Department of Materials Science and Engineering
MŰEGYETEM 1782

Iron and steel making

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Materials Engineering
BMEGEMTBGF1
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Ores

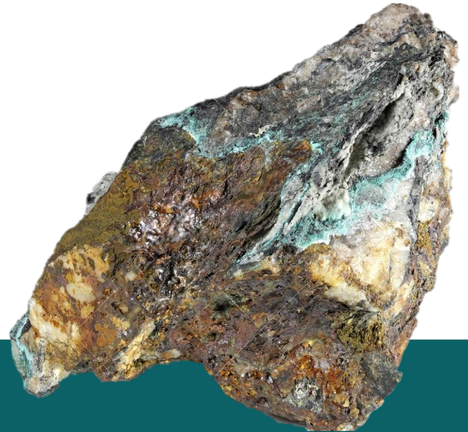
Metals: rarely exist in pure state → mostly in ores

Ore: Metallic and other compounds, mostly oxides

Metallic content:

Iron ores:	30 - 70 % Fe
Copper ores:	0.1 - 0.8 % Cu
Molybdenum:	0.01 - 0.1 % Mo

Four basic way to gain the metallic parts from ore:



- Reduction by carbon
- Electrolytic way
- Metallotermical process
- Dissociation

From ores to metals

1) Reduction by carbon $MeO + C \rightarrow Me + CO$

$FeO + C \rightarrow [Fe] + \{CO\}$

molten metals *gas*

2) Electrolytic way $Al_2O_3 \rightarrow Al_2^{3+} + 3O^{2-}$

on the cathode: $Al^{3+} + 3e^- \rightarrow Al$

3) Metallothermical process

$TiCl_4 + 2Mg \rightarrow [Ti] + 2MgCl$

4) Dissociation $MeX \rightarrow [Me] + [X]$

only at high energy level

costs

The law of mass action

Determines the direction of the reaction from the dynamic equilibrium of the intial materials and the product

$$mA + nB \leftrightarrow A_m B_n$$

$$\frac{[A_m B_n]}{[A]^m \cdot [B]^n} = K(T)$$

Example: desulfurization

$$CaO + FeS \leftrightarrow CaS + FeO$$

$$\frac{(CaS)[FeO]}{[FeS](CaO)} = K(T)$$

$(\,) - in\ slag$

$[\,] - in\ molten\ metal$

$\{\,\} - in\ gas\ phase$

$< > - in\ solid\ phase$

The law of distribution

Shows the distribution of an element in different phases

$$L(T) = \frac{(FeO)}{[FeO]}$$

$( ) - in\ slag$
$[ ] - in\ molten\ metal$
$\{ \} - in\ gas\ phase$
$< > - in\ solid\ phase$

$$L < \frac{(FeO)}{[FeO]}$$ $FeO\ slag \rightarrow molten\ iron$ Oxidation

$$L > \frac{(FeO)}{[FeO]}$$ $FeO\ molten\ iron \rightarrow slag$ Reduction

- The process takes place until the equilibrium is restored
- The slag has a great importance (basic, acidic)

Iron and steel making processes

Iron ore

Blast furnace

Pig iron

Steel making plant

Steel

Foundry → Cast iron

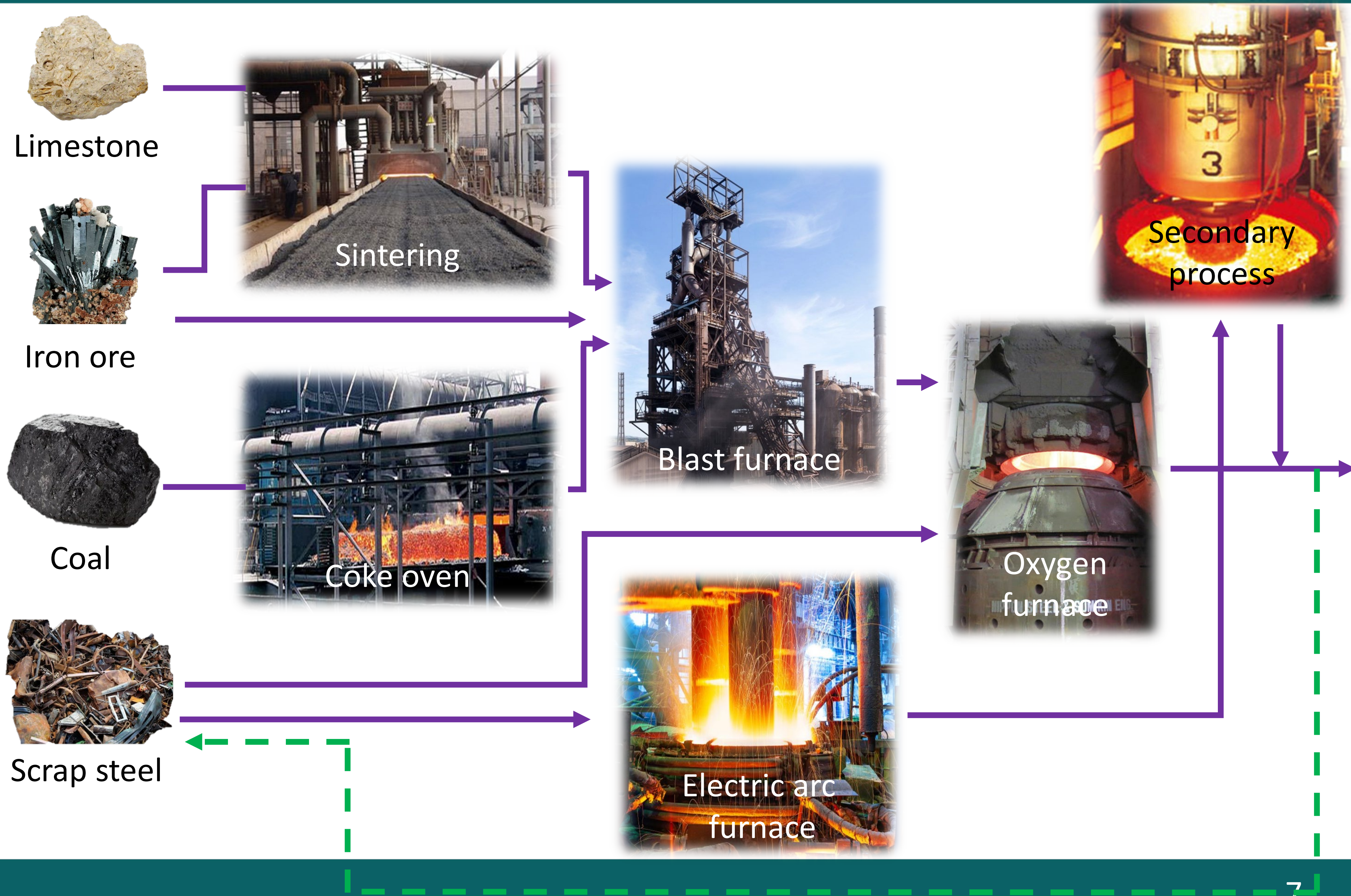
Foundry → Cast steel

Rolling mill → Rolled steel

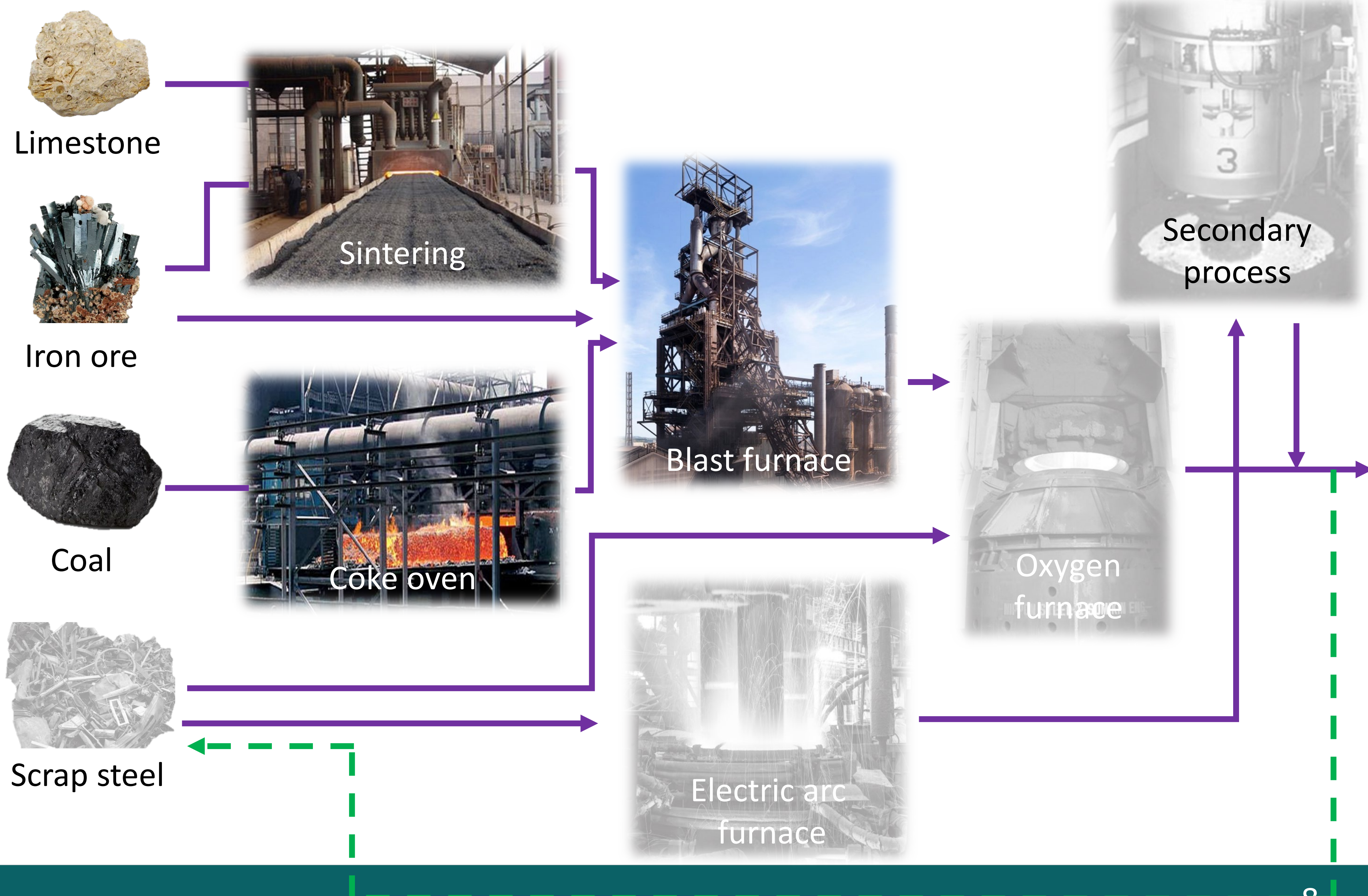
Forge → Forged steel

Wrought steel

Production line of steel



Production line of iron



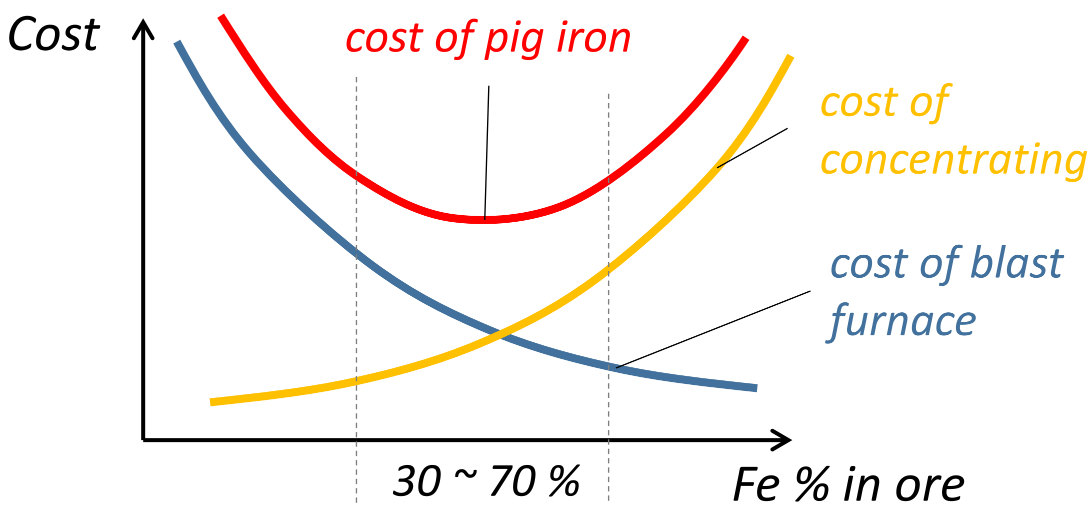
Purpose: Iron ore → Pig iron

ore types: Fe_3O_4 magnetite ~ 70 % Fe
Fe_2O_3 hematite ~ 70 % Fe
$FeCO_3$ siderite ~ 50 % Fe



+ tailings: silicates, sand, other non ferrous
MnO, Al_2O_3, P_2O_5, etc

Total cost vs. Ore quality



Blast furnace

Dimensions:

Diameter: 4 - 10 m

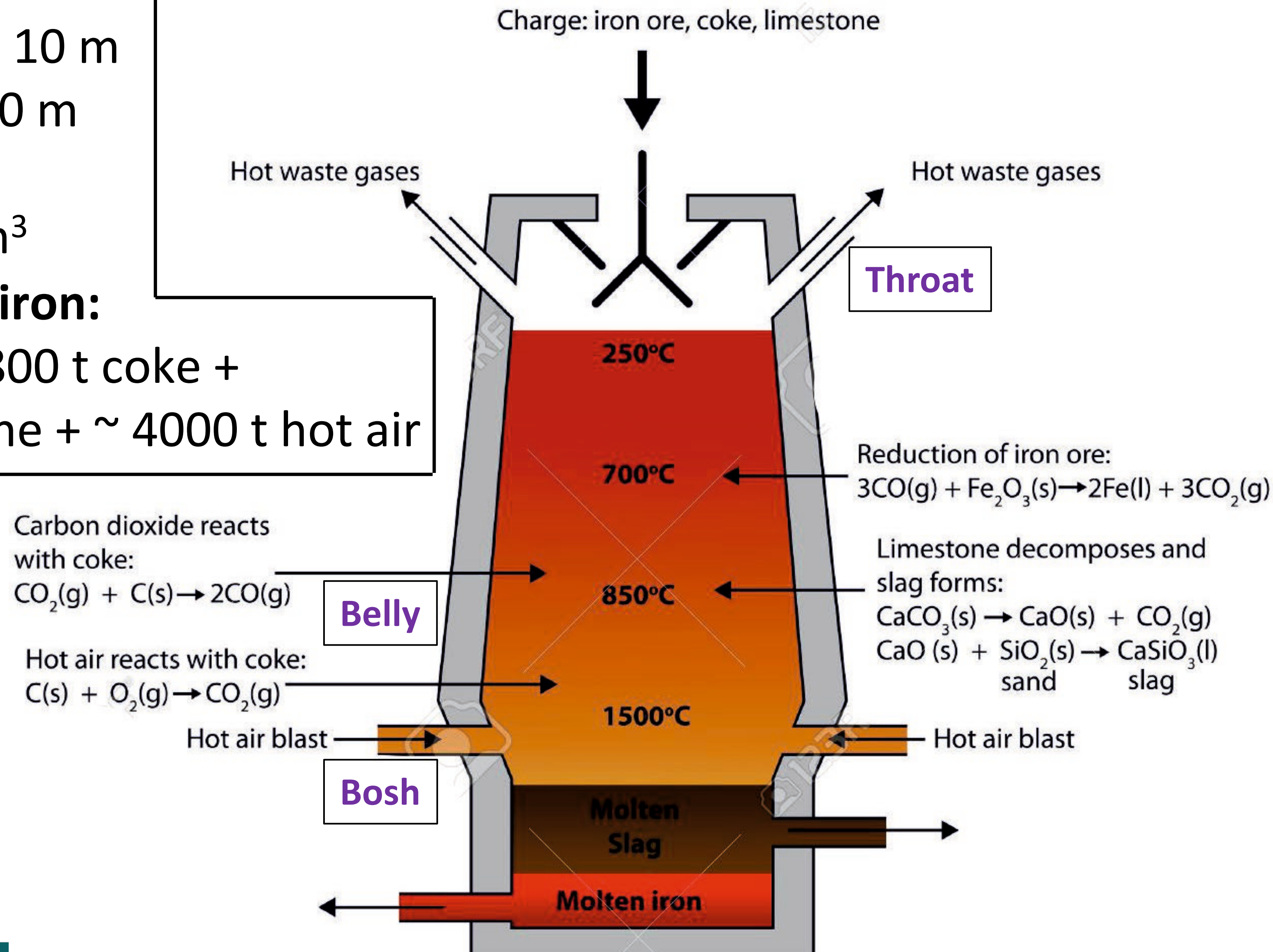
Height: 25 - 30 m

Volume:

300 – 5000 m^3

For 1000 t of iron:

2000 t ore + 800 t coke +
500 t limestone + ~ 4000 t hot air



Processes in blast furnace

Charge moves down (6-8 hours)

- Preheating by gas coke burns more efficient

  Formation of CO: $2C + O_2 \rightarrow 2CO$

  CO reacts with iron ore: $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$
- Coke reduces CO_2 in the gas

  $C + CO_2 \rightarrow 2CO$
- CO reduces the surface of the iron ore *Indirect reduction*

  $FeO + CO \rightarrow Fe + CO_2$
- Slag producing by limestone, dolomite

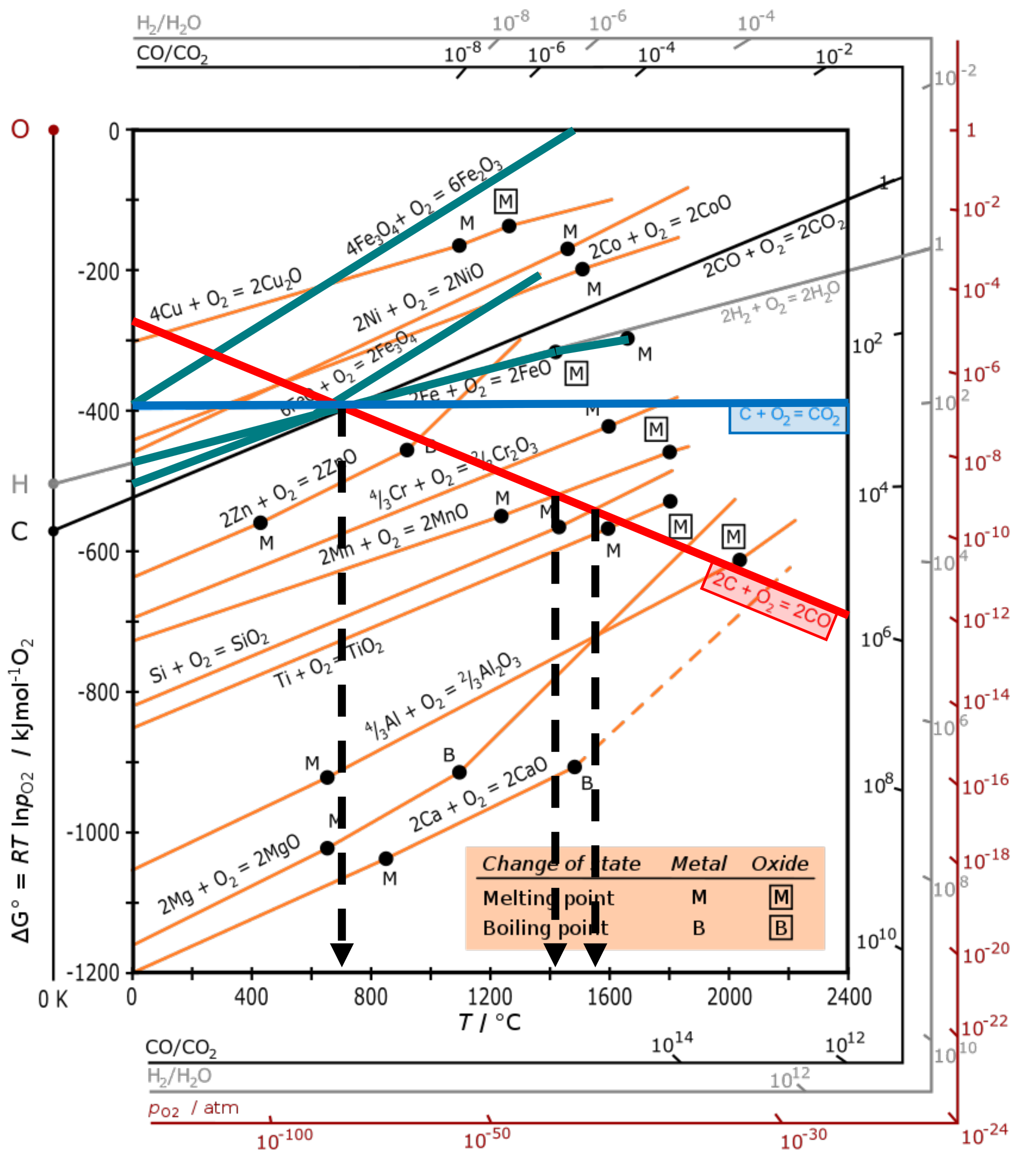
  $CaCO_3 \rightarrow CaO + CO_2$

  $MgCO_3 \rightarrow MgO + CO_2$
- In the bosh the coke burns

  $C + O_2 \rightarrow CO_2 + Heat$
- The coke reduces the molten ore. *Direct reduction*

  $FeO + C \rightarrow Fe + CO$
- Molten limestone + other slag components produce eutectic slag

  Slag floats over molten iron



Ellingham’s diagram for oxides

Line for CO has a negative slope → the stability of CO increases with increasing temperature

Oxides below the carbon line can be reduced by carbon

Reduction of FeO from 690 °C
MnO from ~ 1400 °C
SiO2 from ~ 1550 °C

Processes in blast furnace

Carbon reduces the oxides:

$FeO + C \rightarrow [Fe] + \{CO\}$

$MnO + C \rightarrow [Mn] + \{CO\}$
$SiO_2 + 2C \rightarrow [Si] + \{2CO\}$
} *alloying elements*

$P_2O_5 + 5C \rightarrow [2P] + \{5CO\}$
$SO_2 + 2C \rightarrow [S] + \{2CO\}$
} *impurities*

in molten iron (the products in square brackets)   *gas* (the products in curly brackets)

In blast furnace carbon can reduce	S, P, Cr, Mn, Si, Fe	70-90%
	Ti	10-20%

Desulfurization

- Sodium carbonate based slag

$$Na_2CO_3 + [FeS] + 2\ [C] = (Na_2S) + [Fe] + 3\ \{CO\}$$

$$Na_2CO_3 + [FeS] + 0{,}5\ [Si] = (Na_2S) + [Fe] + 0{,}5\ (SiO_2) + \{CO_2\}$$

- Calcium oxide (quicklime) based slag

$$CaO + [FeS] + [C] = (CaS) + [Fe] + \{CO_2\}$$

$$CaO + [FeS] + 0{,}5\ [Si] = (CaS) + [Fe] + 0{,}5\ (SiO_2)$$

- Calcium carbide

$$CaC_2 + [FeS] = (CaS) + [Fe] + 2\ [C]$$

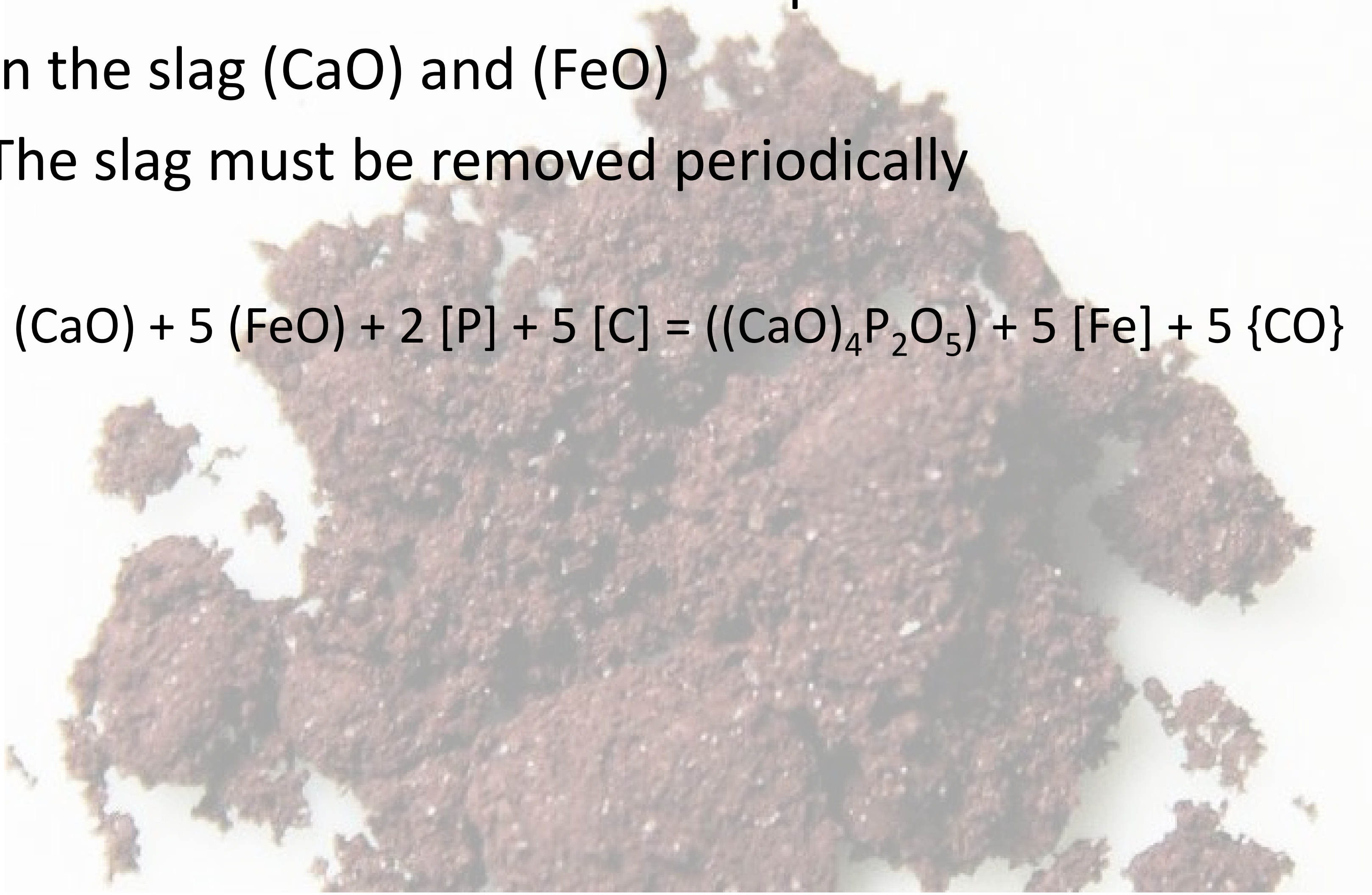
- Magnesium

$$Mg + [FeS] = (MgS) + [Fe]$$

Dephosphorization

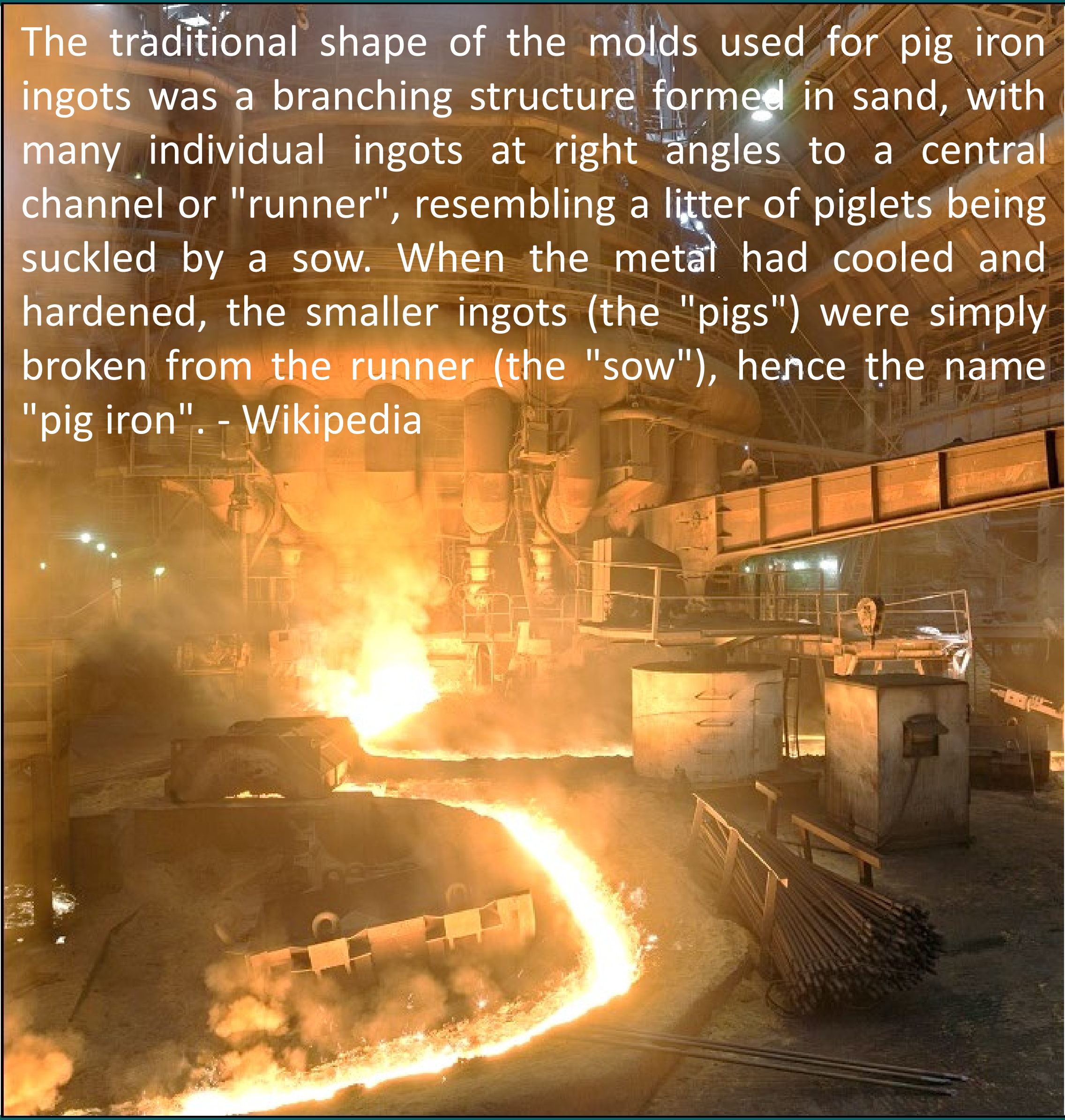
- Basic furnace interior wall is required
- In the slag (CaO) and (FeO)
- The slag must be removed periodically

$$4\ (CaO) + 5\ (FeO) + 2\ [P] + 5\ [C] = ((CaO)_4P_2O_5) + 5\ [Fe] + 5\ \{CO\}$$



Product of blast furnace

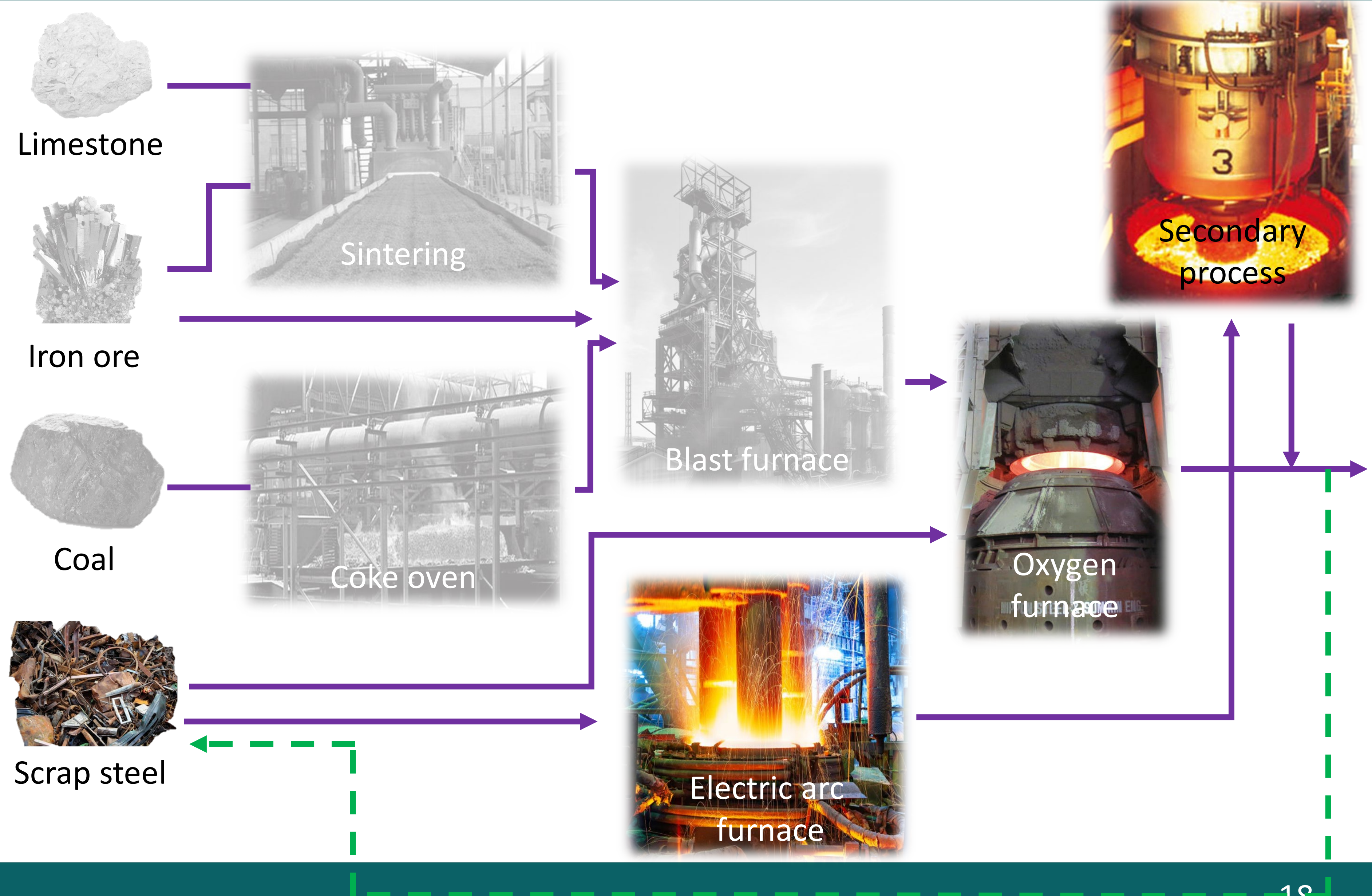
- Slag on the top
- Molten iron on the bottom
- Near eutectic (~ 4 % C)
- ”Pig iron”



The traditional shape of the molds used for pig iron ingots was a branching structure formed in sand, with many individual ingots at right angles to a central channel or "runner", resembling a litter of piglets being suckled by a sow. When the metal had cooled and hardened, the smaller ingots (the "pigs") were simply broken from the runner (the "sow"), hence the name "pig iron". - Wikipedia

Blast furnace tapping

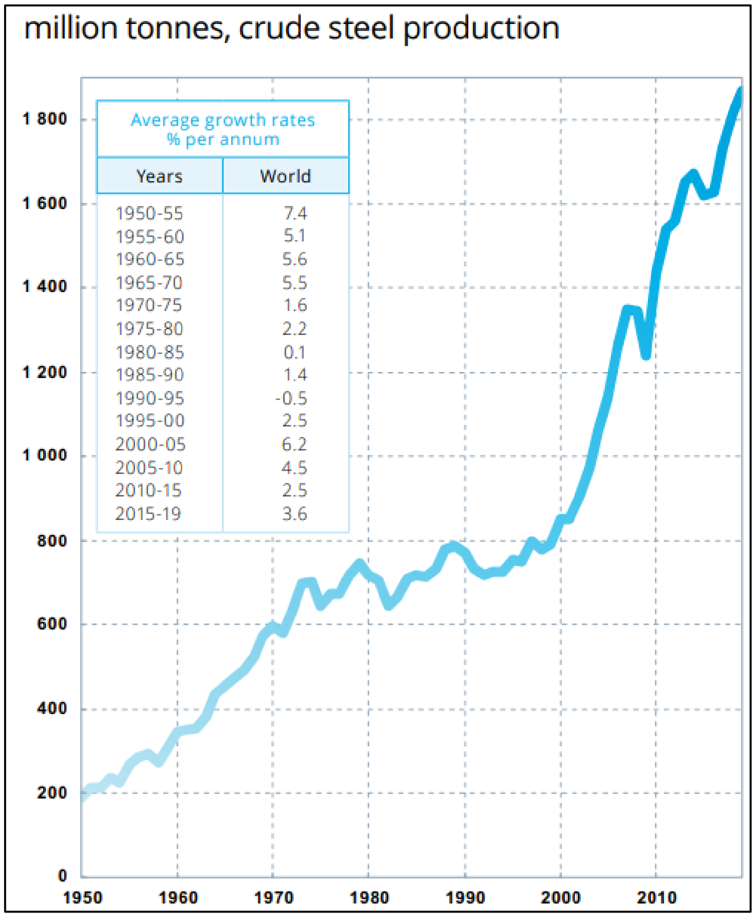
Production line of steel



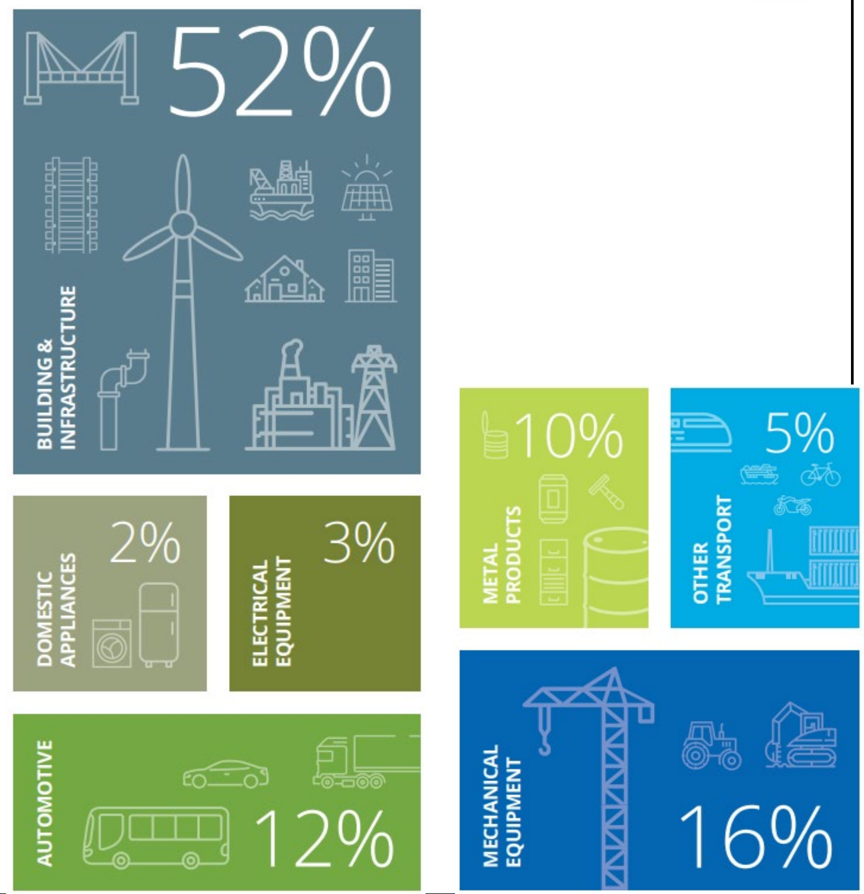
Pig iron → Steel

decrease carbon content

and impurities



Years	World
1950-55	7.4
1955-60	5.1
1960-65	5.6
1965-70	5.5
1970-75	1.6
1975-80	2.2
1980-85	0.1
1985-90	1.4
1990-95	-0.5
1995-00	2.5
2000-05	6.2
2005-10	4.5
2010-15	2.5
2015-19	3.6



Steelmaking steps

1. Charging
2. Deoxidating
3. Alloying
4. Casting
5. Refining

1. Charging

Purpose

- To decrease C, H, P content
- To increase heat
  (lower C % → higher melting point)

Oxidation

- Oxygen content from air
  (Bessemer, Thomas processes)
- Oxidation with slag (Siemens–Martin aka. open hearth, electric arc furnace)
- Oxygen converter, argon – oxygen decarburization, AOD

	Million tonnes	Oxygen %	Electric %	Open hearth %	Other %	Total %
Austria	7.4	90.4	9.6	-	-	100.0
Belgium(e)	7.8	68.3	31.7	-	-	100.0
Bulgaria	0.6	-	100.0	-	-	100.0
Croatia	0.1	-	100.0	-	-	100.0
Czech Republic	4.4	94.7	5.3	-	-	100.0
Finland(e)	3.5	66.8	33.2	-	-	100.0
France	14.4	69.6	30.4	-	-	100.0
Germany	39.7	70.0	30.0	-	-	100.0
Greece	1.4	-	100.0	-	-	100.0
Hungary	1.8	80.1	19.9	-	-	100.0
Italy	23.2	18.1	81.9	-	-	100.0
Luxembourg	2.1	-	100.0	-	-	100.0
Netherlands	6.7	100.0	-	-	-	100.0
Poland	9.0	54.9	45.1	-	-	100.0
Portugal	2.0	-	100.0	-	-	100.0
Romania(e)	3.4	67.6	32.4	-	-	100.0
Slovak Republic	5.3	93.0	7.0	-	-	100.0
Slovenia	0.6	-	100.0	-	-	100.0
Spain	13.6	31.2	68.8	-	-	100.0
Sweden	4.7	66.2	33.8	-	-	100.0
United Kingdom	7.2	78.8	21.2	-	-	100.0
European Union (28)	158.8	59.1	40.9	-	-	100.0
Turkey	33.7	32.2	67.8	-	-	100.0
Others	5.2	49.1	50.9	-	-	100.0
Other Europe	39.0	34.4	65.6	-	-	100.0
Russia(e)	71.9	64.1	33.6	2.3	-	100.0
Ukraine	20.8	71.2	5.8	23.1	-	100.0
Other CIS	8.0	50.7	49.3	-	-	100.0
CIS	100.7	64.5	29.0	6.5	-	100.0
Canada(e)	12.9	60.6	39.4	-	-	100.0
Mexico	18.5	22.8	77.2	-	-	100.0
United States	87.8	30.3	69.7	-	-	100.0
NAFTA	119.1	32.4	67.6	-	-	100.0
Argentina	4.6	45.5	54.5	-	-	100.0
Brazil	32.2	76.1	22.2	-	1.7	100.0
Chile	0.9	76.6	23.4	-	-	100.0
Venezuela	0.1	-	100.0	-	-	100.0
Others	3.9	6.4	93.6	-	-	100.0
Central and South America	41.8	66.1	32.6	-	1.3	100.0
Egypt(e)	7.3	2.5	97.5	-	-	100.0
South Africa	5.7	58.8	41.2	-	-	100.0
Other Africa(e)	3.8	10.6	89.4	-	-	100.0
Africa	16.7	23.5	76.5	-	-	100.0
Iran	25.6	9.6	90.4	-	-	100.0
Saudi Arabia	8.2	-	100.0	-	-	100.0
Other Middle East(e)	10.4	-	100.0	-	-	100.0
Middle East	44.2	5.5	94.5	-	-	100.0
China(e)	996.3	89.6	10.4	-	-	100.0
India	111.2	43.8	56.2	-	-	100.0
Japan	99.3	75.5	24.5	-	-	100.0
South Korea	71.4	68.2	31.8	-	-	100.0
Taiwan, China	22.0	61.9	38.1	-	-	100.0
Other Asia(e)	40.9	36.3	63.7	-	-	100.0
Asia	1 341.1	81.6	18.4	-	-	100.0
Australia	5.5	73.2	26.8	-	-	100.0
New Zealand	0.7	100.0	-	-	-	100.0
Total of above countries	1 867.5	71.9	27.7	0.3	0.0	100.0

The countries in this table accounted for approximately 99.9% of world crude steel production in 2019.
(e) = estimate.

Worldsteel Association: World Steel in Figures 2020

2. Deoxidating

Purpose

- To reduce increased [O] content due to charging

Deoxidizing elements

- Mn, Si, Al, (Ca, Ti, Zr, Mg, etc.) (remember Ellingham's diagram) → Slag formation
- [FeO] + Me → Fe + (MeO)

Vacuum deoxidation

- Reducing partial pressure
- CO is forming, which is removed by vacuum

2. Deoxidized steel

Rimmed

- Little or no deoxidizing element
- P, S segregation in the middle → „pure" Fe rim around
- <0.25 % C, <0.6 % Mn
- For cold-working: bending, heading, drawing

Capped

- Starts as rimmed
- Cap = covering the ingot, or deoxidizing element
- Less segregation and impurities
- Sheet and strip metals, because of good surface conditions

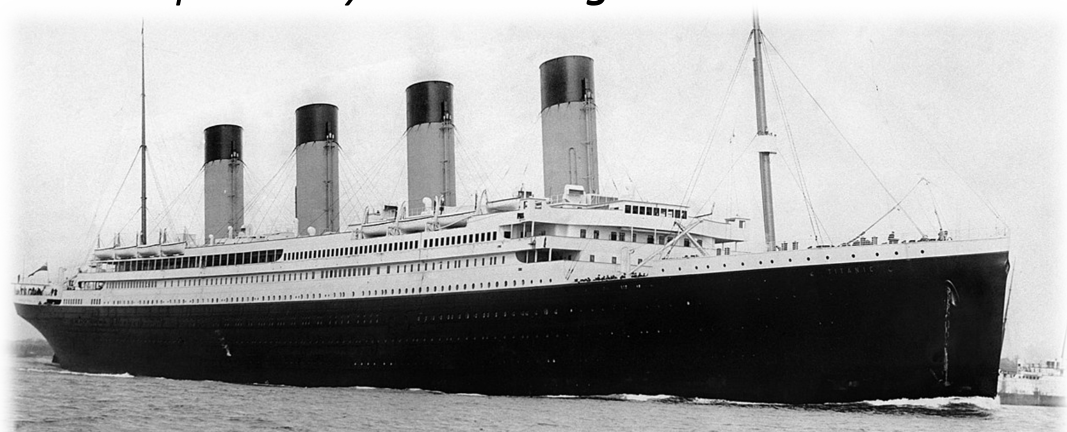
Semi-killed

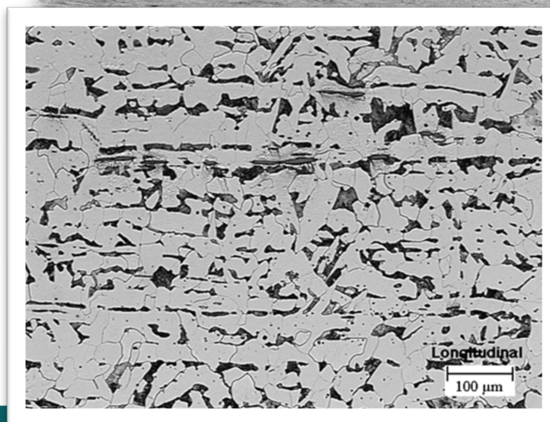
- Mostly deoxidized but CO blowholes
- 0.15 – 0.25 % C
- For rolling and drawing

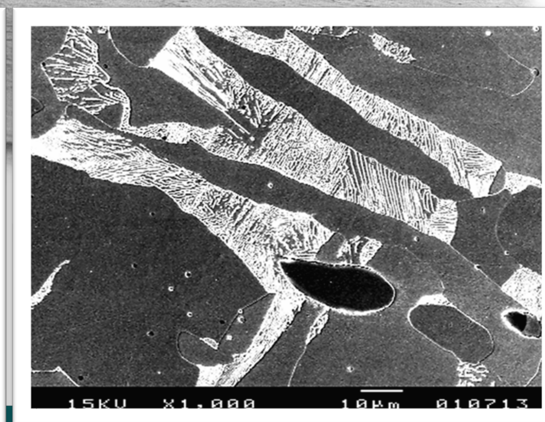
Killed

- Completely deoxidized
- Mn, Si, Al
- Shrinkage defects
- Alloy steels, stainless steels, C > 0.25 %
- For casting

„The fairly ***high oxygen*** *and* ***low silicon*** *content means that the steel has only been partially deoxidized, yielding a semikilled steel. The* ***phosphorus content is slightly higher*** *than normal, while the* ***sulfur content is quite high,*** *accompanied by a* ***low manganese*** *content."*

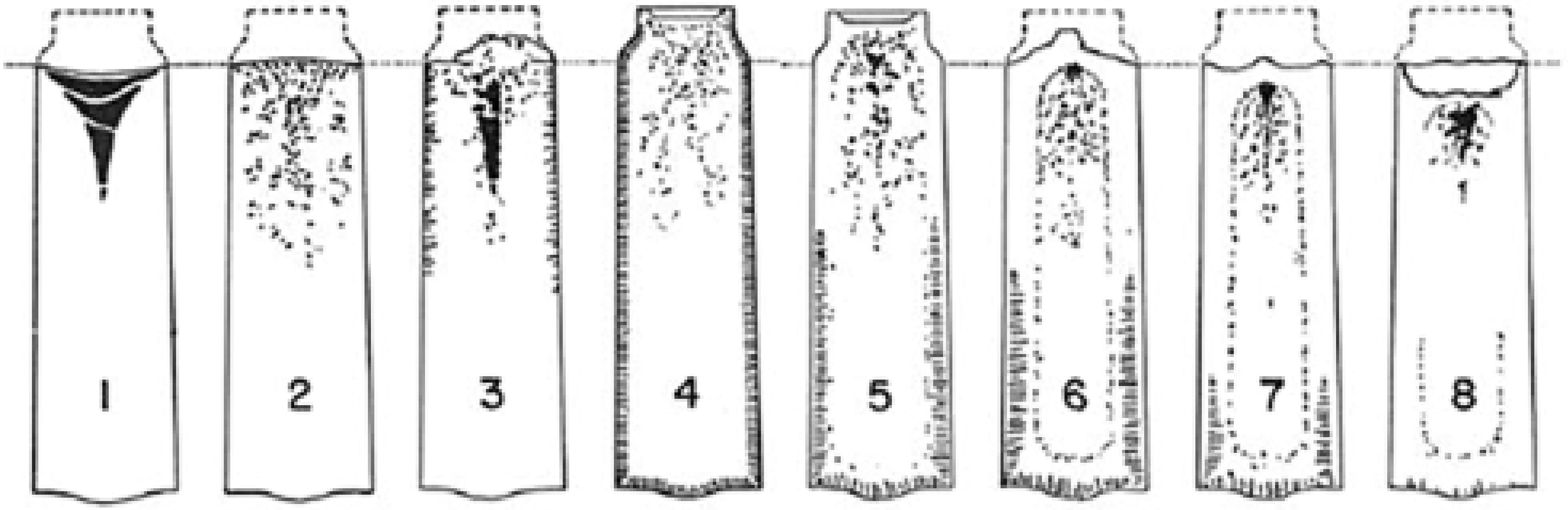






2. Deoxidized steel

Killed Capped Rimmed



3. Alloying

- Alloying elements are added
  - Corrosion, heat resistance
  - Resistance against creep
  - Strenghtening
  - Formability, weldability
- During steel making, or as a secondary process
  - Commonly in ladles, including deoxidation, degassing
- Usually in forms of bulk ferroalloys

Alloying element prices on London Metal Exchange

https://www.lme.com/

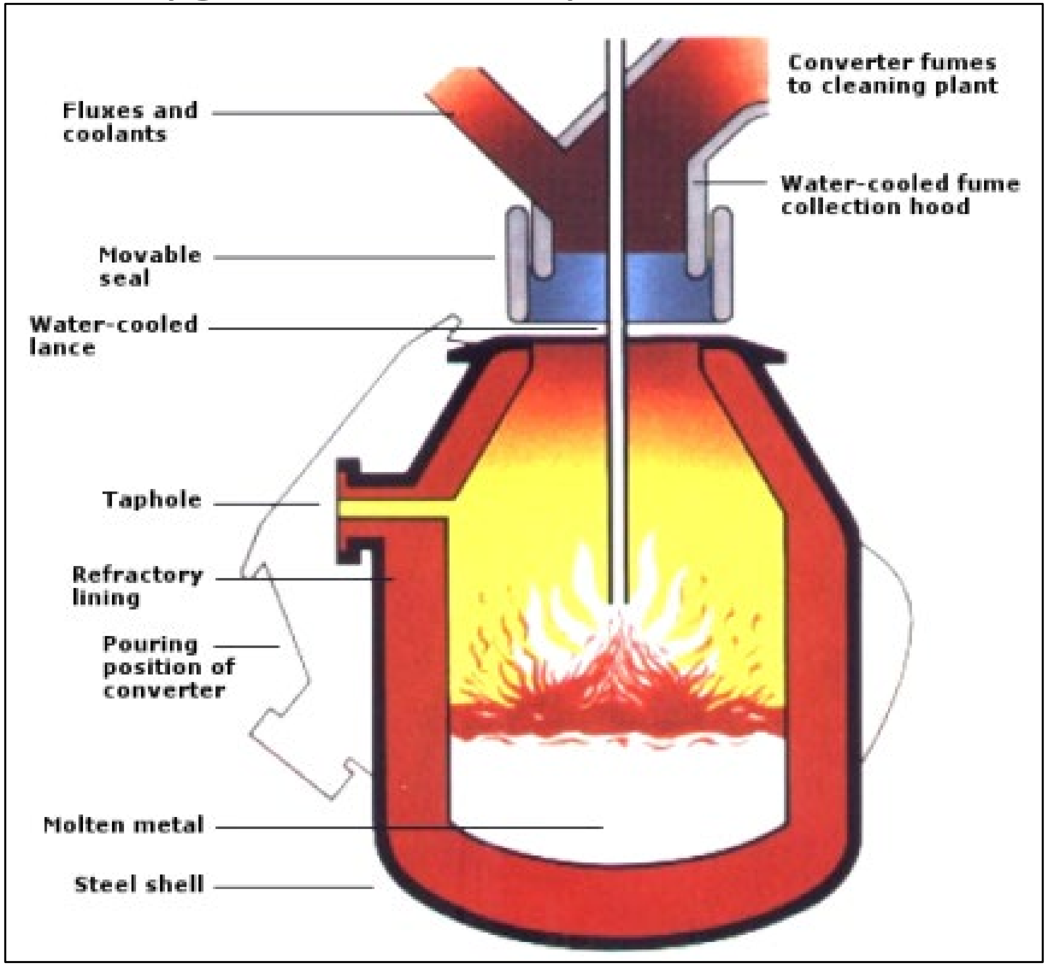
Ferro manganese

Ferro chrome

Ferro nickel

Oxygen converters

Basic oxygen steelmaking, also known as Linz–Donawitz-steelmaking or the oxygen converter process



Oxygen converters

1. Molten pig iron is poured into the ladle
2. Pretreating: desulfurization, dephosphorization
3. Charging: steel or iron scrap (25 – 30 %, high oxygen content), pig iron: 4% C, 0.2–0.8% Si, 0.08%–0.18% P, and 0.01–0.04% S, all of which can be oxidised by the supplied oxygen except sulfur (which requires reducing conditions).
4. Lance "blows" 99% pure oxygen over the hot metal → CO and CO_2 forms, temp. 1700 °C
5. Fluxes (burnt lime, dolomite) added to form slag → basicity
6. After 20 min. 0.3–0.9% C, 0.05–0.1% Mn, 0.001–0.003% Si, 0.01–0.03% S and 0.005–0.03% P
7. Pouring: steel and then slag

Argon oxygen decarburization

- For stainless steels and high grade alloys
- After initial melting the metal is then transferred to an AOD vessel where it will be subjected to three steps of refining; decarburization, reduction, and desulfurization.
- Argon is reducing the partial pressure of {CO} thus the **decarburization** is more efficient

$4\,[Cr] + 3\,\{O_2\} \rightarrow 2\,(Cr_2O_3)$

$(Cr_2O_3) + 3\,[C] \rightarrow 3\,\{CO\} + 2\,[Cr]$

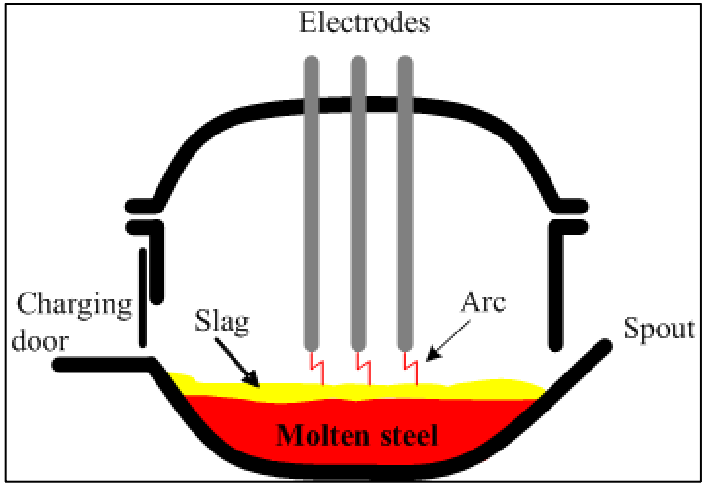
Reduction

Reduction of (Cr_2O_3) with higher affinity alloys as: Al, Si

Desulfurization

$[S] + (CaO) \rightarrow (CaS) + [O]$

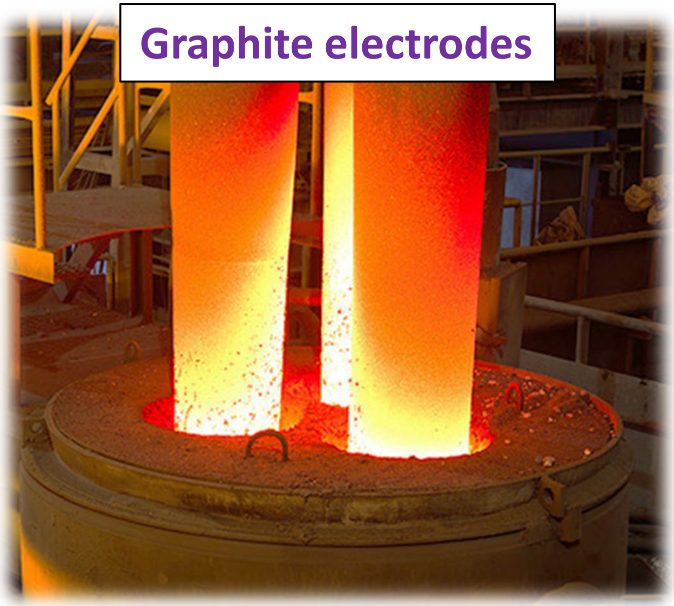
Electric arc furnace



A typical alternating current furnace is powered by a three-phase electrical supply and therefore has three electrodes.

350 – 800 mm diameter
1800 – 3600 mm length
Consumed after 5 – 8 hours

Graphite electrodes



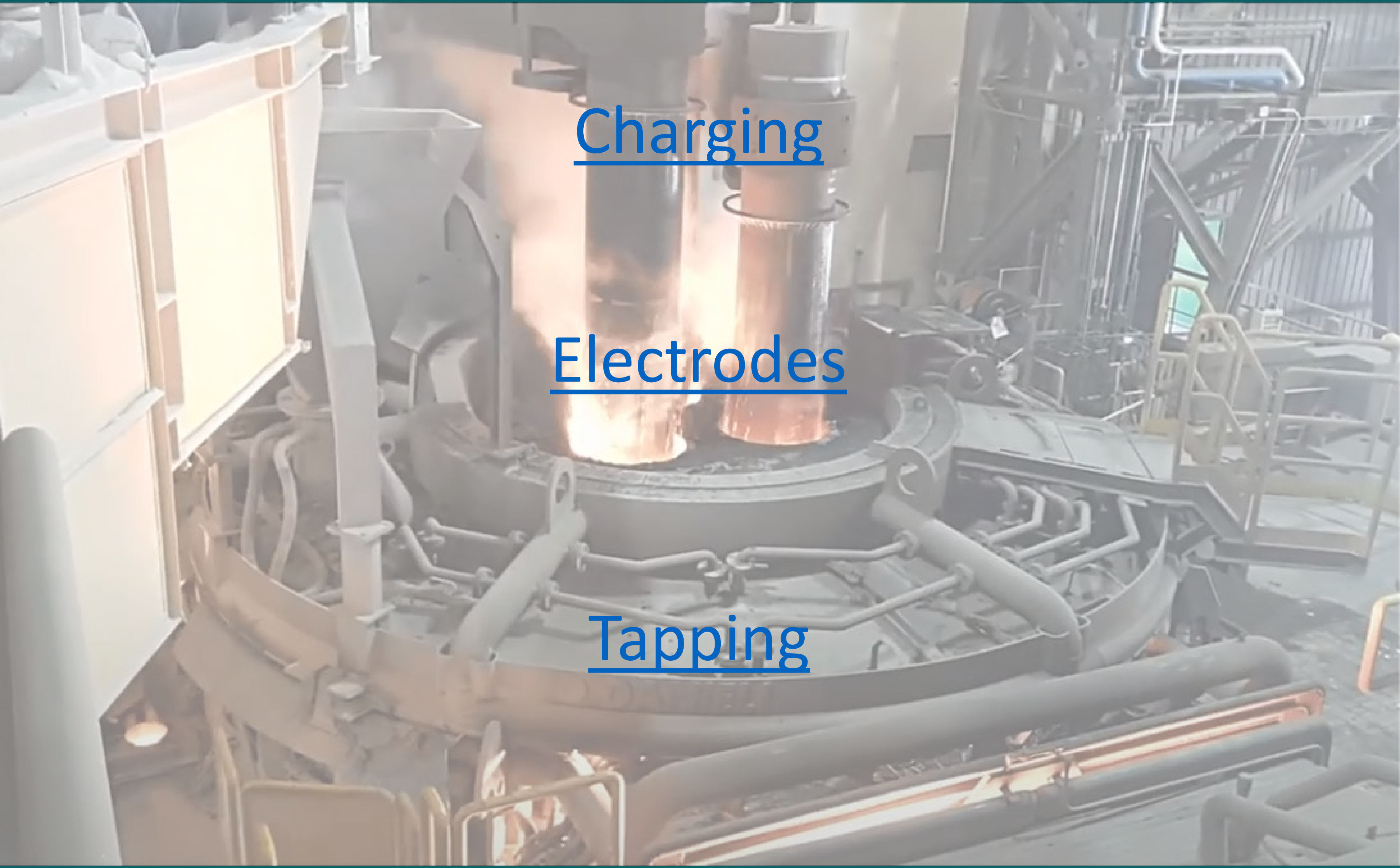
Electric arc furnace

- 0.25 – 350 tonnes capacity
- 100 – 600 Volts, ~ 40000 Amps
- Usually basic refractory walls: CaO, MgO (reducing S % and P %)
- Inert atmosphere → oxidation is done by scrap or oxygen lance
- At higher temperatures (> 3000 °C in the furnace) nitrogen dissociates:

$$\{N_2\} \rightarrow 2\ (N)$$

  - Disadvantage because of aging
  - Advantage if alloying
- For 1 tonne of steel ~ 440 kWh power is required
- Allows steel to be made from a 100% scrap metal feedstock

Electric arc furnace



Charging

Electrodes

Tapping

Induction furnace

- Heat is applied by induction heating of metal
- Heat is generated within the furnace's charge itself
- Charge materials must be clean of oxidation products and of a known composition
- The temperature of the material is no higher than required to melt it; this can prevent loss of valuable alloying elements
- Capacity ~ 1 kg – 100 tonnes
- Fe, steel, Cu, Al

Ingot casting

- Solidification: shrinking, crystallisation, grain-arrangement, mircostructure, segregation

Casting individually

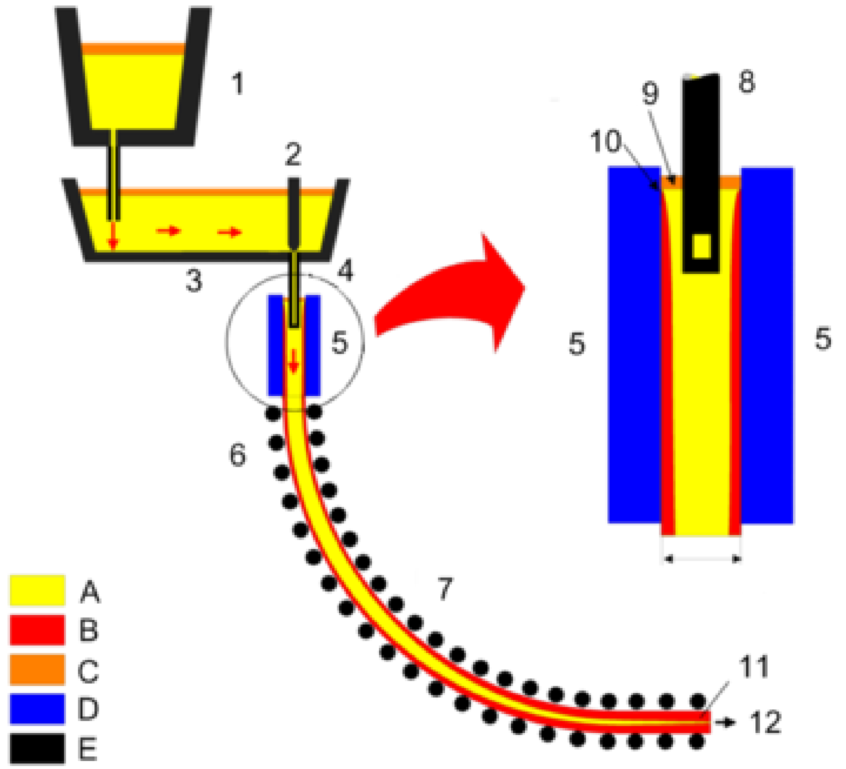
- Simple, productive
- Spattering

Bottom pouring

- Homogenous
- Slow, oxidation

Continous casting

- Molten metal is solidified into a "semifinished" billet, bloom, or slab for subsequent rolling in the finishing mills.



1: Ladle. 2: Stopper. 3: Tundish.
4: Shroud. 5: Mold. 6: Roll support.
7: Turning zone. 8: Shroud.
9: Bath level. 10: Meniscus.
11: Withdrawal unit. 12: Slab.

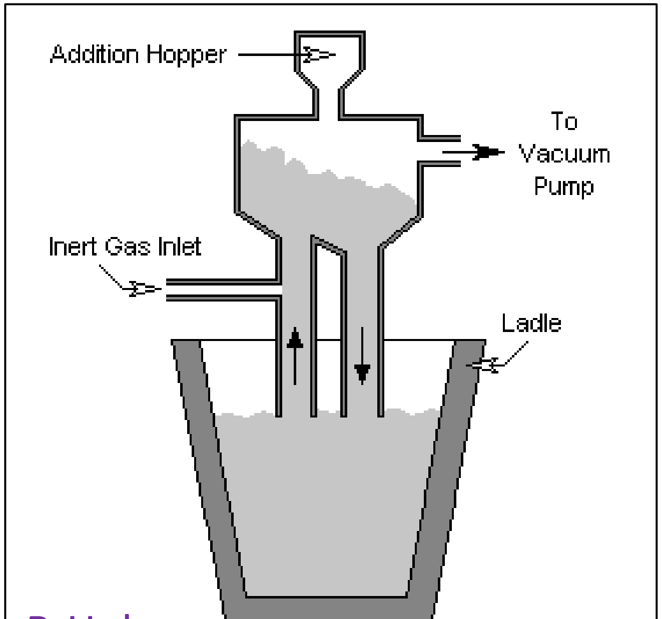
A: Liquid metal. B: Solidified metal.
C: Slag. D: Water-cooled copper plates.
E: Refractory material

[Ingot casting]

[Continous casting]

5. Refining

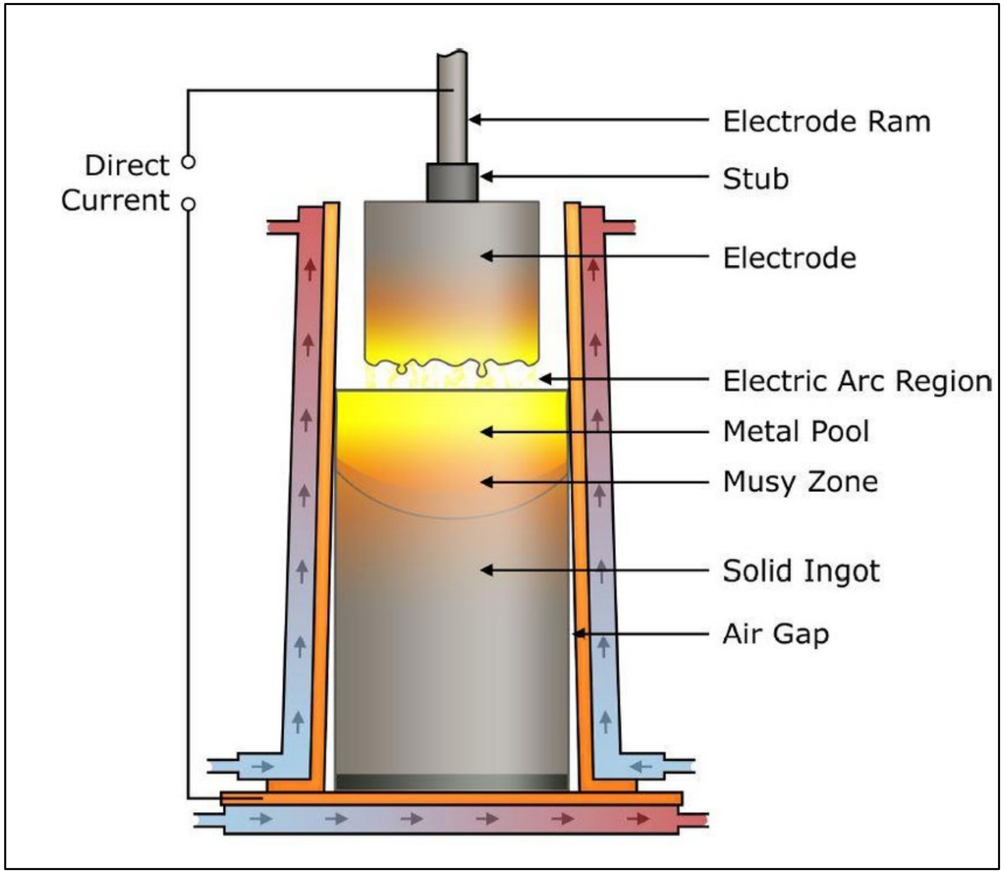
- Remelting and solidification
  - Decrease the dissolved gas content and the amount of inclusions
  - Produce a homogeneous fine-grained crystal structure
  - Produce a homogeneous distribution of alloying elements
- Ladle metallurgy, ladle refining, or secondary steelmaking
  - Deoxidization
  - Degassing
  - Desulfurization - as low as 0.002%
  - Microcleanliness
  - Inclusion morphology
  - Mechanical properties



R-H degasser

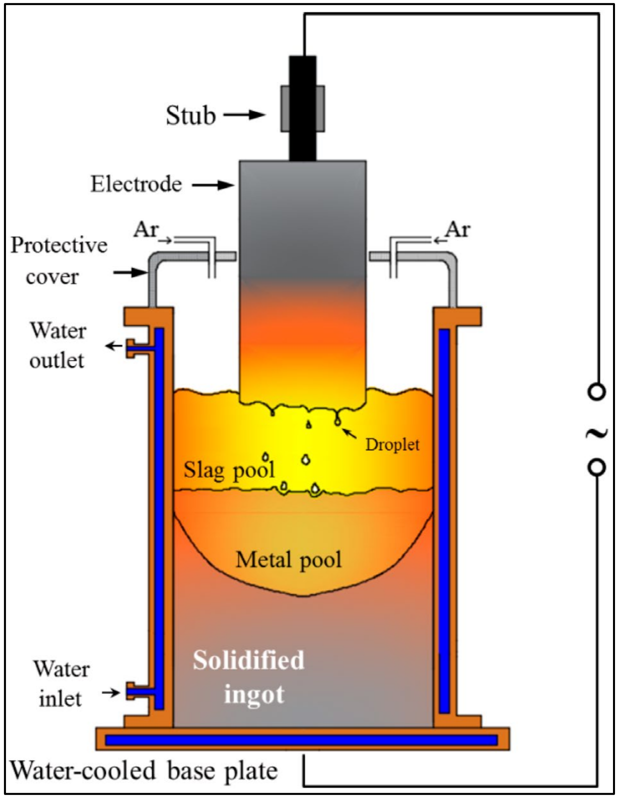
Vacuum arc remelting

- Starting ingot is the electrode
- Vacuum
- Several kA
- Cu crucible
- Air gap
  → no arc
- Stainless steels,
  Ti-alloys
  Alloy steels



Electro-slag remelting

- As-cast alloy as a consumable electrode
- AC current
- New ingot is covered in slag
- Metal droplets travel through the slag to the bottom
- Highly reactive slags (calcium fluoride, lime, alumina, or other oxides are usually the main components)



Thank you for your attention!