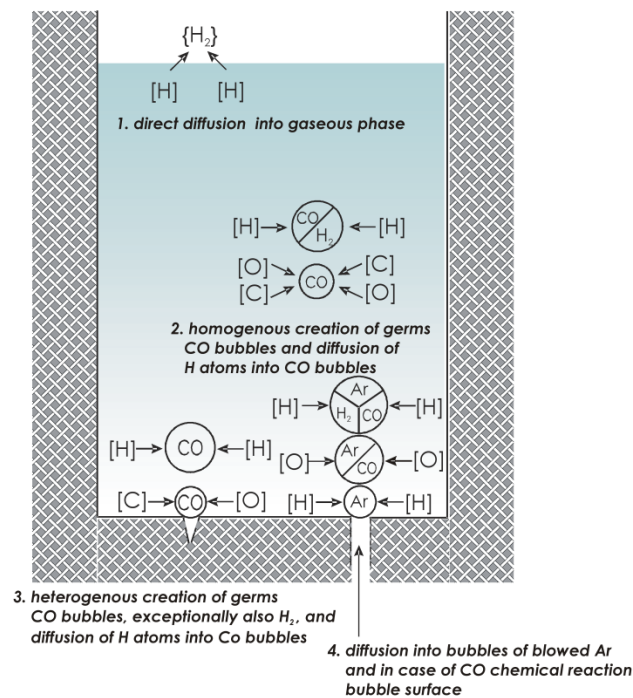


**Fig. 13**   Possibilities of reduction of oxygen, carbon and hydrogen contents in a ladle

## 3.3   Thermodynamic conditions of nucleation of gas bubbles in vacuum

The total pressure $P$ in a bubble of gas, which occurs under the metal surface, equals the sum of three pressures in every moment: external pressure above the metal surface $p_v$, ferrostatic pressure of metal $p_f$ and capillary pressure $p_\sigma$. The ferrostatic pressure is a function of a distance of the bubble from the metal surface h and metal density $\rho$.

$$p_f = h \cdot \rho \cdot g, \quad Pa \tag{40}$$

The capillary pressure depends on metal surface tension $\sigma$ and bubble radius $r$.

$$p_\sigma = \frac{2\sigma}{r}, \quad Pa \tag{41}$$

Then the following applies for the pressure in the bubble

$$P = p_v + h \cdot \varsigma \cdot g + \frac{2\sigma}{r}, \quad Pa \tag{42}$$

The total pressure $P$ increases dramatically along with the bath depth becoming deeper and the bubble radius becoming smaller, as depicted in the **Fig. 14** below.
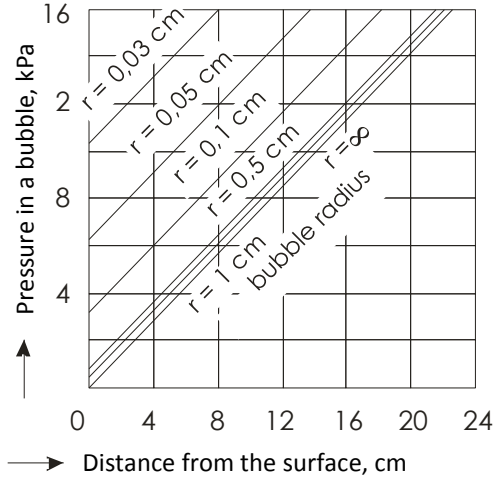


**Fig. 14** Relation of pressure in a bubble to a distance of the bubble from the bath surface and the bubble radius (for $p_v = 0$)

A thermodynamic condition for spontaneous formation of a bubble of hydrogen, nitrogen or carbon monoxide in a liquid metal is such a content of [H], [N] or [C]. [O] in metal, when the respective equilibrium pressures $p_{H_2}$, $p_{N_2}$ or $p_{CO}$ are equal to pressure $P$ at minimum. Then, in accordance with relations (6) and (32), applies

$$p_{(CO,H_2,N_2)} \geq P \tag{43}$$

$$p_{H_2} = \frac{[H]^2}{K_H^2} \cdot f_H^2 \tag{44}$$

$$p_{CO} = K_C \cdot f_C \cdot f_O \cdot [C] \cdot [O] \tag{45}$$

where  $p_{(CO,H_2,N_2)}$  is  equilibrium pressure of hydrogen $p_{H_2}$ or nitrogen $p_{H_2}$ calculated using the Sievert's law, or pressure of carbon monoxide corresponding to equation (45).

Then, with regard to equations (42) and (43), the condition of gaseous bubble nucleation can be written in a form

$$p \geq p_v + h \cdot \varsigma \cdot g + \frac{2\sigma}{r_k} \tag{46}$$

where  $r_k$  is  critical radius of the bubble nucleus, m

The following relation implies from equation (46) for the critical size of a gas bubble nucleus

$$r_k \geq \frac{2\sigma}{p - p_v - h \cdot \varsigma \cdot g} \tag{47}$$

At a defined surface tension of metal, the critical radius of the bubble decreases with an increasing content of hydrogen, nitrogen, carbon and oxygen in metal and corresponding pressure p and decreasing external and ferrostatic pressure. Bubble nuclei of radii $r \geq r_k$ are able of independent existence and further growth, bubbles of $r < r_k$ are dissolved in metal, because considering equations (42) and (46), for $r < rk$ applies $P > p$ and vice versa. For critical radius $r_k$ to have a positive value, equation (47) must have a positive denominator, and then

$$p > p_v + h \cdot \varsigma \cdot g \tag{48}$$

A maximal distance from the bath surface in which bubble nuclei of hydrogen, nitrogen or carbon monoxide can still originate can be calculated from inequality (48).

$$h < \frac{p - p_v}{\varsigma \cdot g} \tag{49}$$

If equilibrium pressures CO, $H_2$ or $N_2$, which relate to their actual contents in steel, are substituted into equation (49), then high probability of CO bubbles nucleation in vacuum even at the atmospheric pressure can be calculated. Probability of nucleation of $H_2$ bubbles and especially $N_2$ bubbles is negligible. It is evident that bubble nuclei near the metal surface are easiest to nucleate, namely within a distance from the surface equal to a bubble radius. On condition ($h = r$), equation (42) can be written in a form

$$P = p_v + r \cdot \varsigma \cdot g + \frac{2\sigma}{r} \tag{50}$$

A curve in **Fig. 15** below is a graphical depiction of the relation of pressure in a bubble to its size near the bath surface according to equation (50).
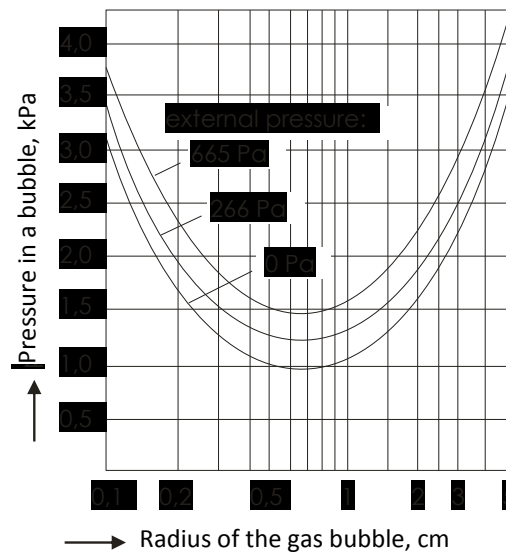


**Fig. 15** Relation of pressure in a bubble near the bath surface to its radius

The curve course implies that in bubbles with a larger as well as less radius than the critical radius $r_k$ the pressure is higher than minimum $P_{min}$. The critical size of the bubble radius near the metal surface, which corresponds to the minimum pressure in the bubble, can be determined from the condition where the first derivation of equation (50) according to $r$ equals zero.

$$\frac{dP}{dr} = \varsigma \cdot g - \frac{2\sigma}{r_k^2} = 0 \qquad (51)$$

This results in a relation for the critical radius of the nucleus

$$r_k = \sqrt{\frac{2\sigma}{\varsigma \cdot g}} \qquad (52)$$

For $\sigma = 1.5$ Nm$^{-1}$, $\varsigma = 7000$ kg.m$^{-3}$, $g = 9.81$ m.s$^{-2}$ applies $r_k = 6.6.10^{-3}$ m

By substituting a relation for $r_k$ into equation (47), an expression for the minimum pressure in the bubble of radius $r_k$ can be derived

$$P_{min} = p_v + 2\sqrt{2\sigma \cdot \varsigma \cdot g} \qquad (53)$$

For $p_v = 0$ Pa applies $P_{min} = 907.8$ Pa $\qquad (54)$

Then a bubble of 6.6 mm radius with the lowest pressure $P = p_v + 907.8$ Pa is the most probable one to nucleate near the bath surface.

## 3.4   Technology of steel refining in vacuum

Reduction of contents of hydrogen and nitrogen during steel vacuum degassing in a ladle is caused particularly by separation of these gases from the bath surface and partially also by their diffusion to gas bubbles of blown argon or carbon monoxide bubbles near the metal surface. The oxygen, or carbon, content decrease is caused both by CO bubbles nucleation in pores of ladle lining as well as on the surface of existing non-metallic inclusions and by transfer of CO into the gaseous phase above the bath surface or to bubbles of blown argon.

Basic methods of steel refining in vacuum cover:

   o   *Steel vacuum refining in a melting furnace (EAF, induction furnace)*
   o   *Steel vacuum refining in a ladle placed in a caisson*
   o   *Steel stream vacuum refining during pouring from a ladle into a ladle in a caisson or during pouring of steel into a mould (in a caisson)*
   o   *Steel vacuum refining in a chamber*
   o   *A lift method DH (Dortmund-Hüttenunion)*
   o   *A circulation method RH (Ruhrstahl-Heraeus)*

### 3.4.1   Vacuum degassing of steel in ladle – VD process

The operating simplicity is an advantage of this method. The basic equipment for steel degassing in ladle comprises an underpressure chamber and an exhaustion system. The underpressure chamber (caisson) consists of a cylindrical housing with a bottom and a lid, see **Fig. 16**. There are holes in the lid to monitor a metal surface during vacuum processing and sometimes there are also connections for feeders of ferroalloys. The exhausting system used for pressure reduction in the underpressure chamber incorporates the following main parts: a vacuum pump, cooling and cleaning equipment, connecting pipeline, auxiliary equipment and measuring instruments. Vacuum pumps are the most important parts of the exhaustion equipment. The most frequently used ones are steam-jet ejector pumps. Ladle vacuum processing is accompanied by intensive boil of steel, therefore the pressure in the chamber

must be reduced gradually. The total time of vacuum processing is typically from 10 to 15 minutes. Steel for ladle vacuum processing must be overheated. A value of this overheating depends above all on the melt weight, chemical composition of the vacuum processed steel, vacuum processing time, in a case of deoxidation and alloying of steel in a ladle also on the amount of added alloying additives.

The molten steel motion intensity can be enhanced using argon fed usually through a permeable block placed in a bottom of the ladle. The steel motion intensity in the ladle can be enhanced also using induction stirring.



Legend:  1 – vacuum system lid
2 – thermal shield
3 – refinement ladle
4 – vacuum caisson
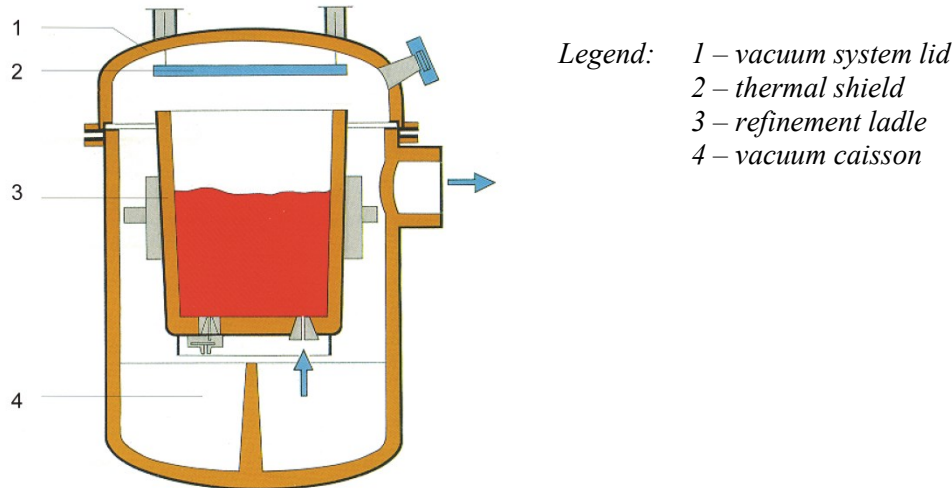
**Fig. 16**  Vacuum degassing of steel in a ladle

### 3.4.2  Vacuum degassing of steel in stream

A method of stream vacuum processing of steel is advantageous above all for casting of ingots for forging. During steel degassing in stream either a mould or a casting ladle is placed in a caisson.

A metal stream becomes cone-shaped as soon as it penetrates the vacuumed space; the cone consists of a large number of droplets. Such a large enlargement of a surface area of the vacuum processed metal allows effective degassing, while intensifying a process of surface reactions at the same time. A cause of the casting stream splashing to droplets is nucleation of CO bubbles immediately after the steel penetration into vacuum. A probability of nucleation of CO bubbles increases markedly with regard to a zero value of the ferrostatic pressure after the steel stream penetration into vacuum.

A critical radius of a bubble nucleus $r_k$ becomes substantially lower for the defined $p_{co}$ according to equation (54), because h = 0 at steel penetrating into the vacuum caisson, thus $p_f = h \cdot g \cdot \varsigma = 0$.

$$r_k = \frac{2\sigma}{p_{CO} - p_v} \tag{54}$$

If vacuum processed steel is cast into a ladle, a degree of steel degassing is still increased as a result of degassing through the bath surface and into argon bubbles. When casting the vacuum processed metal directly into a mould, secondary degassing of steel is substantially lower. It is limited both by a small surface area of the melt in the mould and by a cooling effect of the mould walls.

The equipment for steel vacuum processing in a stream is basically in principle the same as the equipment for degassing in a ladle, as shown in **Fig. 17** and **Fig. 18**.



**Fig. 17**    Stream    degassing    of    steel  **Fig. 18**    Stream    degassing    of    steel
(a ladle – ladle system)                (a ladle – mould system)

In vacuum processing of steel in stream, the ladle – ladle method, a casting ladle is placed into a caisson on a lid of which a tundish is situated and a casting hole of which is sealed with an aluminium disc. After placing the lid and the tundish on their positions, air is pumped-out off the caisson down to the working pressure value and the equipment is ready for casting.
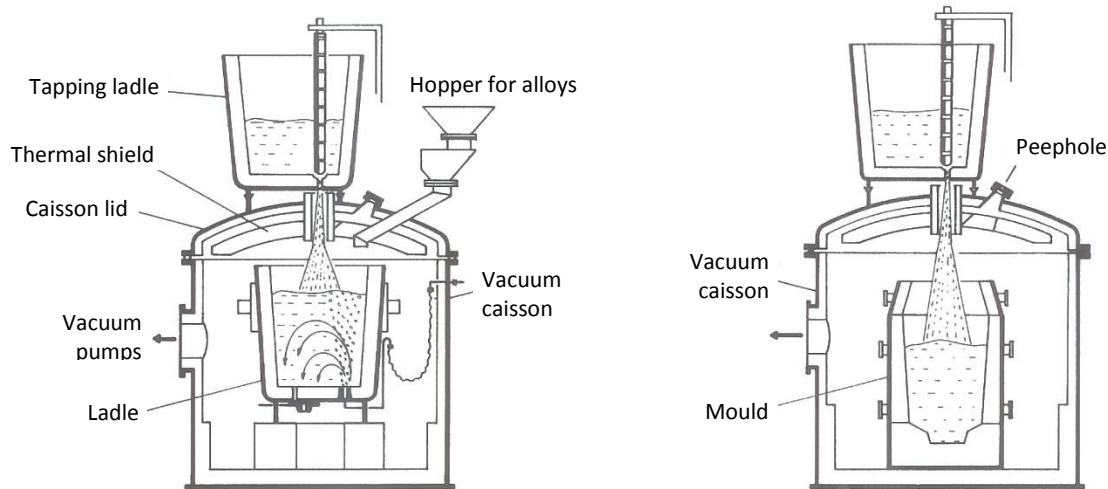
Follow-up, steel is poured from the tapping ladle into the tundish and after reaching a defined height its opening gets opened and the liquid steel stream melts-through the aluminium plug (disc) in a discharge nozzle and flows into the casting ladle placed in the caisson. Velocity of steel flowing from the tapping ladle into the tundish has to be controlled, so that the steel level in the tundish can be high enough all the time, i.e. about two thirds of the tundish height. This requirement is reasoned by the fact that during casting the space inside the caisson is only separated from the outer atmosphere by a layer of the liquid steel in the tundish. As secondary oxidation as well as re-gassing of steel often occurs in the tundish ("pony" ladle), the tundish is often left out in the ladle – ladle system, or the ladle – mould system.

In order to avoid a possibility of an explosion reaction of residual CO and $H_2$ with atmospheric oxygen it is recommended to rinse-out the caisson by an inert gas ($N_2$, Ar) prior to unmaking the underpressure. In the ladle – mould system the procedure is similar. As soon as the steel level reaches a head extension, vacuum is interrupted and during casting of the ingot head part the air is inlet into the caisson, so that the casting velocity slows down. After casting is finished and underpressure is unmade, the mould with the ingot is left inside the caisson until the steel is completely solidified, which is often considered an essential disadvantage of this method.

### 3.4.3   Vacuum degassing of steel in a lift method – DH process

 In the lift method vacuum degassing of steel, often called according to the place of its origin as DH process (Dortmund – Hüttenunion), liquid steel is sucked from the ladle into a special vacuum chamber, see **Fig. 19**.
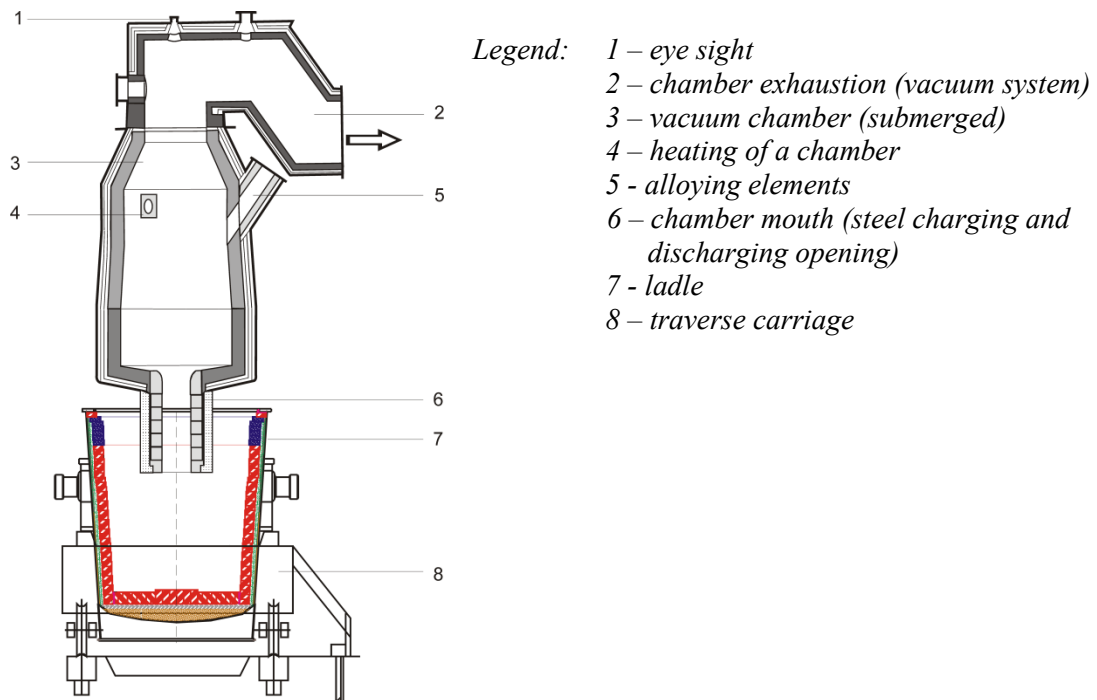
*Legend:*     *1 – eye sight*
                  *2 – chamber exhaustion (vacuum system)*
                  *3 – vacuum chamber (submerged)*
                  *4 – heating of a chamber*
                  *5 - alloying elements*
                  *6 – chamber mouth (steel charging and*
                      *discharging opening)*
                  *7 - ladle*
                  *8 – traverse carriage*

**Fig. 19**     Vacuum degassing of steel by DH process

As a result of a difference in pressure between the vacuum chamber and the outer atmosphere, a column of liquid steel reaching a height around 150 cm is formed in the suction mouth. As a result of the outer pressure a part of the liquid steel inlets to the vacuum chamber, where the very degassing process takes place. After degassing the sucked amount of steel, the vacuum chamber is lifted up (or the ladle lowered down) and the degassed steel flows over back to the ladle.

For complete degassing of steel the content of the ladle must go through the submerged mouth at least three to five times (circulation rate), whereas the total time of vacuuming typically ranges between 15 to 20 minutes. The equipment, aside from the vacuum chamber, incorporates steam-jet ejector pumps, cooling and cleaning system, connecting pipeline, additional mechanisms including lifting, as well as measuring and regulation instruments.

An electrical resistance heating system of the input 300 to 600 kW is usually used for preheating of the chamber prior to vacuum processing. Temperature in the chamber is maintained above 1550 °C. Close attention needs to be paid to the refractory lining of the chamber, especially of the mouth, which is during vacuum processing subjected to heavy wear. The lining temperature should be maintained as high as possible, so that steel cannot solidify on the chamber walls during vacuum processing.

A degree of steel degassing by the lift method is influenced markedly by a number of lifts, which is defined by a ratio of the vacuuming time to the dwelling time of one batch in the chamber. A ratio of the batch weight to the total weight of steel in the ladle has a favourable influence.

Hydrogen content after n-number of lifts can be determined using the equation

$$[H]_n = ([H]_o - [H]_r)\left(1 - K\frac{m}{M}\right)^n + [H]_r \tag{55}$$

where   $[H]_n$       is    hydrogen content after n-number of lifts

$[H]_o$ -$[H]_r$   -   initial equilibrium content of hydrogen in steel and hydrogen content calculated from the Sieverts' law

$m$   -   amount of steel sucked into the chamber at one lift

$n$   -   number of lifts

$M$   -   melt weight

$$K = \frac{[H]_z - [H]_{z+1}}{[H]_z - [H]_r}$$   -   hydrogen proportion removed in one lift from a theoretically possible decrease in hydrogen content

Steel degassing by the DH process not only enables to reduce contents of gases, but also a content of carbon, to homogenize the melt, including deoxidation and alloying at underpressure. Bins fitted with vibration feeders, weighing system and particular closing mechanisms and slipping systems serve for adding alloying elements into the chamber.

### 3.4.4 Vacuum degassing of steel in a recirculating method – RH process

In the lift method vacuum degassing of steel called as RH process (Ruhrstahl − Heraeus), liquid steel is degassed continuously in a vacuum submerged chamber into which steel is transported through a suction tube, see **Fig. 20**.



Legend:    1 – industrial video-camera
2 – vacuum system
3 – RH chamber
4 – chamber temperature raising
5 - argon inlet
6 – submerged inlet tube
7 – blocking vacuum system for feeding of alloying elements
8 – alloying elements filling system
9 – submerged discharge tube
10 – refinement ladle
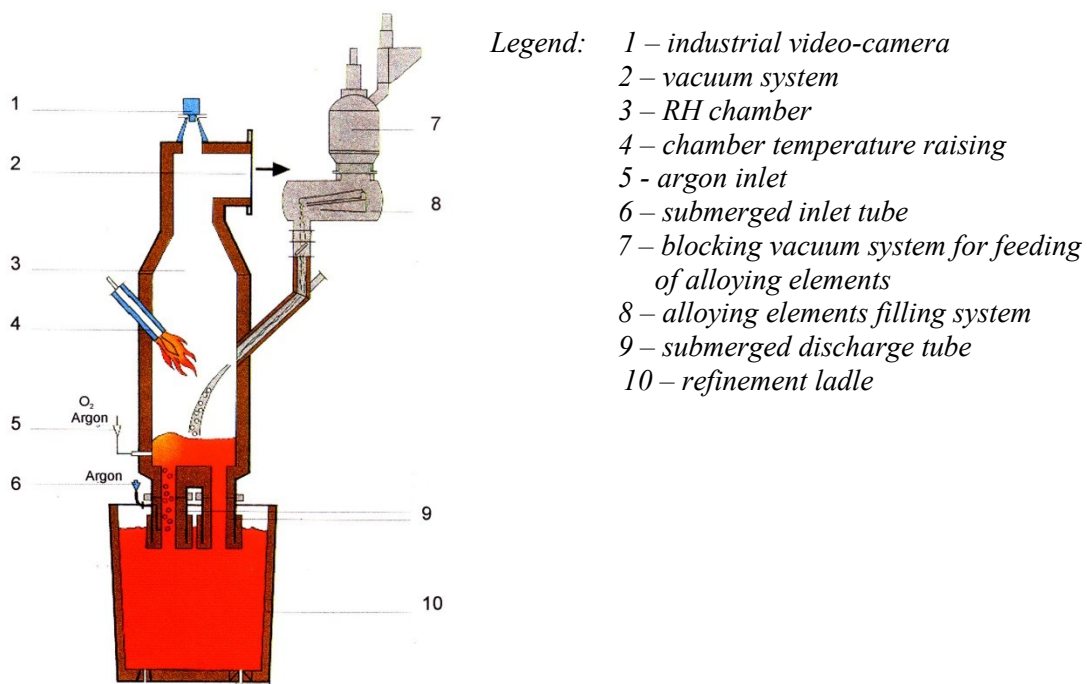
**Fig. 20**     Vacuum degassing of steel by RH process

Feeding of inert gas into a sucking mouth results in origination of a mixture of metal and gas with a lower specific weight and this goes up to the vacuum chamber. Inert gas blowing keeps steel in a turbulent motion all the time. Gases contained in steel are released from individual droplets as well as from the affluxed metal level surface. The process of sucking of steel and its discharge from the vacuum chamber is continuous.  The degassed steel flows-off through the discharge tube back to the ladle. If reduction of hydrogen content in steel by fifty and more percent has to be achieved, then the ladle content must go through the vacuum chamber three to five times.

Before submerging the suction and discharge mouth into the ladle, both openings must be protected with a plate to avoid slag penetrating into the vacuum chamber. Protective covers are melted after submerging into steel and allow the steel ascending up to the chamber. The course of thermal losses is similar to DH process. The vacuum chamber has an independent heating system, typically of a resistance-type.

## Σ Summary of terms of this chapter (subchapters)

o  Mentioned in the part "Subchapters"

## ？ Questions to the topic

o  Questions to this topic correspond to titles of the subchapters in the part "Subchapters"

# 4. STAINLESS STEELS

**Subchapters:**

✓ Principle of corrosion resistance of corrosion resistant steels and alloys

✓ Influence of alloy elements on corrosion properties of alloyed steels

✓ Classification of stainless steels

✓ Decarburization of metal bath with an increased content of chromium

✓ Technological variants of stainless steel making

**Time needed for the study:** individual

**Objective:** After studying this chapter a student will be able to:

- *Define characteristics of corrosion resistance of corrosion resistant steels and alloys*
- *Specify classification of stainless steels*
- *Describe a principle of decarburization of metal bath with an increased content of chromium*
- *Define technological variants of production of stainless steels*

**Lecture**

## 4.1 Principle of corrosion resistance of corrosion resistant steels and alloys

Stainless steels feature enhanced corrosion resistance at standard and elevated temperatures. Of course, these steels also corrode gradually. However, the corrosion process is slow.

If at the corrosion process a protective layer forms on a metal surface, we talk about passivity. A passive layer can be formed by oxides e.g. of iron in nitric acid, on anticorrosion steels by oxides of chromium, titanium etc.

If the ability of passivation of the anticorrosion steel surface at a contact with an oxidation atmosphere has to be ensured, a minimum of 11.7 % of chromium has to be dissolved in the solid solution. As a part of chromium is bonded to carbon as carbide $FeCr_{23}C_6$, the minimum content of chromium in steel has to be % Cr = 11.74 + 14.54 (% C).

In austenitic steels, carbides of chromium are segregated on grain boundaries during slow cooling after casting or forming. In spite of the fact that the diffusion rate of chromium is low, the chromium content may locally drop below 12 %. The steel loses its passivation ability and is subject to intercrystalline corrosion. For steel to be completely resistant against the intercrystalline corrosion, the carbon content must be as low as possible, below 0.02 to 0.03 %.

## 4.2   Influence of alloy elements on corrosion properties of alloyed steels

Effects of particular elements on corrosion properties of alloyed steels can be summarized as follows:

- o *Chromium is a basic element carrying passivability into stainless steels. Other alloying elements can only influence this process; however, they cannot be carriers themselves.*
- o *Nickel takes its part in stabilization of the austenitic structure of stainless steels, by which optimal properties for steel processing are achieved. From the corrosion point of view, nickel contributes to improvement of passivability of stainless steels, in particular in reducing aqueous environments; its influence is highly favourable above all in strong inorganic acids.*
- o *Molybdenum in a combination with chromium has a highly favourable effect on improvement of protective properties of a passivating layer, especially in environments containing chloride ions.*
- o *Manganese in contents from 5 to 10 wt. % has a similar influence on structure properties as nickel; however, these contents are used to achieve different properties than corrosion resistance in steel. Its presence in common contents (i.e. to 2 wt. %) can present itself negatively after the interaction with sulphur, resulting in formation of sulphide $Cr_xMn_{1-X}S$.*
- o *Carbon in most cases has a negative influence on corrosion resistance as a result of a possible bond with chromium. If it is dissolved in a matrix, a negative influence on corrosion resistance is not usually observed.*
- o *Nitrogen is a highly effective austenite-forming element and in many types of austenitic and two-phase steels it is alloyed to high contents as a highly effective substitute for nickel, in particular in the second generation steels, super-austenitic and super-duplex steels, alloyed significantly with molybdenum.*

## 4.3   Classification of stainless steels

Stainless steels are classified according to their structure characteristics. This way the basic types of formed stainless steels can be distinguished – martensitic, ferritic, austenitic and two-phase.

❑   **Ferritic stainless steels**

The simplest and oldest type of stainless steel, in which "corrosion-resistant properties" have been found, are Fe-Cr alloys. The structure stability of the ferritic matrix grows along with the chromium content in steel. Modern types of ferritic stainless steels usually contain 11 up to 29 wt. % of chromium, to 4 wt. % of molybdenum and to 2 wt. % of nickel.

However, wider application of ferritic stainless steels is impeded by worse technological properties (compared to austenitic steels) – low formability and weldability and low ductility, therefore their product line is limited to products with a small cross section, strips, sheets and plates, tubes and pipes, tube plates and tube sheets.

❑   **Austenitic stainless steels**

Highly applicable mechanical and processable properties of austenitic steels have made them an almost universal structural material for construction of many types of equipment where

high corrosion resistance is required. However, they are applicable for a limited atmosphere type only. Pursuant to some statistical data, in 60 - 70 % these steels are damaged by corrosion cracking and slot corrosion.

Development of new austenitic steels makes an effort to eliminate these disadvantages and can be characterized as follows:

- o *Improvement of resistance of austenitic stainless steels to corrosion cracking and local types of corrosion, increasing Cr, Ni, Mo contents, reducing C, P, S contents, additional alloying of steels by N, Cu*

- o *Enhancement of strength properties at simultaneous improvement of corrosion resistance, alloying of steels particularly by nitrogen, possibly by a combination of manganese (up to 8 %), nitrogen and niobium.*

❑ **Two-phase stainless steels**

To reduce disadvantages and to use advantages of classic ferritic and austenitic stainless steels, two-phase stainless steels are used, having higher formability and weldability than ferritic steels and higher resistance to corrosion cracking under stress than austenitic steels (however, lower than ferritic steels). Two-phase stainless steels are alloys with iron content about 60 – 70 wt. %, alloyed with chromium from 17 up to 30 wt.%, nickel 3 up to 13 wt.%, and further molybdenum and nitrogen.

The first generation two-phase steels have very high resistance against spot and slot corrosion due to high contents of chromium and molybdenum. However, welding of these steels results in disturbance of an optimal ferritic to austenitic phase ratio (50 % : 50 %) and thus in degradation of both mechanical properties and corrosion resistance (application of these steels is possible either without welding or with a need of heat treatment after welding).

When using nitrogen as a very cheap austenite-forming element as a substitution for nickel, it was found out that aside from a positive influence on corrosion resistance and improvement of mechanical values of steels, nitrogen slows down transformation of austenite to ferrite at high temperatures and after high-temperature cycles to which steel is subjected during forming or welding the optimal ratio of ferritic to austenitic phase in metal is not disturbed. This type of two-phase stainless steels is called the 2$^{nd}$ generation of two-phase stainless steels.

At present, four basic types of stainless steels are used:

- o *two-phase steels with a low Mo content of 23Cr-4Ni-0.1N type*
- o *22Cr-5Ni-3Mo-0.17N type steels*
- o *25Cr type steels with various contents of Mo, N, Cu, W*
- o *super-duplex stainless steels of 25Cr-7Ni-3.7Mo-0.27N type*

Applicability of two-phase steels is possible in atmospheres at temperatures 220 up to 520 K (-50 to 250°C), where the construction material has to feature a combination of high corrosion resistance and mechanical strength.

## 4.4 Decarburization of metal bath with an increased content of chromium

Stainless steels with high chromium content and low carbon content can be manufactured by ladle oxidation processes under decreased pressure, or more precisely decreased partial

pressure of CO. The most widely used manufacturing procedures for these steels can be divided to two groups:

o *Technologies based on oxidation – vacuum processing (VOD). In these procedures steel from EAF is processed by oxygen blowing into steel in a ladle placed inside a vacuum caisson and it is stirred by an inert gas simultaneously.*

o *The second group covers procedures, where steel molten in AEF is processed in a special converter at the atmospheric pressure. The main representative of this technology is AOD process, where a mixture of oxygen and argon with a variable composition is blown into the converter. A similar process CLU consists in blowing a mixture of oxygen and water vapour into steel. In both the cases the partial pressure of CO in gas bubbles is reduced, moreover, the water vapour acts as a cooling medium.*

Thermodynamic conditions of decarburization of iron melt with an increased chromium content consist in solving the equilibrium of $Fe_{(l)}$-[Cr]-[C]-[O]-$(Cr_mO_n)$-$p_{CO}$ system.

Chipman expressed processes going during decarburization of a melt with a content of carbon and more than 9 % of chromium with the aid of reactions

$$1/4 \ (Cr_2O_3) = 3/4 \ [Cr] + [O] \tag{56}$$

$$[Cr] + [O] = CO_{(g)} \tag{57}$$

$$1/4 \ (Cr_2O_3) + [C] = 3/4 \ [Cr] + CO_{(g)} \tag{58}$$

The temperature dependence of equilibrium constants of reactions (56) to (58) are described in equations

$$log \ K_1 = \frac{12688}{T} + 5,57 \tag{59}$$

$$log \ K_2 = \frac{1138}{T} + 2,07 \tag{60}$$

$$log \ K_3 = \frac{11520}{T} + 7,64 \tag{61}$$

A relation between the equilibrium carbon content and chromium content in a melt can be derived from an equation for the equilibrium constant of reaction (58).

$$[C] = \frac{[Cr]^{3/4} \cdot f_{Cr}^{3/4} \cdot p_{CO}}{K_3 \cdot f_C \cdot a_{(Cr_2O_3)}^{1/4}} \tag{62}$$

This dependence is graphically plotted in Hilty's diagrams, see **Fig. 21** and **Fig. 22**.

Dependencies in **Fig. 21** and **Fig. 22** show that the increased temperature and decreased partial pressure of CO supports carbon oxidation and at the same time reduces chromium oxidation. Especially the decreased pressure has a noticeable influence on a reduction of the equilibrium content of carbon, see **Fig. 21**. However, to achieve the carbon content below 100 ppm in real operating conditions is limited by kinetic parameters, as this is a subcritical carbon content, when further oxygen supply would increase chromium loss. The critical carbon content in steel decreases, while the bath temperature increases, pressure and chromium content decreases and bath stirring intensity increases. Achieving the critical carbon content shows

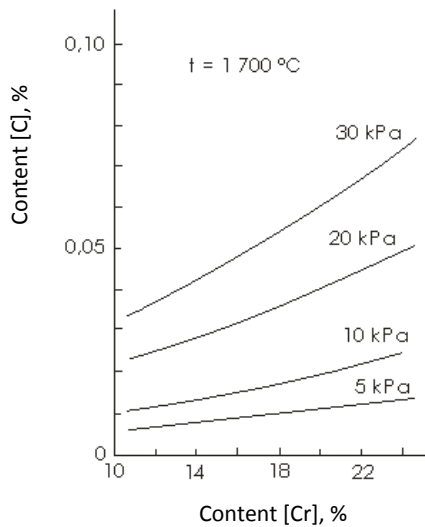itself in flue gas composition, in which, aside from carbon monoxide, also carbon dioxide and oxygen appear.



**Fig. 21** Influence of pressure on the equilibrium between carbon and chromium content at vacuum oxygen decarburization
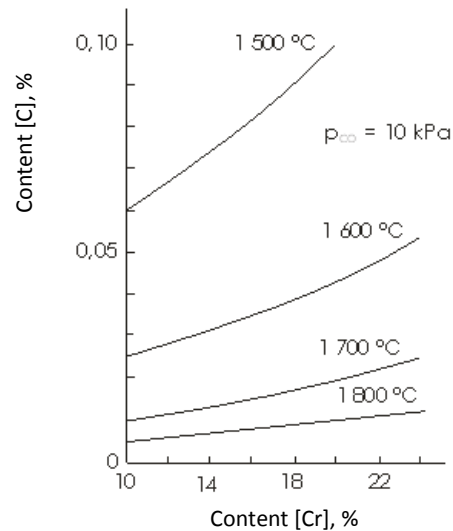
**Fig. 22** Influence of temperature on the equilibrium between carbon and chromium content at vacuum oxygen decarburization

From the point of view of chemical composition, elements increasing carbon activity and decreasing chromium activity influence the molten metal decarburization positively. However, the chromium content itself decreases the carbon activity in stainless steels, thus impairing the bath decarburization. This can be seen in **Tab. 2**.

**Tab. 2** Influence of selected elements on the chromium and carbon activity in anticorrosion steel

| X | C | Mo | Cr | Ni | Si | Mn |
|---|---|---|---|---|---|---|
| $e_{Cr}^{x}.100$ | -11.0 | 0.4 | -0.13 | -0.1 | -1.5 | 0.39 |
| $e_{C}^{x}.100$ | 14.0 | -1.54 | -2.13 | 0.23 | -1.5 | -1.29 |

## 4.5   Technological variants of stainless steel making

Variants used for the manufacture of stainless steels can be divided according to charged materials. Majority of stainless steels are even today manufactured on the basis of alloyed steel scrap. Mainly EAFs are used for melting.

### 4.5.1   EAF → VOD → steel casting system

The system consists in melting of an alloyed charge including dephosphorization and subsequent deep oxygen decarburization in a ladle placed inside a vacuum caisson, see **Fig. 23**. Today the historical system of production of stainless steels is used in small electro-steel works and foundry plants. This is an only method which was and still is used in the Czech Republic. It is applicable for the manufacture of even the most demanding steel grades; however, as to costs it is not able to compete with converter processes of stainless steel making, and this also for the fact that small volumes of the manufactured steel are usually cast into ingots.
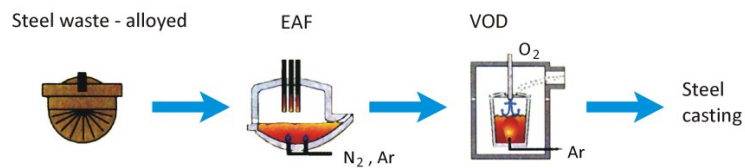
**Fig. 23**    Manufacture of stainless steel by EAF → VOD system

### 4.5.2   EAF → converter → ladle → steel casting system

So far, the largest proportion of corrosion resistant steels have been made by a system of melting the alloyed steel scrap in EAF with following refinement of the molten metal in an atmospheric side-blown AOD converter, see **Fig. 24**. This converter, where vacuum needed for deep decarburization is simulated by Ar-$O_2$ gaseous mixture blown into steel from the side, features high economy of production, high utilization of chromium (~ 98 %) as in VOD and, in addition, a possibility of steel desulphurisation. A disadvantage of this converter is high wear of lining around nozzles, which are only cooled by argon added to oxygen above all by technological reasons.
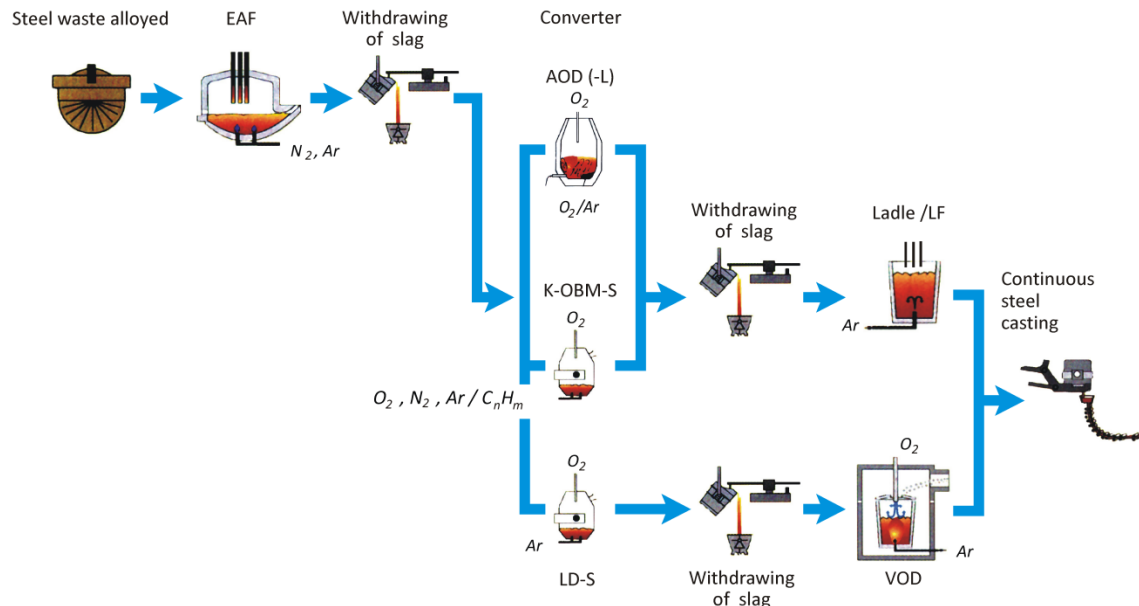


**Fig. 24**   Manufacture of stainless steel by EAF → converter → ladle system

AOD converter has been particularly in Japan steel plants intensified by oxygen blowing through the upper nozzle (AOD-L). For production of special steel grades – high chromium with a low content of carbon and nitrogen – this converter is combined with vacuum equipment (VOD, RH-O, RH-OB, KTB). One of AOD converter variants is CLU converter, into which a mixture oxygen – overheated water vapour is blown through nozzles in the bottom in order to cool the nozzle, to reduce the partial pressure of CO in bubbles and argon consumption.

A converter K-OBM-S (K-BOP) is a perspective substitute for AOD converter. This device is a variant of a bottom-blown converter OBM (Q-BOP). In contrast to AOD converter, it is equipped with double-wall nozzles located in the bottom of the converter. The inner nozzle is used for blowing $O_2$, Ar, $N_2$ into steel in any demanded ratio, while a protective (cooling) hydrocarbon gas (propane, natural gas etc.) is blown through the outer circular ring, see **Fig. 25**.

**Fig. 25** Tuyere of K-OBM-S and AOD converter

## Σ Summary of terms of this chapter (subchapters)

o Mentioned in the part "Subchapters"

## ? Questions to the topic

o Questions to this topic correspond to titles of the subchapters in the part "Subchapters"
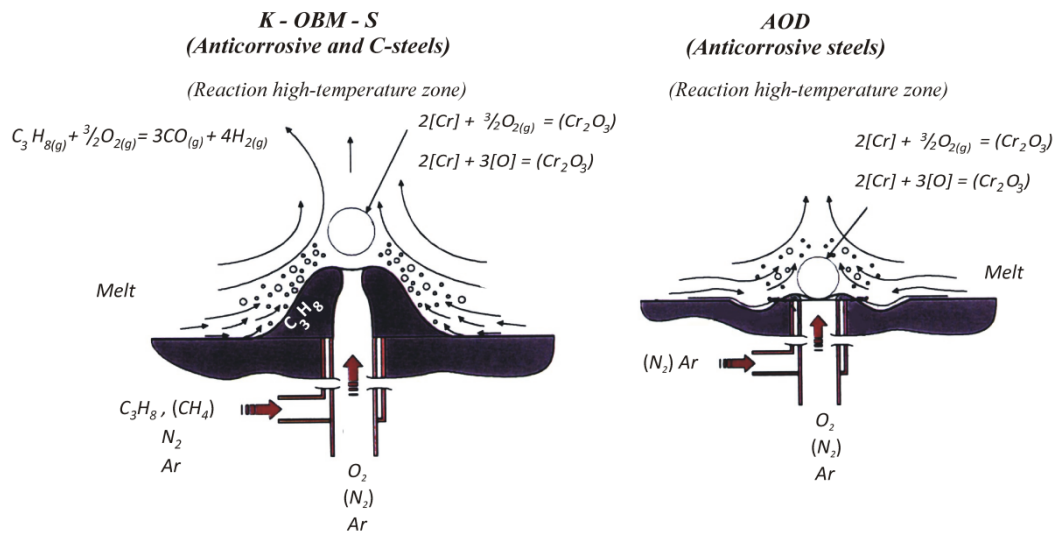
# 5. SYNTHETIC SLAGS

**Subchapters:**

✓ Synthetic slags and their importance for steel refining in ladle

✓ Desulphurization by molten ladle slag

✓ Thermodynamics of steel desulphurization by slag

✓ Thermodynamics of desulphurization at steel deoxidation

✓ Possibility of reduction of oxygen content in steel using molten refining slags

✓ Mechanism and kinetics of steel desulphurization by molten synthetic slag

✓ Possibility of reduction of a content of inclusions in steel by coagulation and coalescence

**Time needed for the study:** individual

**Objective:** After studying this chapter a student will be able to:

- *Characterize synthetic slags*
- *Describe a process of steel desulphurization by ladle slag*
- *Describe thermodynamics and kinetics of steel desulphurization*
- *Characterize a possibility to reduce a content of oxygen and a content of non-metallic inclusions using refining slags*

# Lecture

## 5.1 Synthetic slags and their importance for steel refining in ladle

The function of ladle slag is to increase cleanliness of molten steel, i.e. to absorb non-metallic inclusions, to absorb and bind chemically sulphur in steel, sometimes only to control sulphur content within a demanded range, to protect steel against atmosphere – hydrogen, nitrogen and oxygen and against heat losses, while having a minimal corrosive influence on the ladle lining.

Ladle slag is formed from steel deoxidation products, ladle lining corrosion products and deliberately added additives.

Furnace slag coming into a ladle at steel tapping is an undesirable component due to its high content of FeO. Additives intentionally added into slag ensure a required chemical composition of slag, its fluidity and ability to refine steel. These are mainly lime, calcium carbide, chamotte, wollastonite etc. and more and more often used synthetic slags. Synthetic slags usually contain $Al_2O_3$, CaO, MgO, $SiO_2$, while a minimum of iron oxides, MnO and sulphur. Synthetic slags are added to ladle slags in order to improve physical and chemical properties of ladle slags.

Properties of the refining slag, affected by the above mentioned requirements, include basicity, viscosity of slag, interphase tension between slag and inclusions, or between slag and lining – i.e. the ability of slag to wet inclusions, or the ladle lining. These properties are dependent on chemical composition of slag and its temperature. A speed of slag forming is of the same importance, this means how quickly it achieves required chemical composition and temperature; further, the ability to desulphurize the steel, to absorb inclusions etc. is important, too.

The synthetic slag affects properties of the ladle slag not only by its chemical composition, but, and this is important, also by phase composition and its granularity, this means by parameters taking part in the ladle slag formation speed. For example, a mixture of two high-melting-point oxides CaO ($t_{melt} \sim 2570$ °C) and $Al_2O_3$ ($t_{melt} \sim 2050$ °C) mixed in a mass ratio 1:1 dissolves more slowly in slag than their remolten phase mayenite $12CaO.7Al_2O_3$ with melting temperature of $\sim 1400$ °C.

Chemical and phase composition, a preparation method and granularity of manufactured synthetic slags are different. This relates to a purpose of a synthetic slag application, then to sources of raw materials from which the slag is made and production costs.

Slags with a constant chemical and phase composition are made by remelting processes. These slags are typically of low-melting temperature and easily and quickly assimilate into the ladle slag. However, high quality entails a relatively high price.

The second types of slags are sintered ones, this means only partly transformed into new phases with low liquidus temperatures. As to quality, these slags get near to remolten slags, but they are cheaper.

The third type of slags includes those only blended from original raw materials. These slags feature low price, but decreased homogeneity.

Homogeneity of mixed slags depends on granularity of particular components. Synthetic slags prepared from finely milled materials feature higher homogeneity.

When charged to a ladle, pulverized slags mostly transfer into fly ash; therefore original components are better to be pelletized by adding binding materials.

Synthetic slags charged into a ladle or ladle furnace at steel tapping usually have a main function to make formation of the molten ladle slag more faster. Alkaline ladle slags subsequently make the steel desulphurization process shorter and deeper.

On the contrary, a decrease in the ladle slag basicity and an increase in its viscosity (fluidity reduction) are required for refining of steel with controlled (i.e. increased) sulphur content. For example an addition of wollastonite, or the Slagmag slag, is advisable for this.

## 5.2   Steel desulphurization by molten ladle slag

Sulphur content in steel depends on the following factors during processing in secondary metallurgy equipment:

- o *Oxygen activity in steel, which is mostly determined by aluminium content in steel (an element with the highest affinity for oxygen)*
- o *Slag chemical composition, above all a content of CaO, $SiO_2$, but also $Al_2O_3$ and MgO and a slag weight*
- o *Initial content of sulphur in steel tapped from the primary aggregate (electric arc furnace etc.)*

o *Stirring intensity, so that an interphase interface steel – slag can be renewed and the system can get to equilibrium as close as possible*
o *Temperature*

The sulphur content control can be successfully performed by development of the oxygen activity in steel and by control of basicity and also fluidity of the slag, i.e. the control of chemical composition and temperature in the steel – slag system.

Steel and slag must be stirred intensively all the time, so that the interphase interface can be renewed and the system can get to the equilibrium as close as possible.

### 5.2.1 Thermodynamics of steel desulphurization by slag

As the main desulphurizing agent of ladle slags is calcium oxide, the steel desulphurization process can be described in a reaction:

$$(CaO) + [S] = (CaS) + [O] \tag{63}$$

The synthetic free enthalpy of CaO is more negative than the synthetic free enthalpy of CaS, thus desulphurization according to equation (63) can only occur on condition that the released oxygen is bonded to a stable compound and thus removed-off the reaction system.

From the equilibrium constant of reaction (63)

$$K_S = \frac{a_{[O]}}{a_{[S]}} \cdot \frac{a_{(CaS)}}{a_{(CaO)}} \tag{64}$$

the sulphur content can be expressed by a relation

$$[S] = \frac{1}{K_S} \cdot \frac{a_{[O]}}{f_{[S]}} \cdot \frac{a_{(CaS)}}{a_{(CaO)}} \tag{65}$$

Equation (65) implies that the achievable equilibrium content of sulphur is a function of the oxygen activity in steel, the activity of CaO and CaS in slag and temperature.

The temperature dependence of the equilibrium constant of reaction (63) is expressed by the equation

$$\log K_S = -\frac{4583}{T} + 1{,}05 \tag{66}$$

Within a temperature interval 1550 °C to 1600 °C, $K_S$ value is in a range from 0.0344 to 0.0400. Substituting these values to equation (65) results in the following relation for the equilibrium content of sulphur in steel within the temperature range from 1550 °C to 1600 °C

$$[S] = (29 \text{ to } 25) \quad a_{[O]} \quad \frac{a_{(CaS)}}{a_{(CaO)} \quad f_{[S]}} \tag{67}$$

Equation (67) implies that achieving of low contents of sulphur is only possible in conditions of deeply deoxidized steels at refining by slag with a high activity of calcium oxide, or through a low ratio of $a_{(CaS)} / a_{(CaO)}$.

If steel did not contain elements with a higher affinity for oxygen than iron, the oxygen content in steel is determined by FeO content in slag.

$$Fe_{(l)} + [O] = [FeO] \tag{68}$$

$$\log K_{FeO} = \frac{6320}{T} - 2{,}734 \tag{69}$$

The desulphurization process limited by FeO content in slag can be expressed by using equations (63) and (68).

$$Fe_{(l)} + [S] + (CaO) = (CaS) + (FeO) \tag{70}$$

The following equation expresses the equilibrium constant and its temperature dependence

$$\log K_S^{FeO} = \frac{1\,737}{T} - 1{,}684 \tag{71}$$

$$K_S^{FeO} = K_S \cdot K_{FeO} = \frac{a_{(CaS)} \cdot a_{(FeO)}}{[S] \cdot f_S \cdot a_{(CaO)}} \tag{72}$$

The achievable sulphur content is a function of FeO activity in slag, CaO and CaS activity in slag and temperature.

$$[S] = \frac{a_{(CaS)} \cdot a_{(FeO)}}{[S] \cdot f_S \cdot a_{(CaO)}} \tag{73}$$

Within a temperature interval 1550 °C to 1600 °C, $K_S^{FeO}$ value is in a range from 0.186 to 0.175.

Equation (73) can be then adapted to a form

$$[S] = (5{,}376 \text{ to } 5{,}714) \frac{a_{(CaS)}}{f_S} \frac{a_{(FeO)}}{a_{(CaO)}} \tag{74}$$

This equation implies that low sulphur contents in steel can be only achieved under the slag with a minimal content of FeO (max. 1 to 2 wt. %).

Another condition is a high activity of CaO (min. 45 to 55 wt. %) and low $a_{(CaS)}/a_{(CaO)}$ ratio, exactly like in equation (67). The high activity of CaO in slag requires also a low content of acidic oxide SiO$_2$, so that the slag basicity $B = (\% \, CaO) / (\% \, SiO_2)$ is 3.0 to 3.5 at minimum.

The desulphurizing ability of slag can be also described using the sulphur distribution coefficient between the slag and metal, while CaO activity can be substituted by a content of free CaO in the slag

$$L_S = \frac{(S)}{[S]} \sim K_S^{FeO} \frac{(CaO)_{free}}{a_{(FeO)}} \frac{f_S}{} \tag{75}$$

A content of free CaO equals a difference between the total content of CaO and the content of CaO bonded to acidic oxides.

$$(CaO)_{free} = (CaO) - \frac{112}{60}(SiO_2) + \dots \tag{76}$$

The content of $(CaO)_{free}$ in slag is reduced by acidic oxides, mostly $SiO_2$, which forms calcium silicates with CaO, from which dicalcium silicate $Ca_2SiO_4$ is the most stable one.

The influence of the content of free CaO and iron oxide on the sulphur distribution coefficient in aluminium-calcium slags is shown in **Fig. 26.**
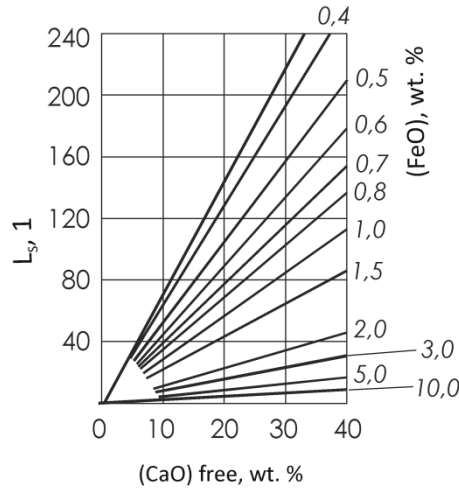


**Fig. 26**   Influence of the content of free CaO and iron oxide on the sulphur distribution coefficient in aluminium-calcium slags

The diagram in **Fig. 26** shows that the $L_S$ distribution coefficient increases noticeably along with the content of free CaO, only while FeO content in slag is low.

The achievable sulphur content at steel refining in ladle also depends on technological parameters, such as the slag weight and the initial sulphur content in steel.

From the substance balance of the process of steel desulphurization by slag and the sulphur distribution coefficient (75) a relation of initial sulphur content *[S]₀* and final sulphur content [S] can be derived

$$\left([S]_0 - [S]\right) = m\left[(S) - (S)_0\right] \tag{77}$$

where $m = \dfrac{m_S}{m_0}$ is slag mass to steel mass ratio

Equation (77) can be adapted

$$[S] = \frac{[S]_0 + m\,(S)_0}{1 + m\,L_S} \tag{78}$$

As the amount of the refining slag is limited (m ~ 0.01 to 0.03), the final sulphur content depends above all on its initial content and the distribution coefficient $L_S$.

## 5.2.2   Thermodynamics of desulphurization at steel deoxidation

Steel desulphurized in ladle by slag has a reduced content of oxygen after the previous deoxidation. This means that the oxygen content in steel according to equation (63) is not usually determined by FeO content in slag, but by a content of a deoxidizing element with the highest affinity for oxygen in steel. From elements typically used for deoxidation (Mn, Si, Al), this is aluminium.

At deoxidation of steel by aluminium

$$\frac{2}{3}[Al] + [O] = \frac{1}{3}(Al_2O_3) \tag{79}$$

the equilibrium constant of this reaction and the follow-up oxygen activity is expressed by relations (80) and (81).

$$K_{Al} = \frac{a_{(Al_2O_3)}^{1/3}}{[Al]^{2/3} \cdot f_{Al}^{2/3} \cdot a_{[O]}} \tag{80}$$

$$a_{[O]} = \frac{a_{(Al_2O_3)}^{1/3}}{K_{Al} \cdot [Al]^{2/3} \cdot f_{Al}^{2/3}} \tag{81}$$

The temperature dependence of this equilibrium constant in the presence of CaO-Al$_2$O$_3$ slag is expressed by equation (82)

$$\log K_{Al} = \frac{21263}{T} - 6,862 \tag{82}$$

The process of steel desulphurization in the presence of deoxidizing aluminium can be expressed by a combination of equations (63) and (79)

$$(CaO) + [S] + \frac{2}{3}[Al] = (CaS) + \frac{1}{3}(Al_2O_3) \tag{83}$$

The equilibrium constant of reaction (83) and its temperature dependence are expressed by equations (84) and (85).

$$K_{S,Al} = K_S \cdot K_{Al} = \frac{a_{(CaS)} \cdot a_{(Al_2O_3)}^{1/3}}{a_{(CaO)} \cdot [S] \cdot f_{[S]} \cdot [Al]^{2/3} \cdot f_{Al}^{2/3}} \tag{84}$$

$$\log K_{S,Al} = \frac{16680}{T} - 5,813 \tag{85}$$

The value $K_{S,Al}$ of temperatures 1550 °C to 1600 °C is 2171 to 1237. The following can be derived from equation (84) for the equilibrium content of sulphur in steel deoxidized by aluminium

$$[S] = \frac{a_{(CaS)} \cdot a_{(Al_2O_3)}^{1/3}}{K_{S-Al} \cdot a_{(CaO)} \cdot f_{[S]} \cdot f_{Al}^{2/3} \cdot [Al]^{2/3}} \tag{86}$$

and with regard to values of constants $K_{S,Al}$ for temperatures 1550 °C and 1600 °C

$$[S] = \frac{(4,6 \text{ to } 8,1) \ 10^{-4}}{[Al]^{2/3}} \ \frac{a_{(CaS)}}{a_{(CaO)}} \frac{a_{(Al_2O_3)}^{1/3}}{f_{[S]}} \frac{}{f_{Al}^{2/3}} \tag{87}$$

In the above mentioned equation (87) the relation of sulphur to oxygen in steel is expressed by means of aluminium content in steel.

While values of activity coefficients can be calculated using interaction coefficients, the ratio of activities of CaS, Al$_2$O$_3$ and CaO for a particular steel grade has to be determined empirically.

## 5.3 Possibility of reduction of oxygen content in steel using molten refining slags
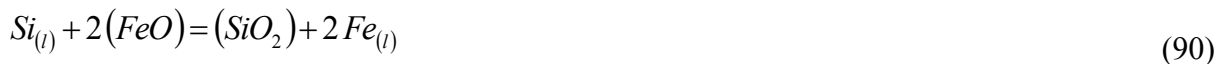
Steel refining by the synthetic slag can create conditions for diffusion deoxidation of steel. A thermodynamic condition of the diffusion deoxidation of steel is a lower activity of FeO in slag than the oxygen activity in steel.

Considering reaction (68), the following condition must be met

$$a_{(FeO)} < K_O \cdot a_{[O]} \tag{88}$$

where $K_O$ is distribution coefficient of oxygen between slag and metal

The low activity of FeO in slag can be ensured by deoxidation (deactivation) of slag by granulated aluminium powder, ferrosilicon or calcium carbide.

$$2\,Al_{(l)} + 3\,(FeO) = (Al_2O_3) + 3\,Fe_{(l)} \tag{89}$$

$$Si_{(l)} + 2\,(FeO) = (SiO_2) + 2\,Fe_{(l)} \tag{90}$$

$$(CaC_2) + 3\,(FeO) = (CaO) + 2\,CO_{(g)} + 3\,Fe_{(l)} \tag{91}$$

While calcium carbide can be used for highly alkaline slags and ferrosilicon for slags with low alkalinity, aluminium can be used for both of the slag types.

In the past, steel deoxidation by the molten synthetic slag was often performed in electro-steel works. The synthetic slag was pre-fused in a ladle to temperature of 1700 to 1750 °C. Steel from EAF was tapped into the ladle from the top down. After the steel having impacted the surface, as a result of permeation of both phases, a significant enlargement of the contact surface of steel and slag as well as intensive stirring occurred. By this kinetic conditions for a fast progression of refining reactions are ensured, and also for coagulation and coalescence of inclusions and their absorption by the molten slag.

This process is also called "perrening" pursuant to its discoverer – Perrin. Originally, acidic slags were used for deoxidation (50 to 60 % of SiO$_2$, 10 to 15 % of Al$_2$O$_3$, 10 to 15 % of CaO+MgO). SiO$_2$ oxide decreases FeO activity in acidic slags as a result of the reaction

$$(SiO_2) + (FeO) = (FeSiO_3) \tag{92}$$

When using the alkaline slag for steel refining, above all steel desulphurization occurs, on condition that the synthetic slag does not contain FeO (and MnO) and the steel is deoxidized at the same time.

For steel refining by the pre-fused alkaline molten synthetic slag, the most frequently used ones are aluminium-calcium slags containing 50 to 56 % of CaO, 40 to 44 % of Al$_2$O$_3$, 1 to 4 % of MgO, 2 to 3 % of SiO$_2$, max. 1 % of FeO. This slag fuses just at temperature 1450 °C and at 1600 °C has viscosity lower than 0.2 Pa.s. For its preparation, caustic lime and raw materials based on corundum with high Al$_2$O$_3$ content are used. During steel refining, discharging of the ladle slag containing FeO into the refining ladle must be avoided.

The slag consumption ranges from 2 to 6 % of the steel mass. The efficiency of steel refining by synthetic slag increases along with a degree of emulsification of metal and slag. The emulsification degree increases along with an increase in the discharged metal flow height, along with an increase in velocity of the metal pouring into the ladle and along with an increase in the slag amount.

## 5.4 Mechanism and kinetics of steel desulphurization by the molten synthetic slag

Transfer of sulphur from the steel into the fused slag comprises the following partial stages:

- o *Diffusion of sulphur atoms from the metal volume to the interphase boundary metal – molten slag and simultaneous diffusion of $O^{2-}$ anions to this interphase interface*
- o *Adsorption of sulphur on the interphase interface followed by the electrochemical reaction with present oxygen anions:*

$$\left(O^{2-}\right)+S_{ads} \Leftrightarrow \left(S^{2-}\right)+O_{ads} \tag{93}$$

- o *Diffusion of $S^{2-}$ anions through a slag layer containing a product of desulphurization CaS to free $Ca^{2+}$ cations in the slag. At the same time, oxygen diffusion from the interphase interface into the metal volume occurs, too.*
- o *The equilibrium reaction of sulphur anions with calcium cations in the molten slag.*

$$\left(Ca^{2+}\right)+\left(S^{2-}\right)=\left(CaS\right) \tag{94}$$
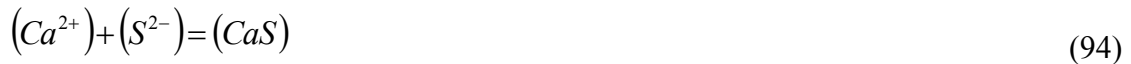
Free oxygen anions, which accompany the sulphur transfer from the metal to the slag, are present in the slag as a result of dissociation of calcium oxide

$$\left(CaO\right)=\left(Ca^{2+}\right)+\left(O^{2-}\right) \tag{95}$$

A limiting stage of the process of metal desulphurization by the molten slag is diffusion of $S^{2-}$ anions in the slag phase, which has viscosity higher than the molten steel by 1 to 2 orders of magnitude. On this condition, a kinetic equation of desulphurization by the molten slag can be written in a form

$$-\frac{d[S]}{d\tau} = \frac{D_{(S)} \cdot F}{\delta V}\left[(S)_p - (S)\right] \tag{96}$$

where $D_{(S)}$    is diffusion coefficient of sulphur, or more precisely of $S^{2-}$ anions, in slag, $m^2.s^{-1}$

$\delta$    - diffusion layer thickness, m

$F/V$    - specific surface of a slag droplet, $m^{-1}$

$(S)_p, (S)$ - content of sulphur ($S^{2-}$ anions) in a surface and a volume of a slag droplet, wt. %

As the sulphur diffusion from the surface into the volume of the slag phase runs most slowly, the sulphur content in the slag surface is permanently in equilibrium with the sulphur content in the metal volume with regard to equation (75).

$$(S)_p = L_S \cdot [S] \tag{97}$$

Then, for the desulphurization rate by the molten slag also applies

$$-\frac{d[S]}{d\tau} = \frac{D_{(S)} \cdot F}{\delta V} \{L_S[S] - (S)\} \qquad (98)$$

According to equation (98) the desulphurization rate decreases along with time, because the sulphur content in the metal decreases, while the sulphur content in the slag volume increases. The distribution coefficient $L_S$, which is a thermodynamic characteristic of the desulphurization process and depends above all on the slag composition, affects also the desulphurization kinetics.

Another important factor, which affects the rate of desulphurization by the molten synthetic slag, is a size of the specific surface between the slag and metal phase and the slag viscosity affecting $D_{(S)}$ value. Emulsification of the slag when the metal flowing from the furnace impacts the fused slag in a ladle is a highly effective method for enlargement of the specific surface F/V.

## 5.5    Possibilities of reduction of a content of inclusions in steel by coagulation and coalescence

When refining steel by synthetic slags, aside from deoxidation and desulphurization, a significant decrease in a content of non-metallic inclusions also occurs, leading to an increase in steel microcleanliness. A reason is joining of inclusions into larger complexes and their transfer into slag droplets. In a case of liquid inclusions joining, this is coalescence; solid inclusions formed e.g. at coagulative deoxidation by ferrosilicon or aluminium are joined by coagulation. Thermodynamic conditions of coalescence and coagulation of inclusions relate to the interphase tension between inclusions and between an inclusion and steel. The surface energy of two inclusions in steel before their connection can be expressed

$$W_1 = \sigma_{V_1-k} S_1 + \sigma_{V_2-k} S_2 \qquad (99)$$

and after the connection by a relation

$$W_2 = \sigma_{V_1-k} S_1^| + \sigma_{V_2-k} S_2^| + \sigma_{V_1-V_2} S_3 \qquad (100)$$

where  $\rho_{V1-k}, \rho_{V2-k}$  is interphase tension between inclusions and steel, $Nm^{-1}$
   $S_1, S_2$       -   areas of inclusion surfaces before their connection, $m^2$
   $S_1^|, S_2^|$       -   areas of surfaces between inclusions and steel after their connection, $m^2$
   $S_3$          -   area of connection of inclusions, $m^2$

A change in the surface energy corresponding to the connection of two inclusions can be expressed as a difference of equations (91) and (100).

$$\Delta W = W_2 - W_1 = \sigma_{V_1-V_2} S_3 - \sigma_{V_1-k}\left(S_1 - S_1^|\right) - \sigma_{V_2-k}\left(S_2 - S_2^|\right) \qquad (101)$$

The thermodynamic condition of spontaneous joining of inclusions is a decrease in the surface energy and thus $\Delta W < 0$. In the case of liquid inclusions, the interphase tension $\sigma_{V1-V2}$ gets close to zero and thus connection of inclusions by coalescence is always accompanied by a decrease in the surface energy. Connection of solid inclusions by coagulation is supported by high interphase tension between inclusions and metal with the low interphase tension between inclusions $\sigma_{V1-V2}$. At forced coalescence and coagulation, as a result of an intensive metal motion the amount of inclusions in steel decreases very quickly, e.g. in 1 second their number in 1 kg of steel can drop from $10^9$ down to $10^2$.

## Σ   Summary of terms of this chapter (subchapters)

- o  Mentioned in the part "Subchapters"

## ?   Questions to the topic

- o  Questions to this topic correspond to titles of the subchapters in the part "Subchapters"

# 6. STEEL REFINING BY BLOWING OF FINE-GRAINED ADDITIVES

**Subchapters:**

✓ Principle of blowing of fine-grained additives

✓ Mechanism and kinetics of steel desulphurization by pulverized lime

✓ Method of blowing of pulverized additives

✓ SL process

✓ Inputting cored wires into the steel

**Time needed for the study:** individual

**Objective:** After studying this chapter a student will be able to:

- *Characterize a principle of blowing of fine-grained additives*
- *Define a mechanism and kinetics of steel desulphurization*
- *Describe basic methods and technologies of blowing of pulverized additives*

**Lecture**

## 6.1 Principle of blowing of fine-grained additives

From the point of view of a state of matter of the used additive, this method of ladle refining of steel belongs to the area of refining by solid matters. However, it represents a relatively independent chapter, both in term of the technological design and in term of achieved effects.

This ladle refining method can be successfully used for desulphurization, deoxidation of steel and modification of inclusions, then for alloying and carburization of steel depending on the used type of the blown pulverized medium. As far as steel alloying, an increase in yield can be achieved especially for ferroalloys with high metal-loss, such as FeTi, e.g. for titanium to 70 up to 80 %. When blowing carburizers into a ladle, utilization of the agent as high as 100 % can be achieved. Nevertheless, this method of refining has found widespread application in desulphurization, deoxidation of steel and modification of inclusions.

## 6.2 Mechanism and kinetics of steel desulphurization by pulverized lime

The mechanism of steel desulphurization by pulverized lime assumes the existence of two interphase interfaces:

- ○ *Interphase interface metal - $CaS_{(s)}$*
- ○ *Interphase interface $CaS_{(s)}$ - $CaO_{(s)}$*

On this condition, the sulphur transfer from the metal into the solid phase volume can be described as follows:

- o *Diffusion of sulphur atoms from the metal volume to the interphase boundary metal - $CaS_{(s)}$ and simultaneous diffusion of $O^{2-}$ anions through CaS layer from the interphase boundary $CaO_{(s)}$ - $CaS_{(s)}$ to the boundary $CaS_{(s)}$ - metal*
- o *Adsorption of sulphur on the boundary metal - $CaS_{(s)}$ followed by the electrochemical reaction with present oxygen anions*

$$O^{2-} + S_{ads.} \Leftrightarrow S^{2-} + O_{ads.} \tag{102}$$

- o *Diffusion of $O^{2-}$ anions through a layer of desulphurization products from the boundary metal - $CaS_{(s)}$ to the boundary $CaS_{(s)}$ - $CaO_{(s)}$. At the same time, desorption and diffusion of oxygen atoms from the interface $CaS_{(s)}$ – metal into the metal volume occurs.*
- o *Reaction of anions of sulphur and $CaO_{(s)}$ on the interphase boundary $CaS_{(s)} – CaO_{(s)}$*

$$CaO_{(s)} + S^{2-} \Leftrightarrow CaS_{(s)} + O^{2-} \tag{103}$$

Regarding high temperatures at which metal desulphurization occurs, adsorption and desorption processes and reactions on both of the interphase boundaries can be excluded as the slowest stage of the desulphurization process. The desulphurization rate is then limited above all by sulphur diffusion in metal and in CaS layer. At low contents of sulphur in metal, the desulphurization process is limited particularly by diffusion of sulphur atoms in metal, which has penetrated into pores between and inside grains of solid calcium oxide and where only atomic diffusion can occur. In a case of higher contents of sulphur in metal an increase in thickness of CaS layer occurs and then a limiting member of the process is diffusion of $S^{2-}$ anions through this layer to the interphase interface $CaS_{(s)}$ - $CaO_{(s)}$.

The thermodynamic and kinetic analysis of the desulphurization process in blowing pulverized materials into steel results in the following conclusions, which are conditions for high effectiveness of this steel refinement method:

- o *pulverized lime, which is the cheapest desulphurizing medium, needs to be supplemented by fluidizing materials, which increase a velocity of diffusion processes while decreasing activity of formed CaS*
- o *lime has to have a content of sulphur and oxides entraining oxygen into metal as low as possible*

## 6.3   Method of blowing of pulverized additives into steel

In order to achieve a high degree of desulphurization the additives based on calcium or magnesium are fed into steel through a nozzle submerged deep in a ladle (approximately 5/6 to 6/7 of the ladle depth). Argon is used as the carrier gas, exceptionally nitrogen. The carrier gas amount is determined depending on the amount of the added addition and a requirement for optimal stirring of metal. The equipment scheme is depicted in **Fig. 27**.

During steel tapping from a furnace, holding of slag in the furnace is performed, because this is the oxidation slag. The bath surface is covered by the covering slag, the most frequently $CaO – SiO_2 – Al_2O_3$ mixture in a ratio $CaO/SiO_2:Al_2O_3 = 0.3 – 0.4$, and this in an amount of c. 6 kg/t of steel. The total blowing time usually does not exceed 10 to 15 minutes. The ladle is covered with a lid during blowing.
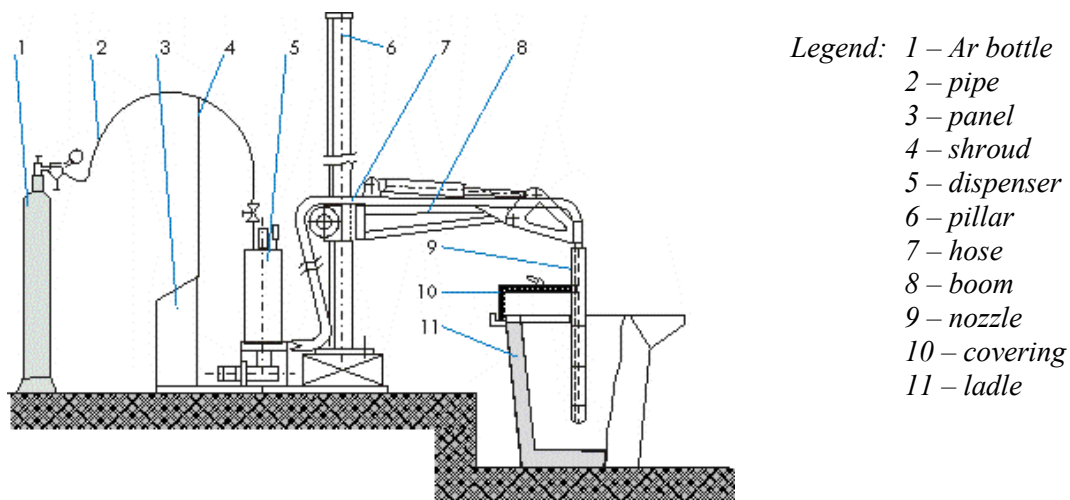
**Fig. 27**    Scheme of equipment for blowing pulverized substances into a ladle

A condition for achieving a high degree of desulphurization and final contents of sulphur below 0.01 % is a reduction of the oxygen content in steel down to 6 to 8 ppm. The specified oxygen content can be achieved through steel deoxidation by aluminium in a ladle with an alkaline lining. The chamotte lining has lower thermodynamic stability, so $SiO_2$ reduction from the ladle stones occurs. Oxygen transfer from the ladle lining into steel makes it more difficult to achieve the oxygen content in steel below 20 ppm. While, for example, in a dolomite lined ladle the sulphur content in steel can be decreased below 0.01wt. % at its initial content of 0.03 wt. %, in a case of a chamotte lined ladle the initial sulphur content should not exceed 0.02 wt. %.

❑   **SL process**

The principle of SL process (Scandinavian Lancers) consists in steel desulphurization and modification of inclusions by pulverized additives blown into steel through lances immersed in a ladle. The lance can have a ceramic plug on its end and in this case it rests on the ladle bottom. Gas with pulverized materials is blown through 3 to 6 outlets under an angle of 120° towards the bottom in a distance c. 30 cm from the ladle bottom. Pulverized lime in a mixture with CaSi, possibly $CaC_2$ or aluminium is used for steel desulphurization. Argon consumption is 0.6 to 1.2 $m^3.min^{-1}$, while for lime 8 to 15 $kg.t^{-1}$; from that 30 to 50 % for injection and the rest into the covering slag. Temperature decrease is 3 to 5 $°C.min^{-1}$. Granularity of lime should be to 0.6 mm, granularity of CaSi to 2 mm. Efficiency of desulphurization ranges between 80 to 90 %.

Chemical composition of used refining mixtures in this process is shown in **Tab. 3**.

**Tab. 3** shows that besides calcium compounds, mixtures of magnesium with lime and fluorite or only mixtures of lime with aluminium oxide are used. An achieved degree of steel desulphurization is around 90%, while the final content of sulphur may reach values below 0.002 wt. %, independently of its initial content.

When blowing mixtures containing CaSi into steel, favourable modification of shapes of inclusions in steel occurs, easier floatation of inclusions and as a result of this an increase in microcleanliness of steel. At the same time, steel fluidity also increases, which has an extraordinary significance for continuous casting of steel or casting at low temperatures.

**Tab. 3**   Chemical composition of refining mixtures

| Refining additive | Chemical composition | Amount of additive blown into steel kg.t$^{-1}$ | Additive needed for 90 % deS kg.t$^{-1}$ |
|---|---|---|---|
| CaSi | 54 % Si, 40 % Ca | 2 – 3 | 2.9 |
| CaSi | 62 % Si, 30 % Ca, 8 % Al | 2 – 4.5 | 3.87 |
| CaC$_2$ | 80 % CaC$_2$, 15 % CaO (50 % CaO) | 1 – 3 | 4.24 |
| Mg (CaO/CaF$_2$) | 5 – 20 % Mg, 60 – 80 % CaO, 10 % CaF$_2$ | 1 - 3 | 2.2 |
| CaO/CaF$_2$ | 90 % CaO, 10 % CaF$_2$ | 3 – 5 | 3 |
| CaO – Al$_2$O$_3$ | 50 % CaO, 50 % Al$_2$O$_3$ | 1 – 5 | 4 |
| CaO – Al$_2$O$_3$ - CaF$_2$ | 70 % CaO, 20 % Al$_2$O$_3$, 10 % CaF$_2$ | 1 – 5 | 3 |
| CaMg | 45 % Ca, 55 % Mg | 1 – 2 | 1.5 |

## 6.4   Inputting cored wires into the steel

Besides injection of pulverized matters, there is a technology of adding cored wires and Al wire into the molten steel. This technology has a similar principle as the injection of pulverized matters, but with lower thermal losses, achieving of accurate deoxidation and alloying on the lower limit of the prescription along with a possibility of modification of inclusions.

Inputting cored wires into the steel represents a method with the following goals:

  o *Controlled and deep deoxidation of steel*
  o *Defined metal-loss Al = 98 % for deoxidation*
  o *Accurate, economy alloying on the lower limit of the prescription through inputting cored wires*
  o *Modification of Ca – Si, Ca – Fe inclusions*
  o *Desulphurization*

The method of inputting Al wire into the steel consists in:

  o *Al wire (of a thickness of 3 to 10 mm) is unreeled from a drum and subsequently input (shot-in) by a velocity of 2.5 to 5 m·s$^{-1}$ through the slag into the steel in a ladle; the velocity must be of such a value, so that the wire becomes molten at the bottom (or above the bottom) of the ladle. All the Al is used for the steel deoxidation, while an undesirable metal-loss of Al in the slag and atmosphere above the bath is minimized.*
  o *During the steel processing an inert gas is blown and Al wire inputting must not be performed in a place against the current of the blown inert gas, so that a metal-loss into the slag cannot occur. Al inputting is then carried out into the descending current of the blown inert gas.*
  o *During the steel processing a manipulator for measuring steel temperature and oxygen activity is used, so that homogenous steel is achieved for determination of an amount of the input Al; the temperature and oxygen activity is measured and follow-up, on the basis of the found out parameters, the amount of e.g. Al as a deoxidizing*

*agent for the oxygen activity decrease to a demanded level can be determined. Utilization of Al wire reaches 98 % and this is an economic deoxidation with a minimum and constant metal-loss.*

The method of inputting cored wires into the steel consists in:

o *Cored wire is filled with alloying elements – ferroalloys FeTi, FeV etc.) or with additives for modification of non-metallic inclusions (CaSi, CaFe, CaAl etc.).*

o *The very inputting (shooting-in) of cored wires is performed after a decrease in the oxygen activity to a required level (deoxidation). In this case the cored wire enters the steel by a speed of 0.3 to 2 m.s$^{-1}$through the slag into the steel in the ladle. All the content of the cored wire is used for alloying or modification of inclusions, because it is released only as down as at the bottom of the ladle after dissolution of the steel sheath.*

o *During the steel processing an inert gas is blown and injection of the cored wire must not be performed in a place against the current of the blown inert gas, but into the descending current of the blown inert gas.*

o *By a selection, amount, type or a combination of cored wires the inclusions of required compositions can be formed (for example liquid ones),*

**Fig. 30** shows an example of equipment for inputting Al wire and cored wires.



**Fig. 30**    Example of equipment for inputting Al wire and cored wires

∑    **Summary of terms of this chapter (subchapters)**

o Mentioned in the part "Subchapters"

?    **Questions to the topic**

o Questions to this topic correspond to titles of the subchapters in the part "Subchapters"

# 7.   LADLE FURNACES

**Subchapters:**

- ✓ Types of ladle furnaces
- ✓ Ladle furnace - LF
- ✓ Ladle furnace with chemical temperature raising - IR-UT, CAS-OB
- ✓ Refining equipment ASEA
- ✓ Refining equipment VAD
- ✓ ISSM equipment

**Time needed for the study:** individual

**Objective:** After studying this chapter a student will be able to:

- *Define types of ladle furnaces*
- *Describe basic types of ladle furnaces - LF, CAS-OB*
- *Characterize a principle of inputting cored wires*

**Lecture**

## 7.1   Types of ladle furnaces

Development of ladle furnaces relates to the development and aims of secondary metallurgy. At present, ladle furnaces are already an integral part of equipment of all modern steelworks. Ladle furnaces can be divided according to several criteria:

- o *according to the steel temperature raising method:*
  - *Arc temperature raising - electric arc*
  - *Chemical temperature raising with the aid of Al, Si*
- o *according to the working pressure:*
  - *Atmospheric pressure (ladle furnace LF)*
  - *Vacuum (ladle furnace ASEA, VAD)*
- o *according to the steel stirring method:*
  - *Ar blowing through a porous block on the ladle bottom*
  - *Induction stirring of steel*

Advantages of ladle furnaces can be summarized in the following items:

- o *Possibility to decrease the steel tapping temperature*
- o *Reduction of the furnace lining wear*
- o *Increase in the furnace production by transferring the refining stage of the primary aggregate to the ladle furnace*
- o *Possibility to synchronize a furnace aggregate with CCM*
- o *Intensive refining effect – intensive deep desulphurization*
- o *Slag has the same or higher temperature than steel in the ladle furnace (lower viscous slags, better desulphurization of steel)*

o  *Accurate casting temperatures for CCM ranging from ± 2.5 to 5 °C*

## 7.2   Ladle furnace - LF

A ladle furnace LF represents a basic aggregate of ladle metallurgy with temperature raising using electric arc. The temperature raising using the electric arc works on the same principle as in a case of the electric arc furnace, whereas requirements for output of transformer are approximately 6times lower. By electric arc heating the steel temperature is maintained on a stable level or can be slightly increased according to a requirement of production technology and the manufactured steel grade.

During steel processing in a ladle furnace LF, the steel stirring using argon blown through a porous block in the bottom of the ladle is typically performed to ensure homogenization (from a minimal to maximal flow rate). Besides the steel temperature raising and homogenization, the ladle furnace LF allows additional alloying or microalloying of the steel using feed hoppers or feeders of cored wires as auxiliary equipment.

One of the main functions of the ladle furnace is deep desulphurization of steel using the refining slag. To meet the above mentioned requirement, the ladle slag is formed from products of the steel deoxidation and from slag-forming additives added during tapping and slag-forming additives added during the steel processing in the ladle furnace LF. Covering electric arcs by slag increases its temperature, thus makes the process of desulphurization and absorption of non-metallic inclusions faster and increases the lining service life and endurance towards radiating heat at the same time. **Fig. 28** shows an example of basic parts of a ladle furnace LF.
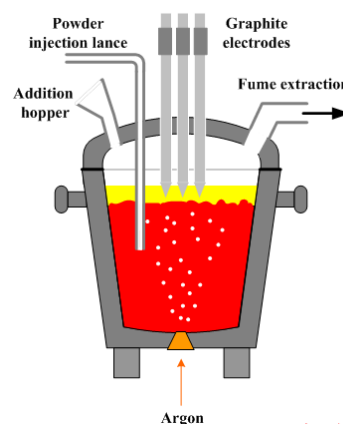
*a) graphite electrodes*

*b) open door of the ladle furnace*

*c) ladle furnace LF in operation*

*d) basic scheme of the ladle furnace LF*

**Fig. 28**   Display of basic parts of a ladle furnace LF

## 7.3  Ladle furnace with chemical temperature raising - IR-UT, CAS-OB

Ladle furnaces with chemical temperature raising and oxygen lance CAS-OB (*Composition Adjustment by Sealed Argon Bubbling-Oxygen Blowing*) and IR-UT (*Injection Refining with Temperature Raising Capability*) are alternatives to ladle furnaces LF.

CAS-OB and IR-UT ladle furnaces are standardly equipped with oxygen lances, through which $O_2$ is blown onto the bath surface, along with equipment for adding granulated Al or FeSi into the reaction region. The reaction region forms an open eye of the bath that is defined by the so-called snorkel (an iron-concrete bell). This bell is put down onto the surface after the eye has been created by argon blowing. Follow-up, $O_2$ is blown and Al or FeSi added. The very separation of slag from metal with the help of the so-called snorkel is performed during heating, which is carried out at the beginning of the steel processing. During processing, argon is blown into the steel, both through the porous block in the ladle bottom and from the top through a lance.

Heating of the steel by addition of Al or FeSi occurs according to the following equations:

$$2Al_{(s)} + 3/2\ O_{2(g)} \rightarrow (Al_2O_3) \qquad \Delta H << 0 \qquad \Delta H = -31\ 000\ kJ\ /\ kg\ Al \qquad (104)$$

$$Si_{(s)} + O_{2(g)} \rightarrow (SiO_2) \qquad \Delta H << 0 \qquad \Delta H = -29\ 000\ kJ\ /\ kg\ Si \qquad (105)$$

Equations (104) and (105) imply that this is a highly exothermic reaction, whereas by adding 1 kg of Al per 1 t of steel and an amount of 0.6 $m^3$ of $O_2$ the steel is heated by 35 °C. In a case of adding 1 kg of Si per 1 t of steel and an amount of 0.8 $m^3$ of $O_2$ the steel is heated by 33 °C. **Fig. 29** shows a depiction of basic parts of a ladle furnace CAS-OB.



*a) snorkel of CAS-OB ladle furnace in operation*
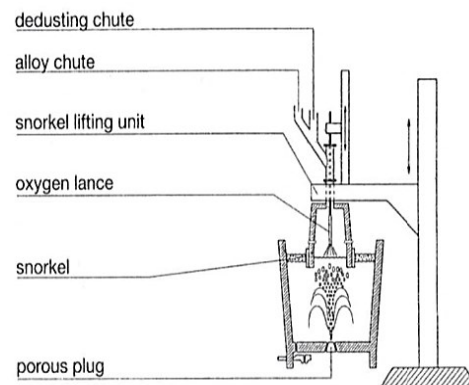
*d) basic scheme of CAS-OB ladle furnace*

**Fig. 29**   Display of basic parts of CAS-OB ladle furnace

## 7.4  Refining equipment ASEA

ASEA refining equipment allows temperature raising of steel and, aside from the steel desulphurization, all refining operations, such as the steel deoxidation, alloying, vacuum oxygen decarburization and also vacuum degassing of steel.

ASEA refining equipment incorporates the following parts: refining ladle, equipment for arc heating of molten steel, equipment for vacuum processing, equipment for induction stirring and auxiliary equipment.

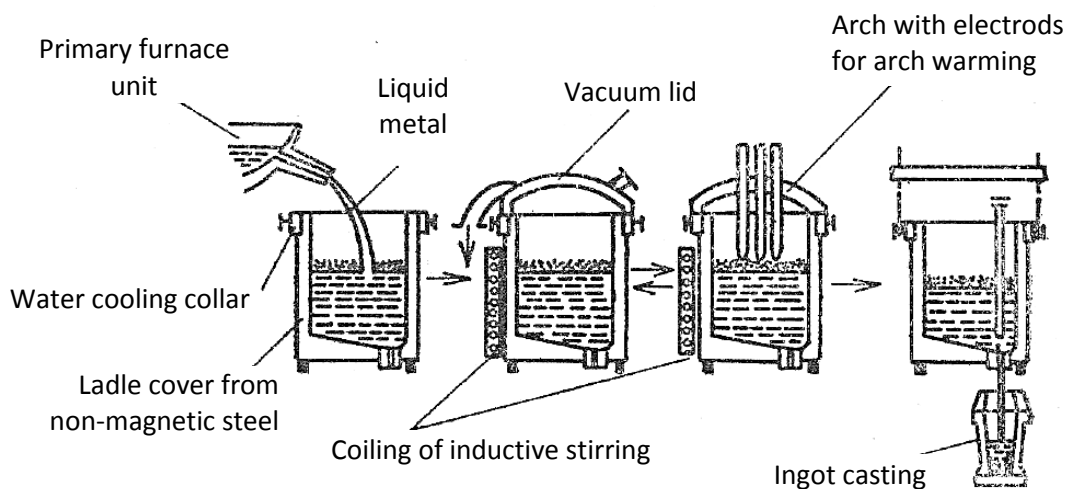**Fig. 31** shows a depiction of ASEA process.

**Fig. 31**    Schematic depiction of ASEA process

The most widely used type is an arrangement, where the refining ladle moves on the transport carriage with an induction stirrer between two working standpoints. In the first standpoint heating of the metal by electric arc is performed and in the second standpoint vacuum processing is performed.

**Fig. 32** shows a depiction of the particular working standpoints of ASEA refining equipment.
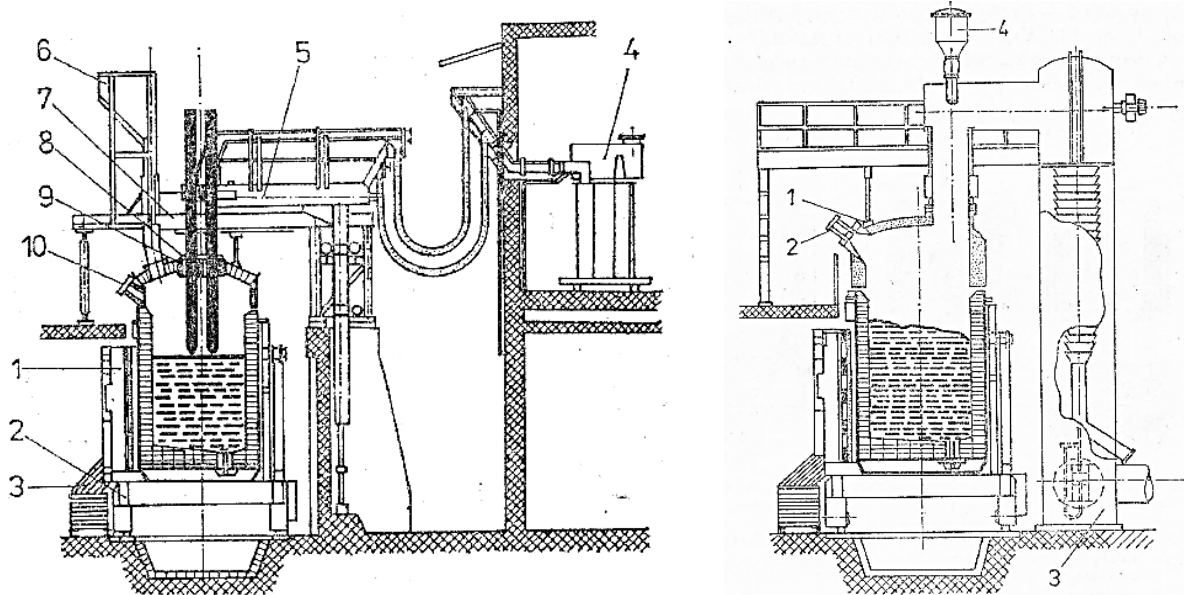


*Legend: 1 – induction stirrer, 2 – transport carriage, 3 – pliant cords cooled with water, 4 – ladle transformer, 5 – electrodes holder, 6 – store tank for dosing of alloying ingredients, 7 – unit for arch lifting, 8 – gasket, 9 – ring cooled with water, 10 – check peephole*

*Legend: 1 – check peephole, 2 – TV camera, 3 – vacuum system with dust separator and gas cooler, 4 – store tank for dosing of alloying and deoxidation ingredients*

  *a)standpoint of electric arc heating*          *b)vacuum processing standpoint*

**Fig. 32**    The most frequent arrangement of ASEA refining equipment

The equipment for arc heating is equipped with a dome with three graphite electrodes extending downwards onto the refining ladle. Alloying elements are added in the heating

standpoint through a feeder going through the dome, whereas at the moment of alloying the arc heating is interrupted. In the standpoint for the steel vacuum processing the ladle is covered with a vacuum-tight lid connected with a vacuum station via pipeline.

Compared to the classical pouring ladle, ASEA refining equipment has a greater height to width ratio. The higher height is needed, so that there is an adequate free space for a move of the steel in the ladle. Another difference in comparison with the classical ladle is a necessary application of non-magnetic austenitic stainless steel as material for the ladle shell. This is a condition for induction stirring using coils located on the transport carriage. Stirring is ensured by a magnetic current flowing through the ladle wall. A schematic depiction of the magnetic field for various arrangements of stirrers is shown in **Fig. 33**.
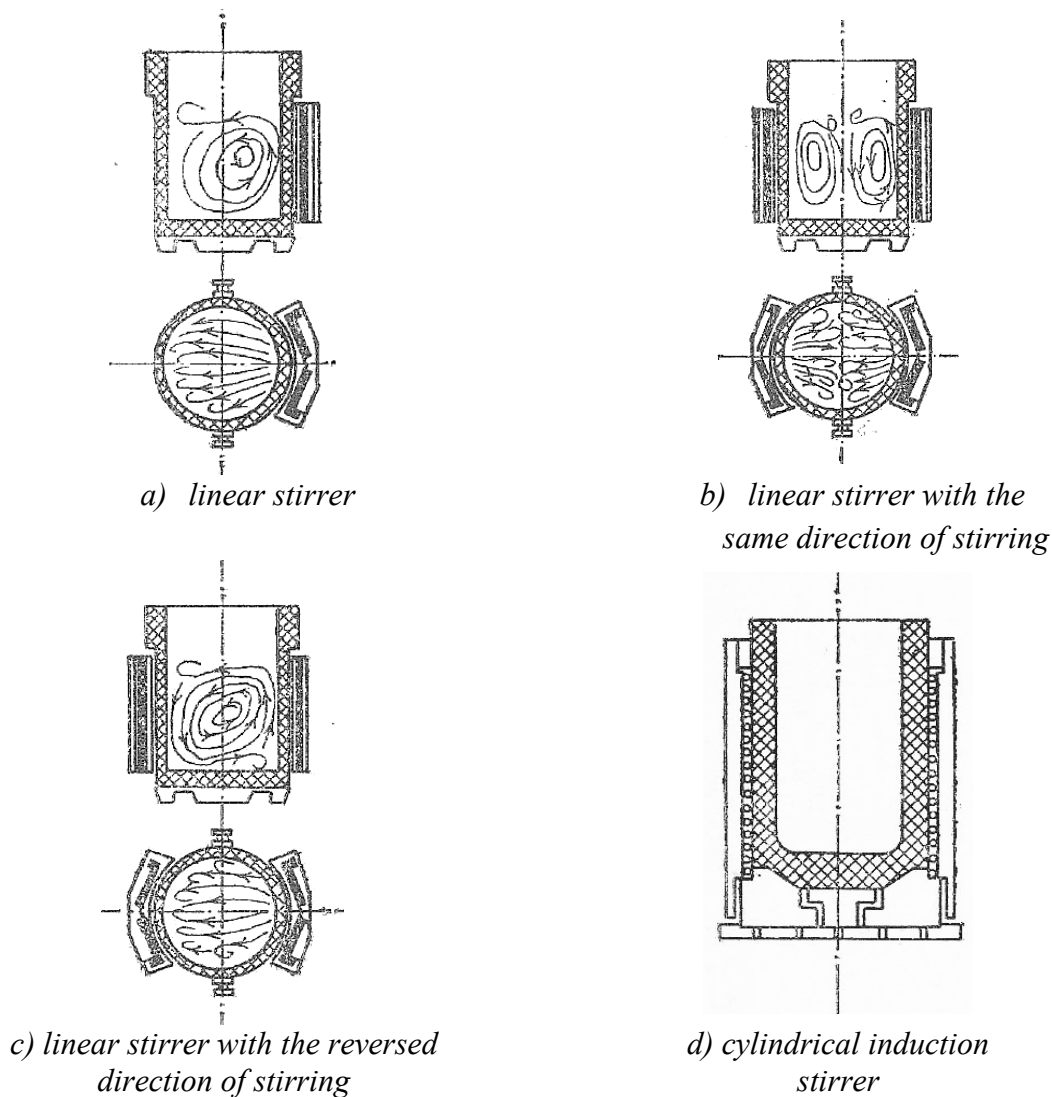


*a)  linear stirrer*

*b)  linear stirrer with the same direction of stirring*

*c) linear stirrer with the reversed direction of stirring*

*d) cylindrical induction stirrer*

**Fig. 33**    Schematic depiction of the magnetic flow in the ASEA ladle with various arrangement of induction stirring

## 7.5    Refining equipment VAD

VAD (*Vacuum Arc Degassing*) equipment represents another variant of ladle processing of steel. The equipment allows all metallurgical operations, i.e. vacuum degassing, arc heating, argon stirring of steel, alloying, deoxidation, decarburization and above all desulphurization.

In VAD process all refining operations are performed in one working standpoint in a vacuum-tight chamber. Stirring of steel in the ladle is only performed by argon blowing through a permeable block built in the ladle bottom, whereas electric arc heating runs at reduced pressure about 20 to 35 kPa. This more simple arrangement does not require a ladle with a stainless steel shell, which brings along a favourable effect of lower costs compared to ASEA equipment.

**Fig. 34** shows a scheme of VAD equipment.
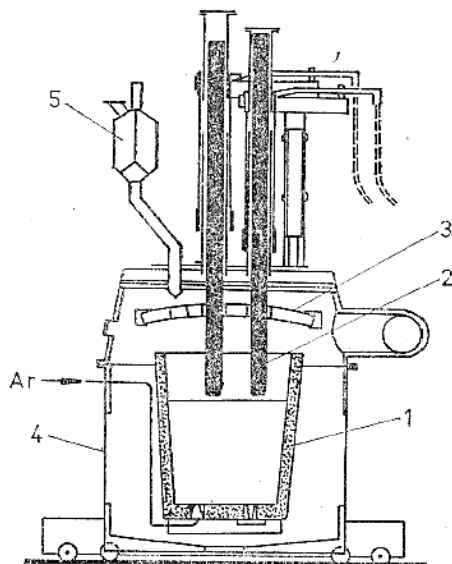


Legend: 1 – ladle with steel
2 – electrodes
3 – heat-isolating shield
4 – vacuum chamber (caisson)
5 – store tank for dosing of alloying and deoxidation ingredients

**Fig. 34**    Schematic depiction of VAD equipment

Refining in the VAD process is performed in a ladle placed in a vacuum chamber connected to a system of steam-jet ejector pumps. At the end of vacuum processing the caisson pressure is equalized by nitrogen feeding-in. On the upper part of a lid, there is a system of reserve boxes with feed hoppers and vacuum closure enabling to add alloying and deoxidizing additives during processing.

For heating, graphite electrodes are used; their parts above the lid are enclosed in vacuum-tight tubes. A move of electrodes and tubes is enabled using a special telescopic seal between the outer and inner tube. Temperature and chemical homogenization during refining is provided by argon blowing. As the equipment works under the decreased pressure, the argon amount ensuring effective stirring of the bath is substantially lower (0.03 to 0.06 $m^3 \cdot t^{-1}$ of steel) compared to refining by argon under the atmospheric pressure (0.06 to 1.2 $m^3 \cdot t^{-1}$ of steel).

## 7.6   ISSM equipment

ISSM equipment (*Integrated System of Secondary Metallurgy*) allows chemical temperature raising and following vacuum processing of steel in a ladle placed inside a vacuum caisson. The base of this technological equipment is a hermetically closed caisson inside which a ladle with the molten steel continuously stirred by an inert gas is placed during the refining process at the deep vacuum. The equipment is further equipped with an oxygen lance through which $O_2$ is blown onto the bath surface along with an Al wire feeder into the so-called reaction region, where steel is heated using chemical temperature raising of the molten steel.

ISSM equipment is also fitted with a vacuum sluice with a possibility of modification of slag chemical composition by feeding slag-forming additives (lime, synthetic slags). In addition, the equipment is fitted with a feeder of cored wires to ensure steel deoxidation, alloying or microalloying and a possibility of modification of aluminate inclusions (CaSi and CaFe) along with containers for ferroalloys.

The following metallurgical effects can be achieved in the ISSM equipment: decarburization to a required limit in anticorrosive steel making, deoxidation of the molten steel using the carbon reaction – VCD process, active utilization of slag on the refining effect by removing inclusions and desulphurization according to the requirement for the manufactured steel, achieving of steel degassing below 1.5 ppm of hydrogen and below 30 ppm of nitrogen, deoxidation to 30 ppm value of the total oxygen content, possibility of chemical temperature raising, ensuring of high temperature and chemical homogeneity, possibility of accurate alloying including microalloying additives with high rate of utilization of alloying elements.

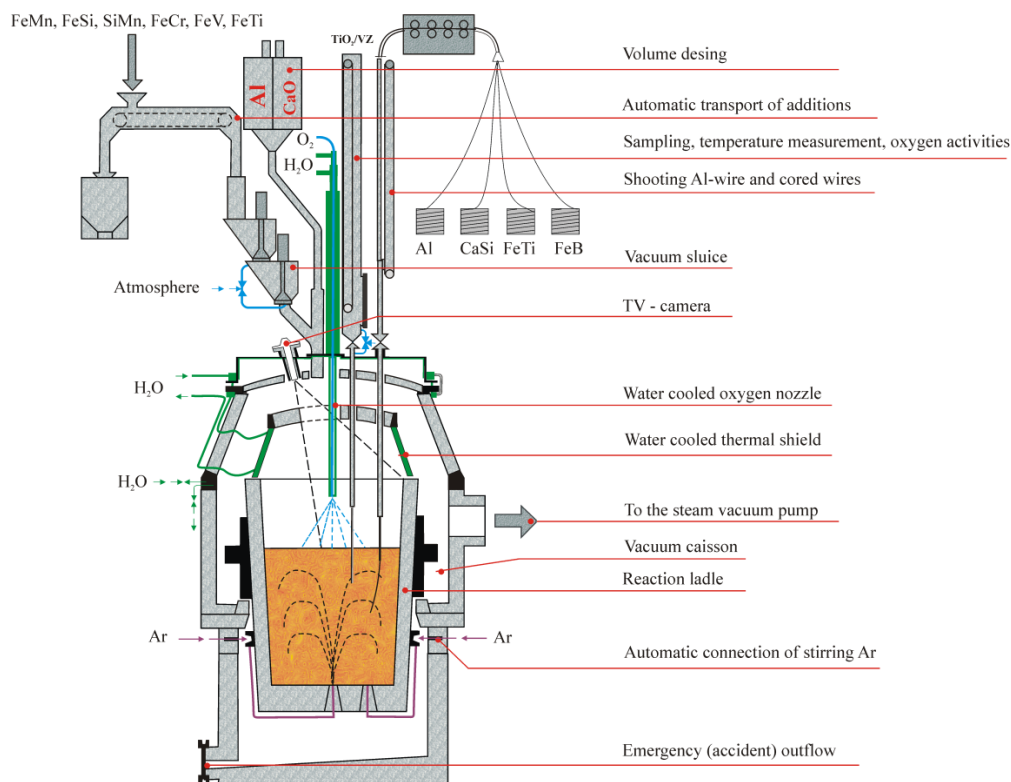**Fig. 35** shows a schematic depiction of ISSM equipment.



**Fig. 35**    Schematic depiction of ISSM station

## Σ    Summary of terms of this chapter (subchapters)

o    Mentioned in the part "Subchapters"

## ❓    Questions to the topic

o    Questions to this topic correspond to titles of the subchapters in the part "Subchapters"