Department of Materials Science and Engineering

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 ways to gain the metallic parts from ore:

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

↑ Costs ↓

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

$TiCl_4 + 2Mg \rightarrow [Ti] + 2MgCl_2$

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 initial 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

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

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

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

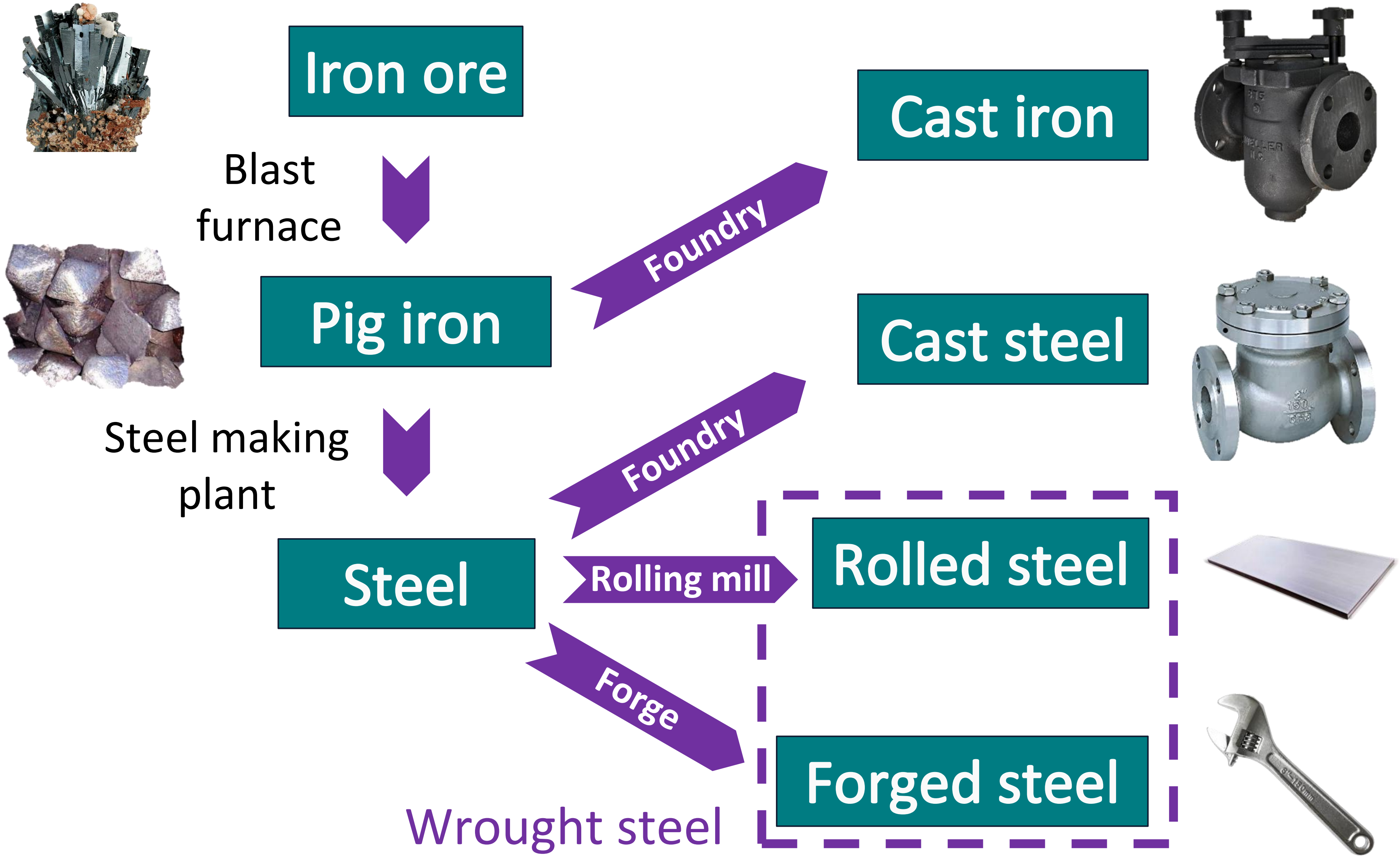
Oxidation

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

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

Foundry

Cast iron

Steel making plant

Steel

Foundry

Cast steel

Rolling mill

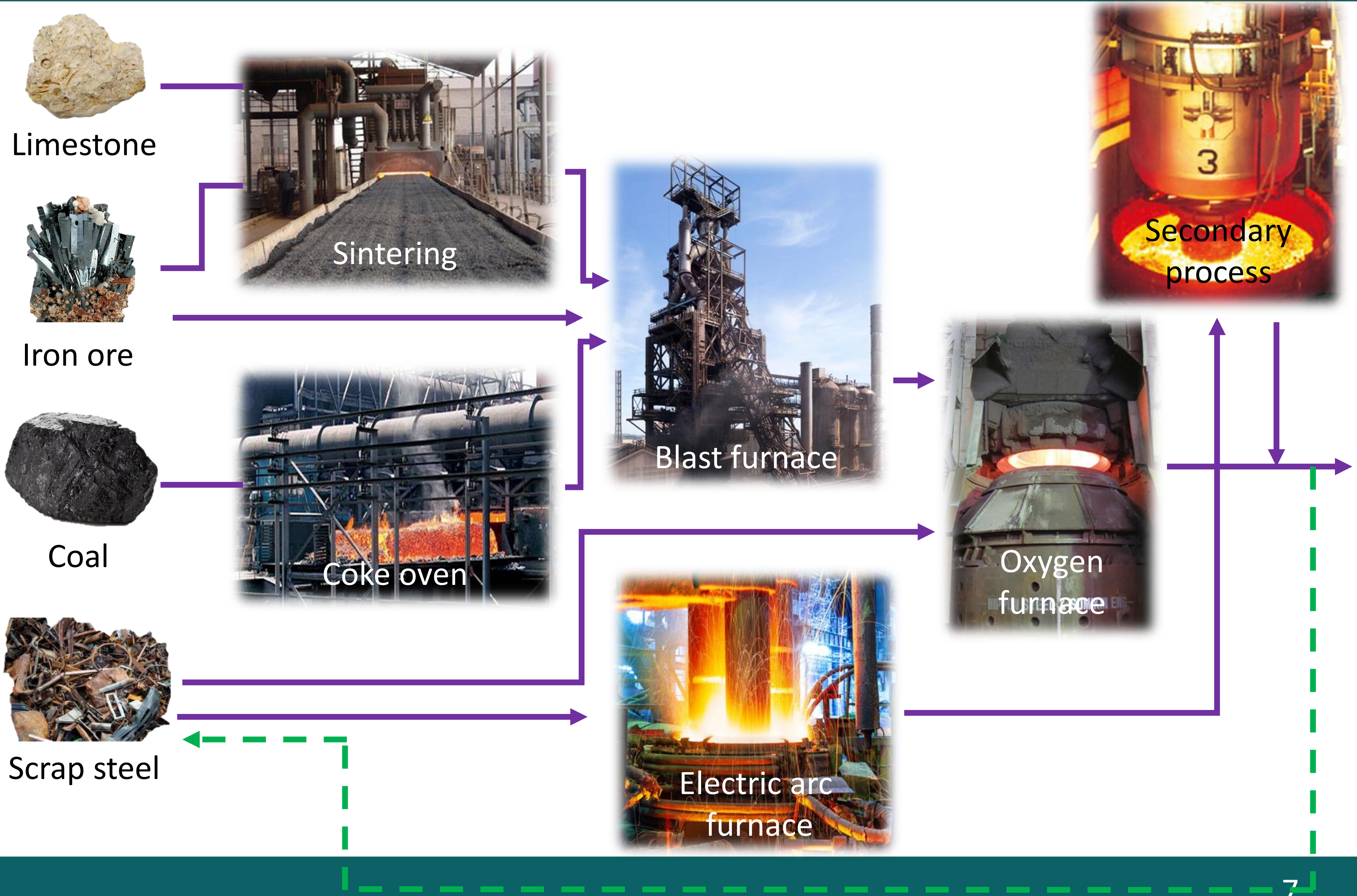
Rolled steel

Forge

Forged steel

Wrought steel

Production line of steel



Limestone

Iron ore

Coal

Scrap steel

Sintering

Coke oven

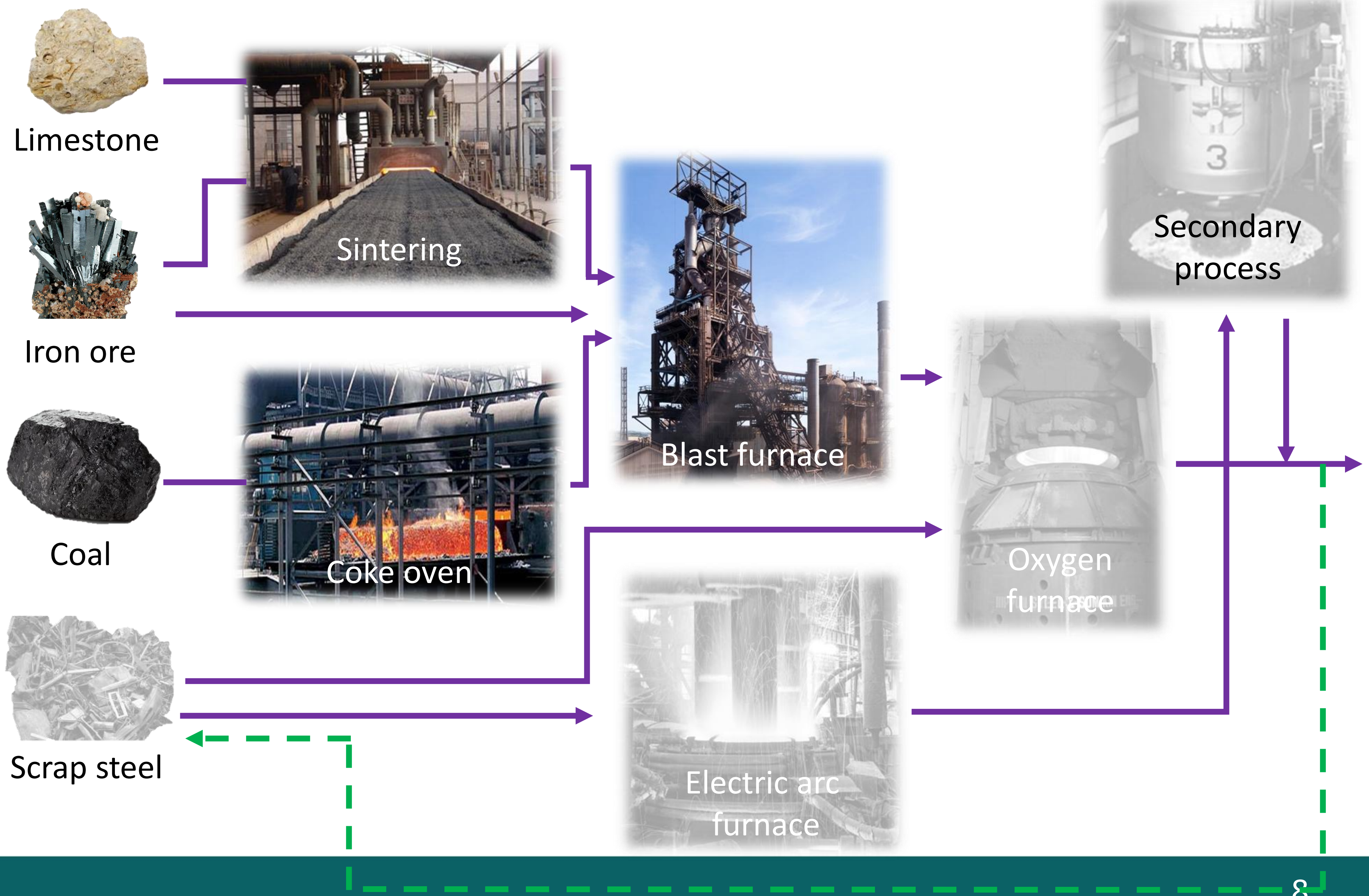
Blast furnace

Oxygen furnace

Electric arc furnace

Secondary process

Production line of iron



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Oxygen furnace

Secondary process

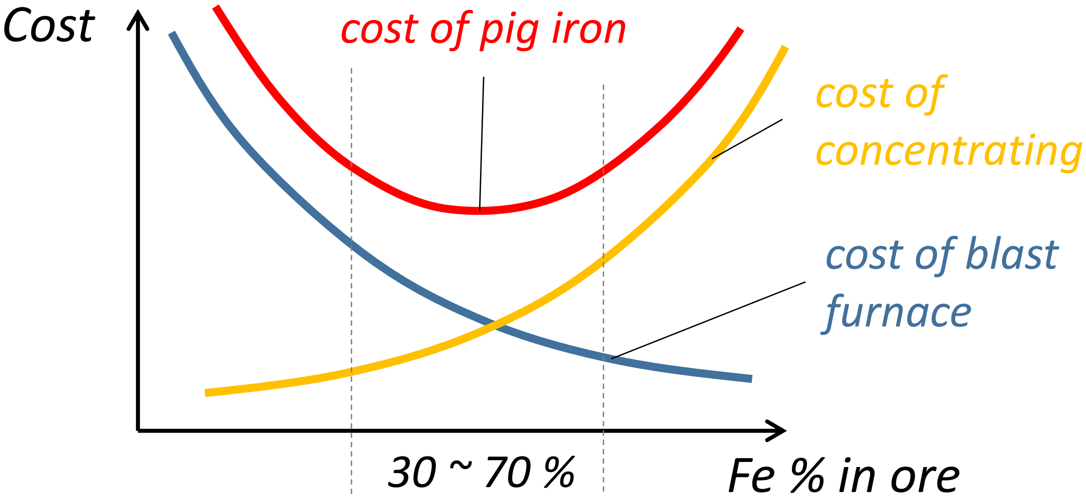
Iron making

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

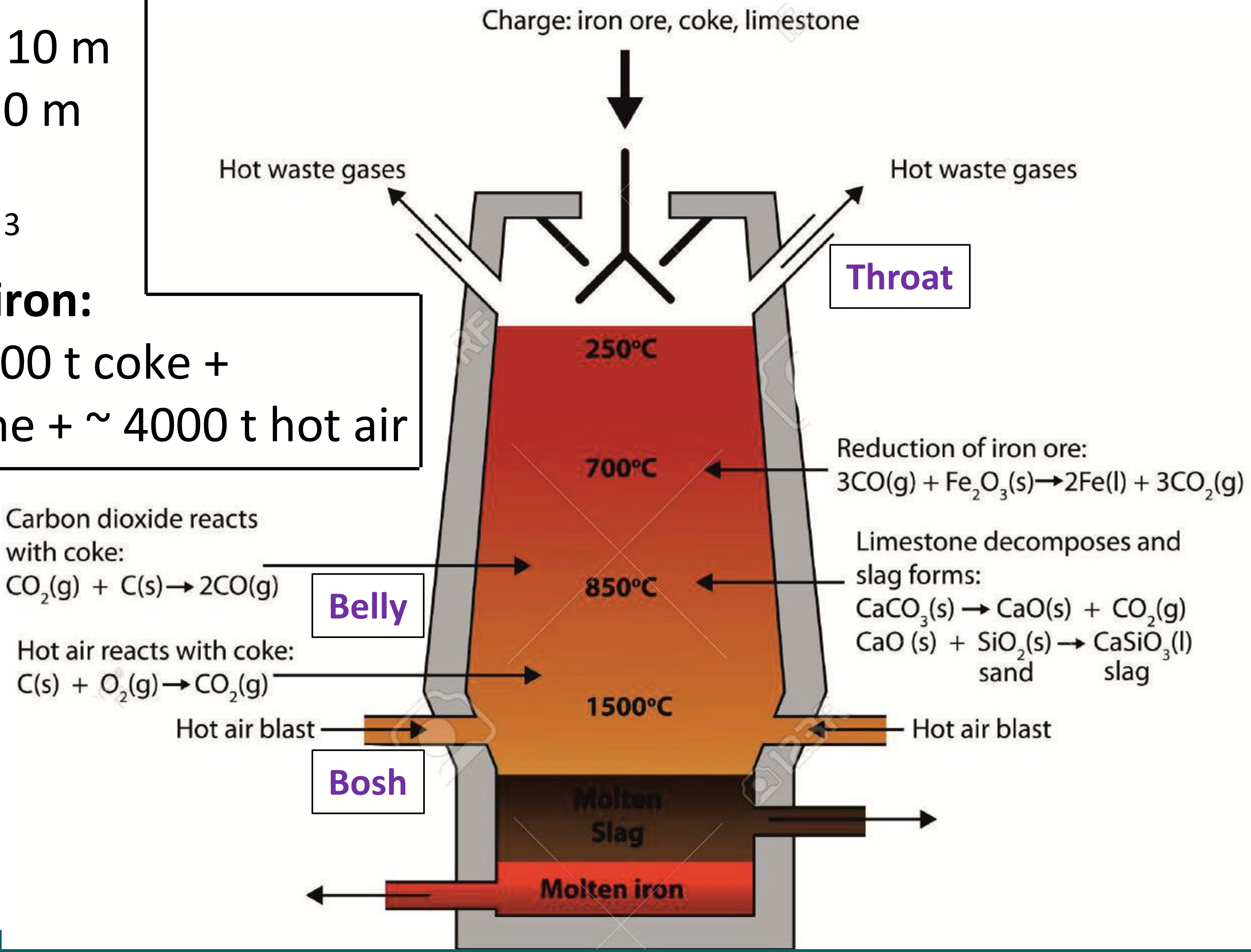
Volume:

300 – 5000 m^3

For 1000 t of iron:

2000 t ore + 800 t coke +

500 t limestone + ~ 4000 t hot air

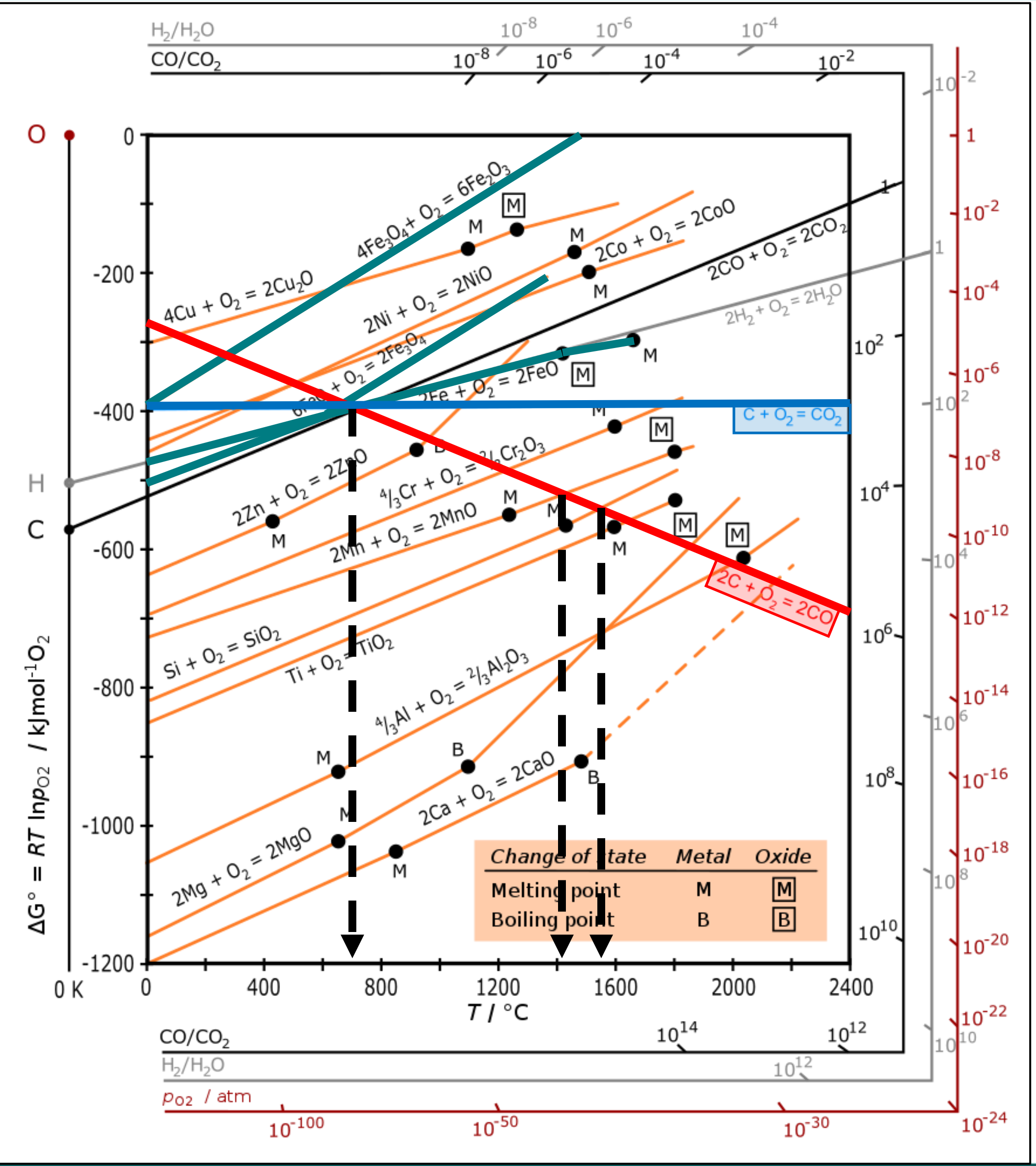


Processes in blast furnace

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
  $C + O_2 \rightarrow CO_2 + \text{Heat}$
- 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

Thermodynamics



Ellingham’s diagram for oxides

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

Oxides above the carbon line can be reduced by carbon

Reduction of FeO from 690 °C

MnO from ~ 1400 °C

SiO_2 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

gas

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

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

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

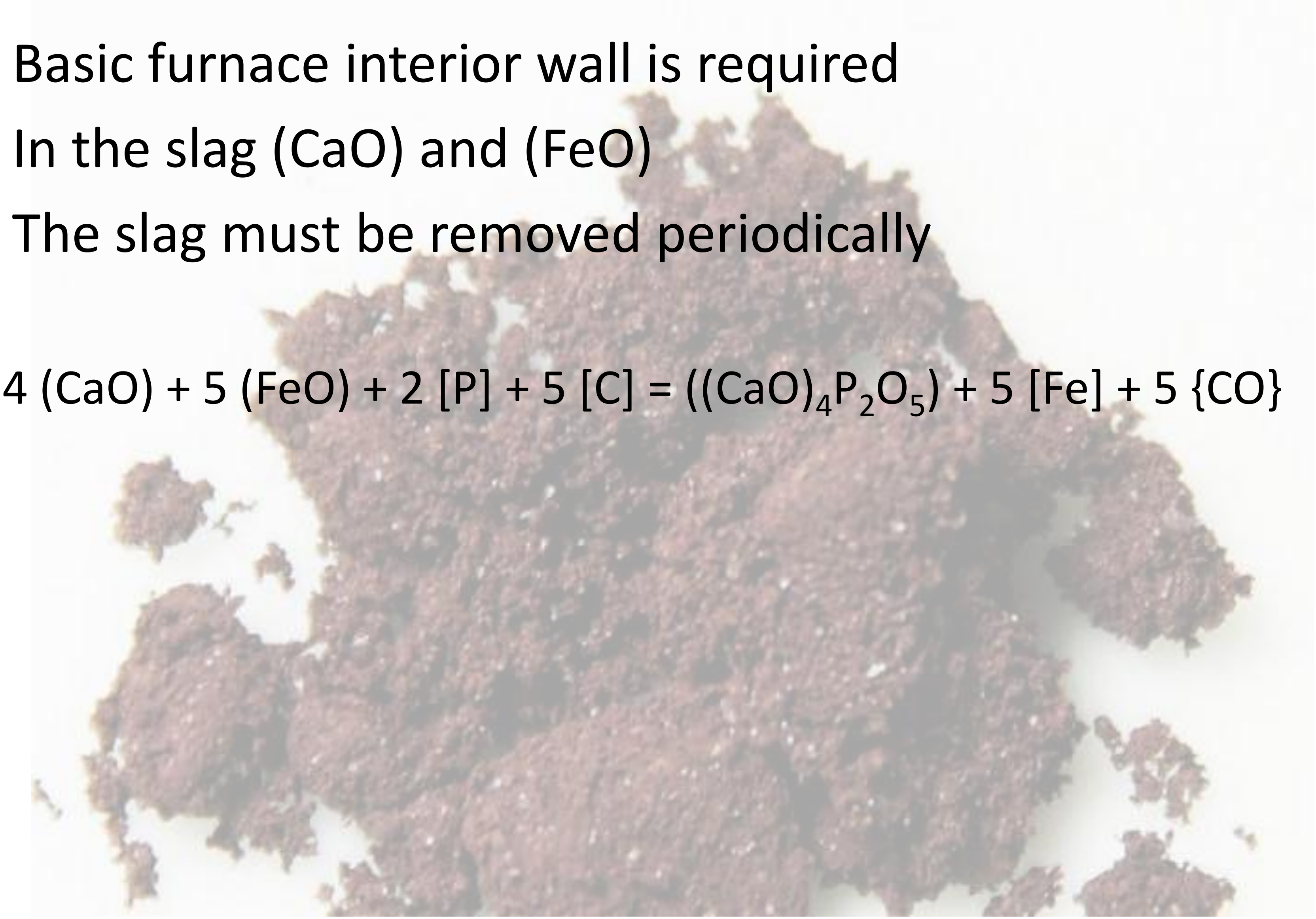
- Calcium carbide

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

- Magnesium

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

Dephosphorization



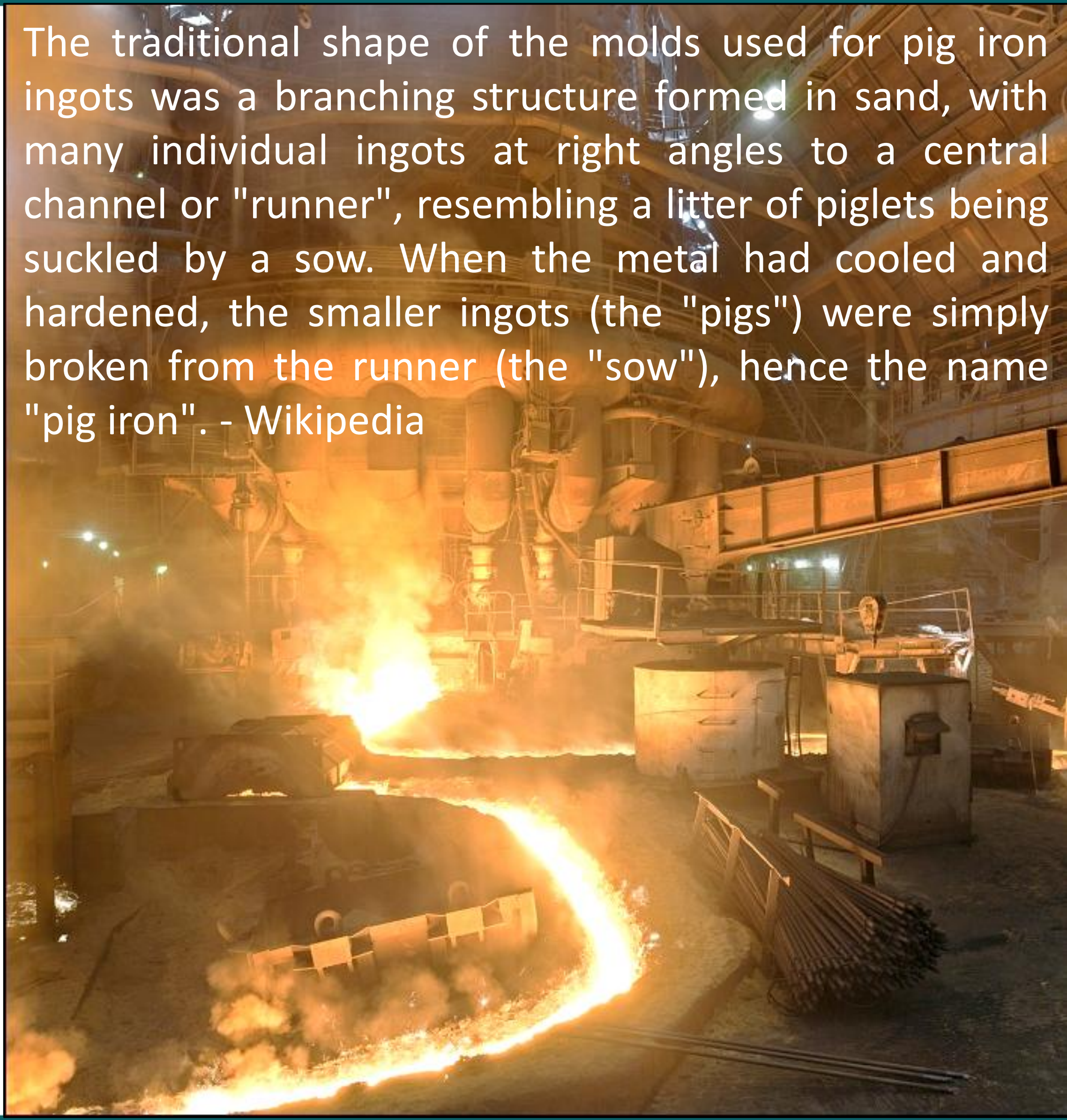
- Basic furnace interior wall is required
- In the slag (CaO) and (FeO)
- The slag must be removed periodically

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

Product of blast furnace

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

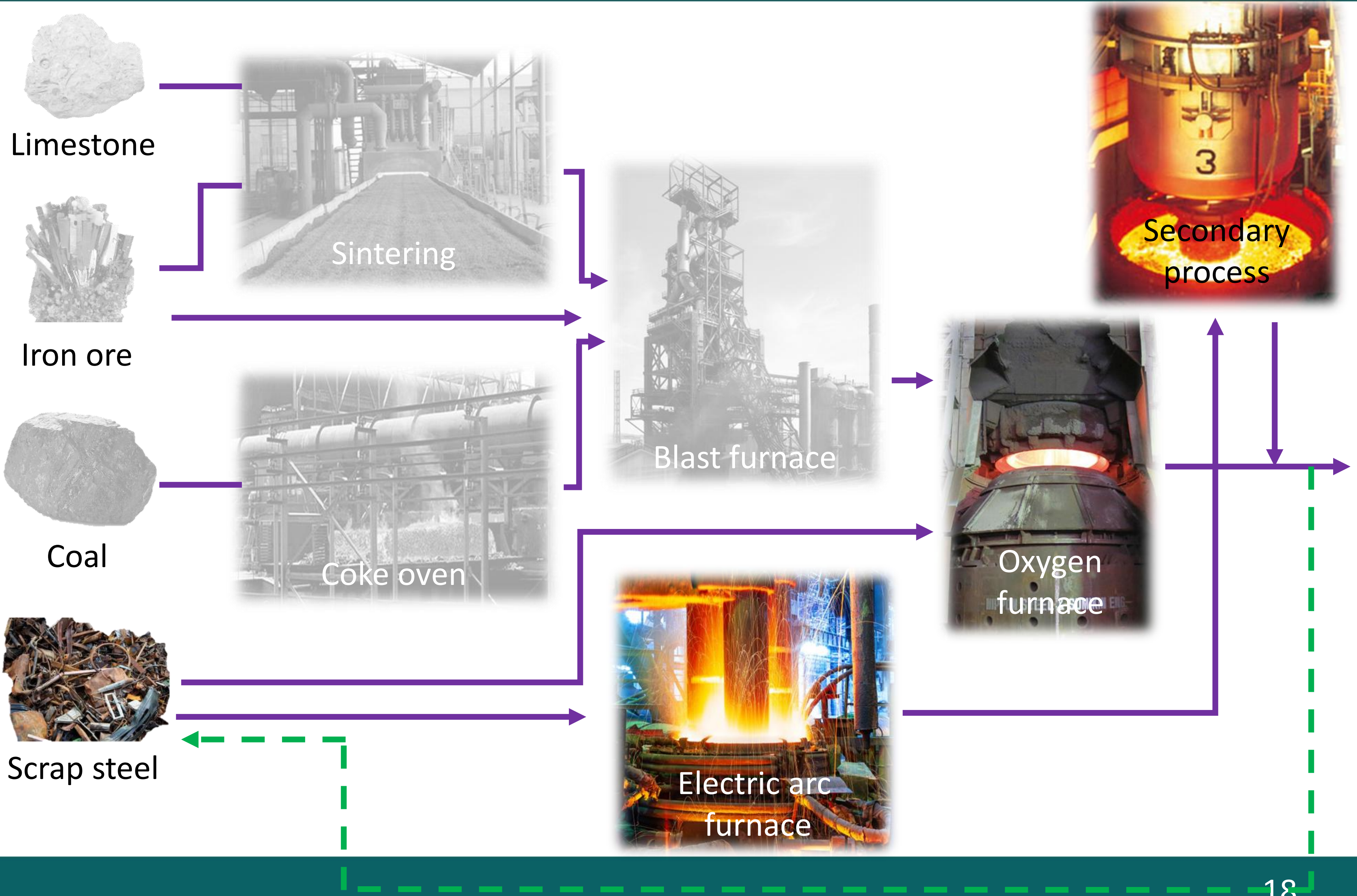
The traditional shape of the molds used for pig iron ingots was a branching structure formed in sand, with many individual ingots at right angles to a central channel or "runner", resembling a litter of piglets being suckled by a sow. When the metal had cooled and hardened, the smaller ingots (the "pigs")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



Blast furnace tapping

[Blast furnace tapping]

Production line of steel



Limestone

Iron ore

Coal

Scrap steel

Sintering

Coke oven

Blast furnace

Electric arc furnace

Oxygen furnace

Secondary process

Steelmaking

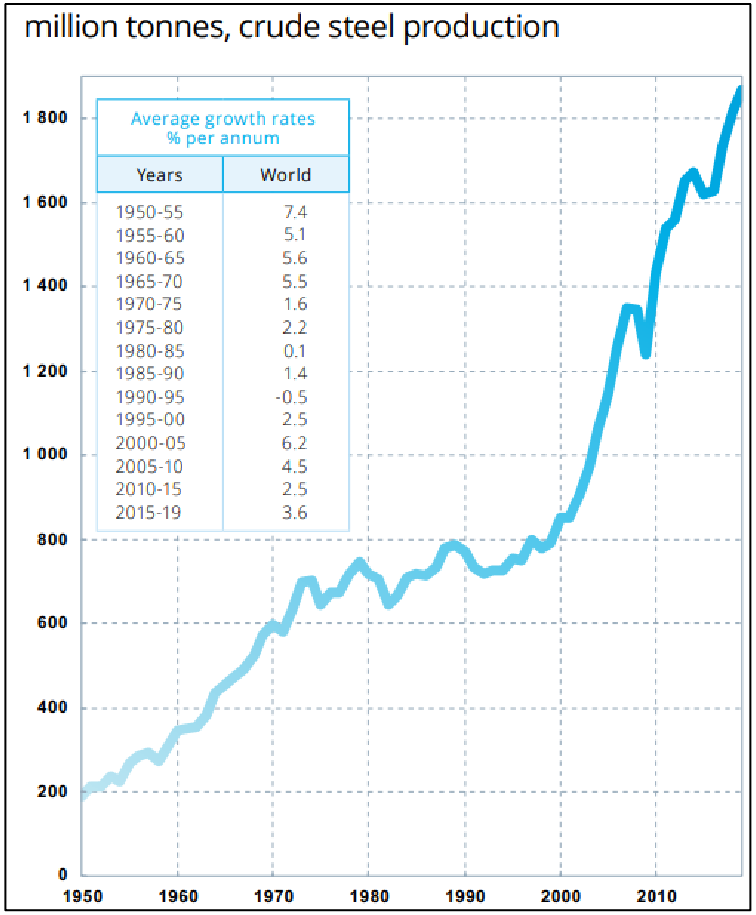
Pig iron

decrease carbon content

→

and impurities

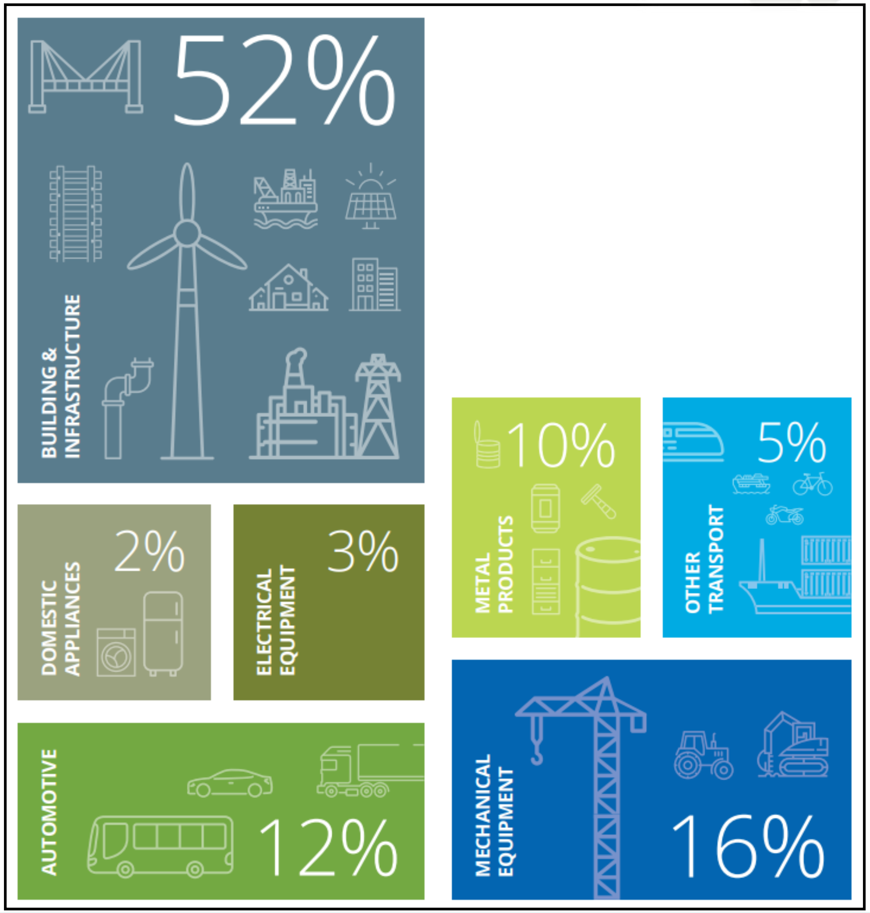
Steel



million tonnes, crude steel production

Average growth rates
% per annum

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



Worldsteel Association: World Steel in Figures 2020

Steelmaking steps

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

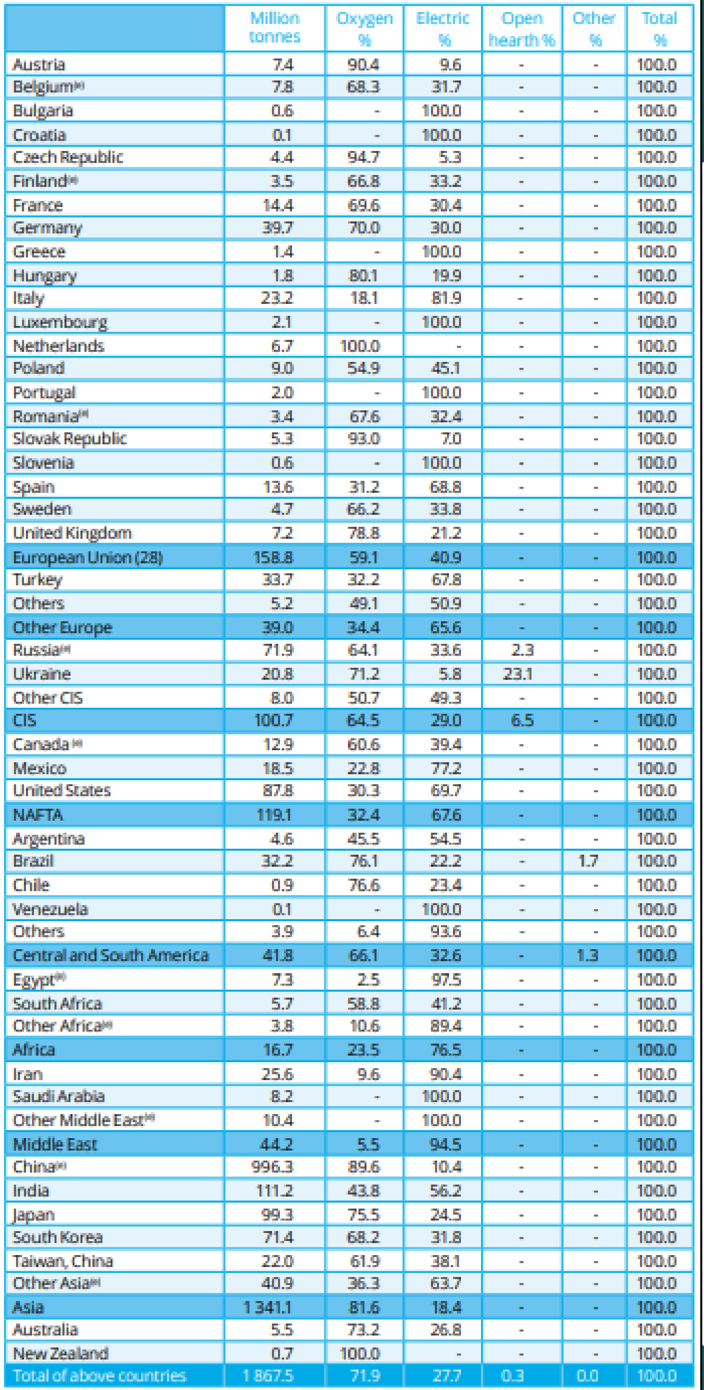
1. Charging

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. Dezoxidating

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

2. Deoxidized steel

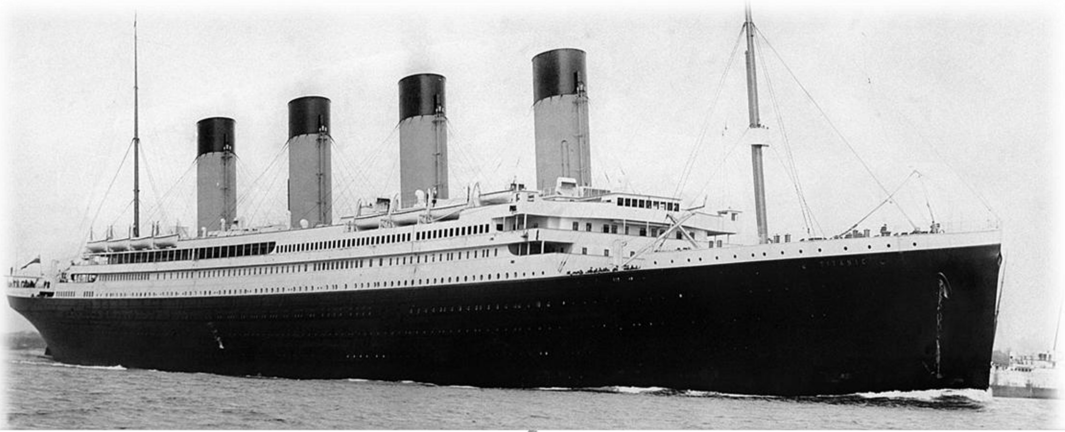
Semi-killed

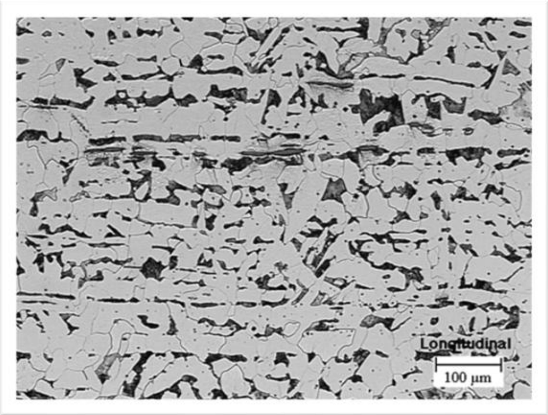
- Mostly deoxidized but CO blowholes
- 0.15 – 0.25 % C
- For rolling and drawing

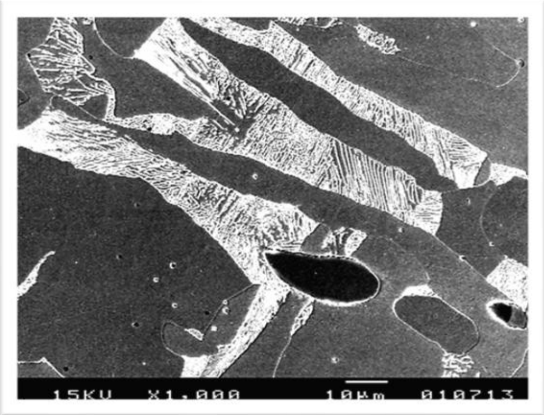
Killed

- 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.”*

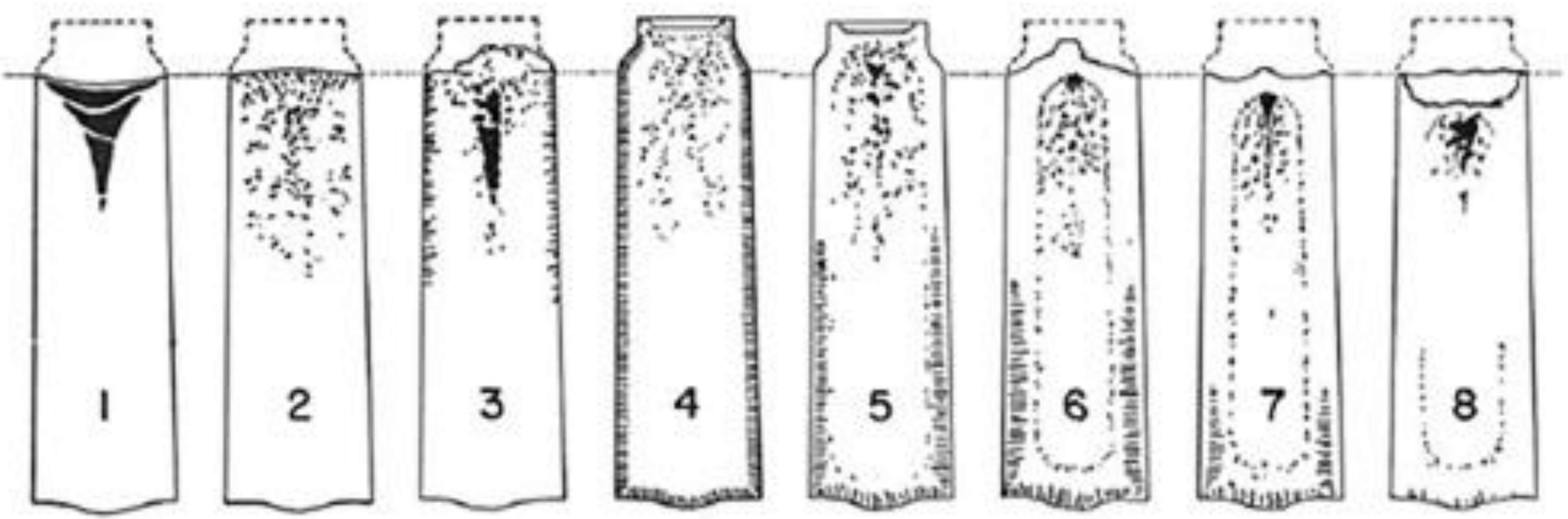






2. Deoxidized steel

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/

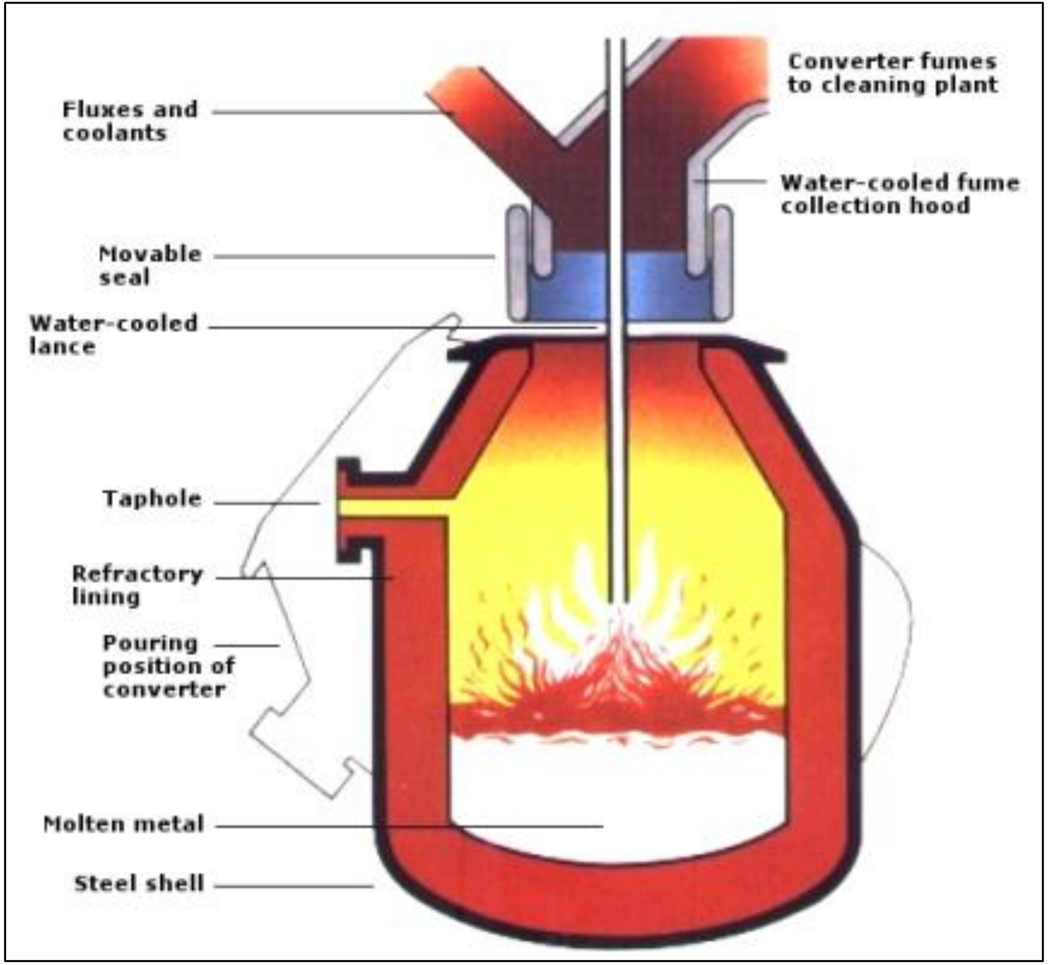
Ferro manganese

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

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

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

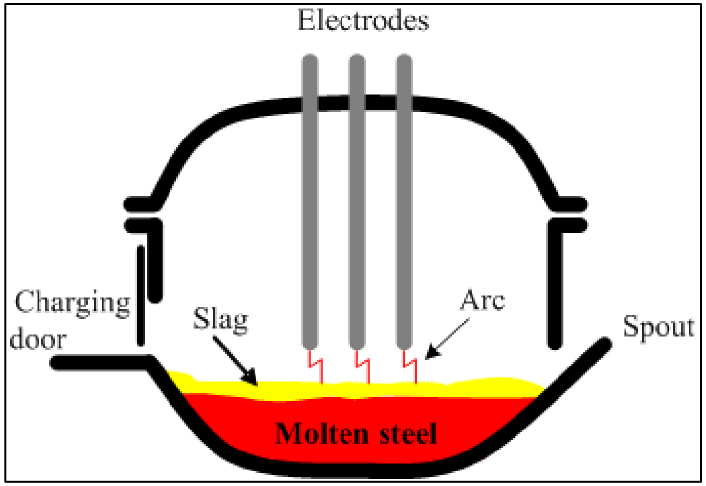
Reduction

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

Desulfurization

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

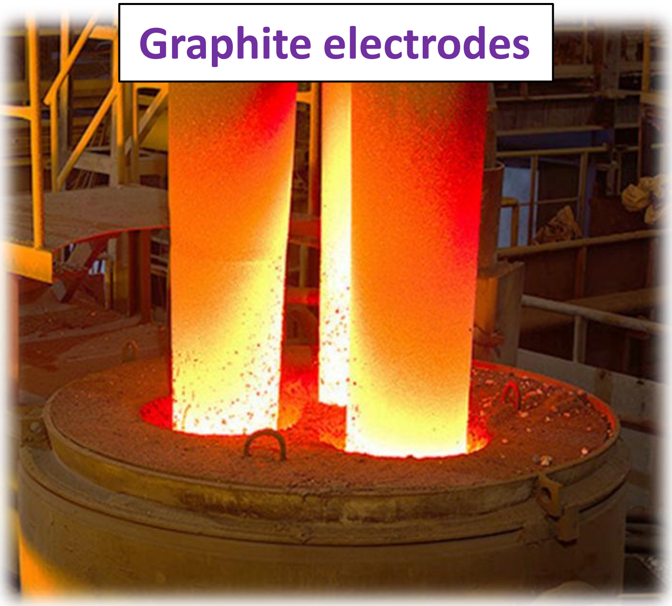
Electric arc furnace



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



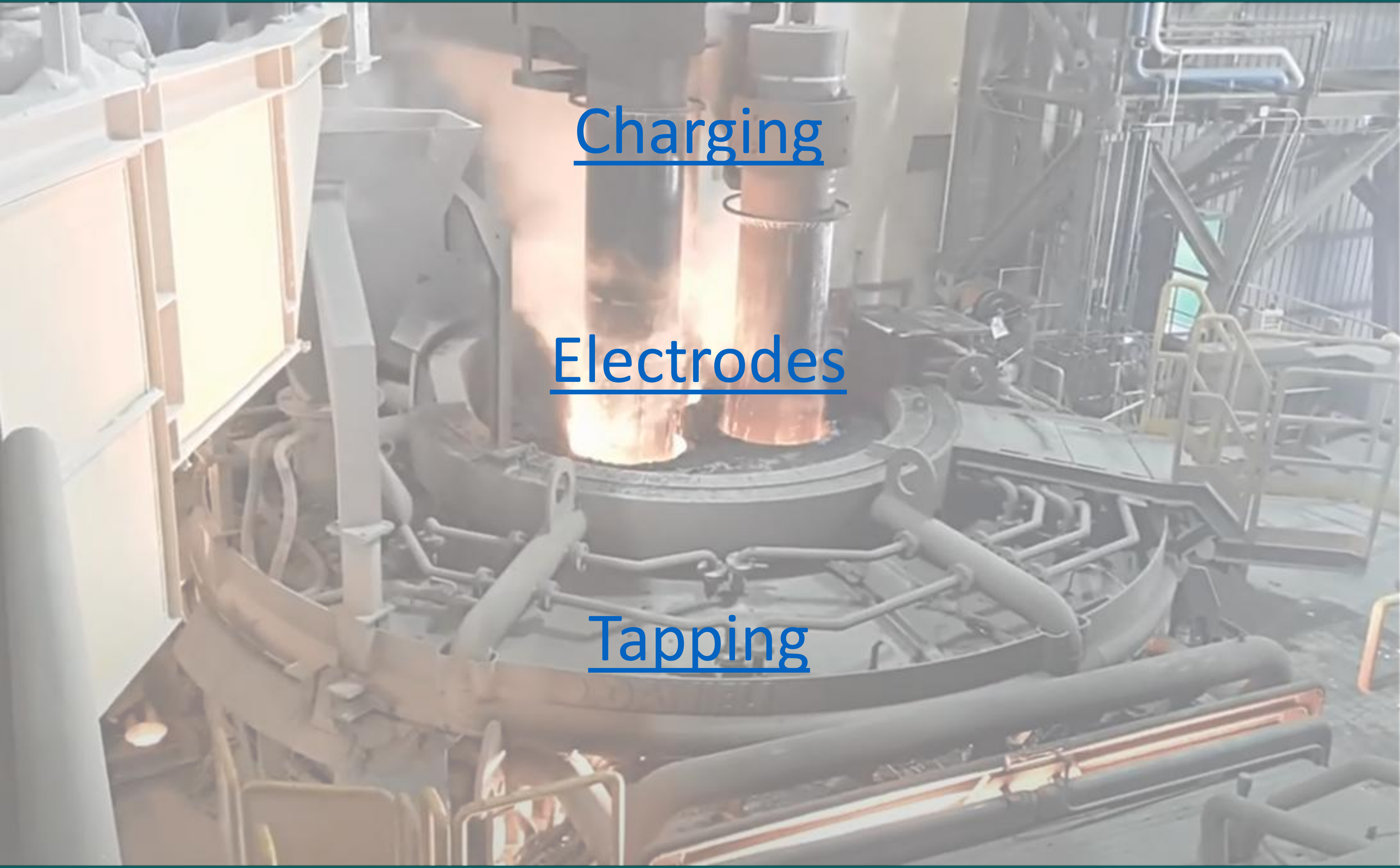
Electric arc furnace

- 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

4. Casting

Ingot casting

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

Casting individually

- Simple, productive
- Spattering

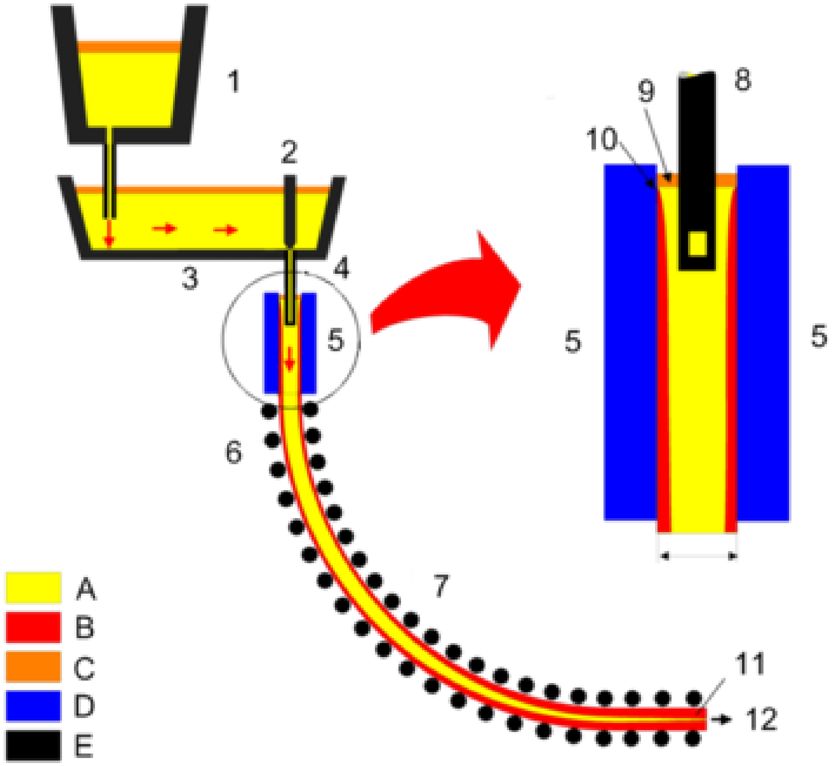
Bottom pouring

- Homogenous
- Slow, oxidation

4. Casting

Continous casting

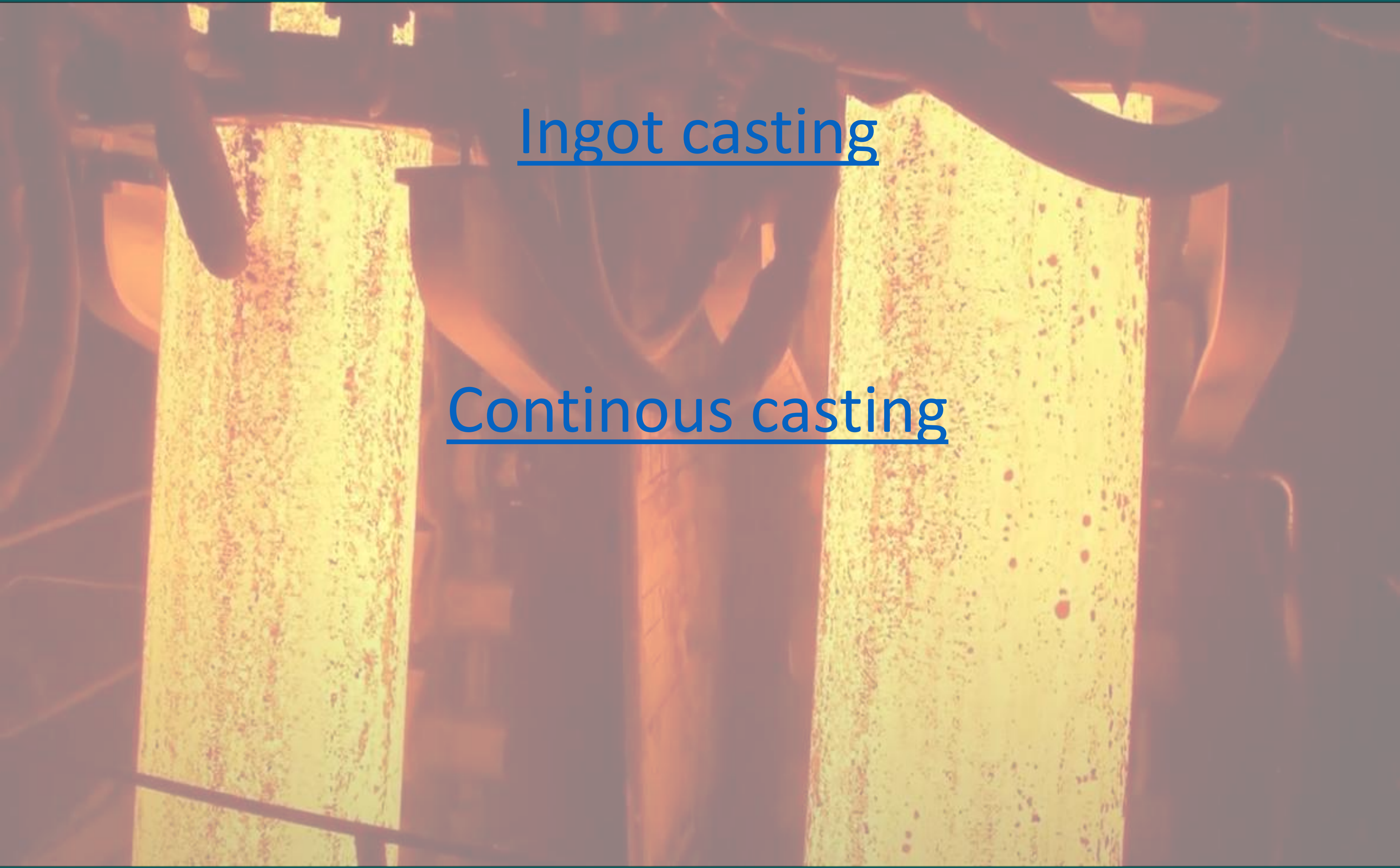
- Molten metal is solidified into a "semifinished" billet, bloom, or slab for subsequent rolling in the finishing mills.



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

Casting

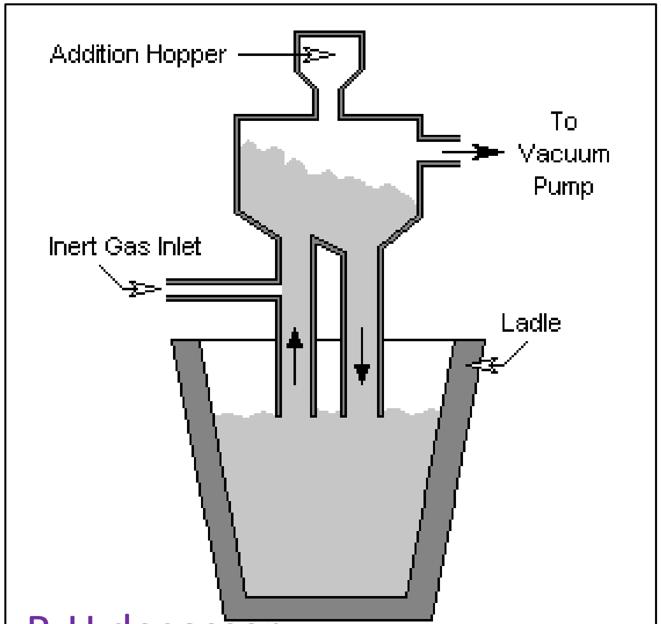


Ingot casting

Continous casting

5. Refining

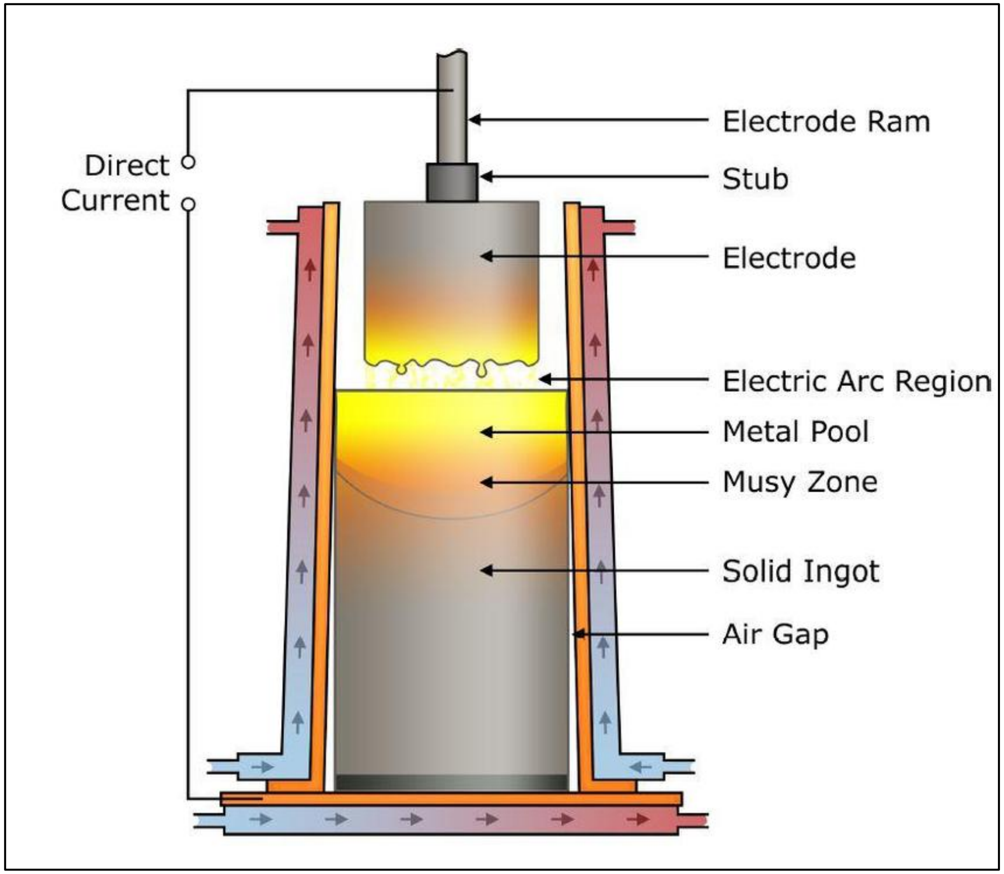
- Remelting and solidification
  - Decrease the dissolved gas content and the amount of inclusions
  - Produce a homogeneous fine-grained crystal structure
  - Produce a homogeneous distribution of alloying elements
- Ladle metallurgy, ladle refining, or secondary steelmaking
  - Deoxidization
  - Degassing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

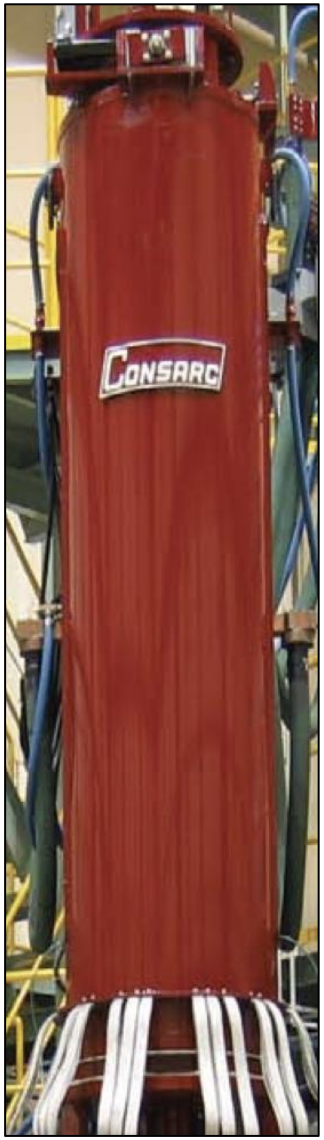


R-H degasser

Vacuum arc remelting

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

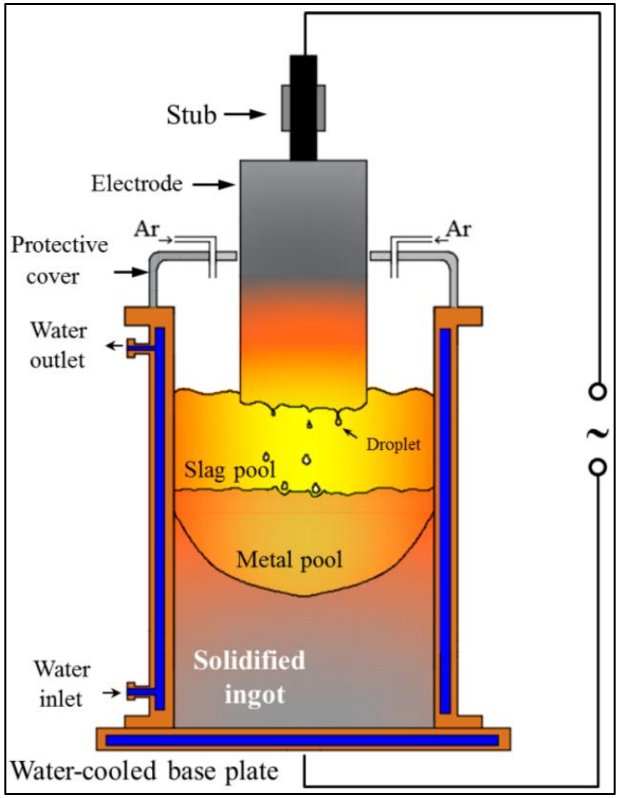




5. Refining

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!