# Metallurgical Engineering

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First Edition, 2012

ISBN 978-81-323-2794-3

*Published by:*
**Orange Apple**
4735/22 Prakashdeep Bldg,
Ansari Road, Darya Ganj,
Delhi - 110002
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# Metallurgy

**Metallurgy** is a domain of materials science that studies the physical and chemical behavior of metallic elements, their intermetallic compounds, and their mixtures, which are called alloys. It is also the technology of metals: the way in which science is applied to their practical use. Metallurgy is distinguished from the craft of metalworking.

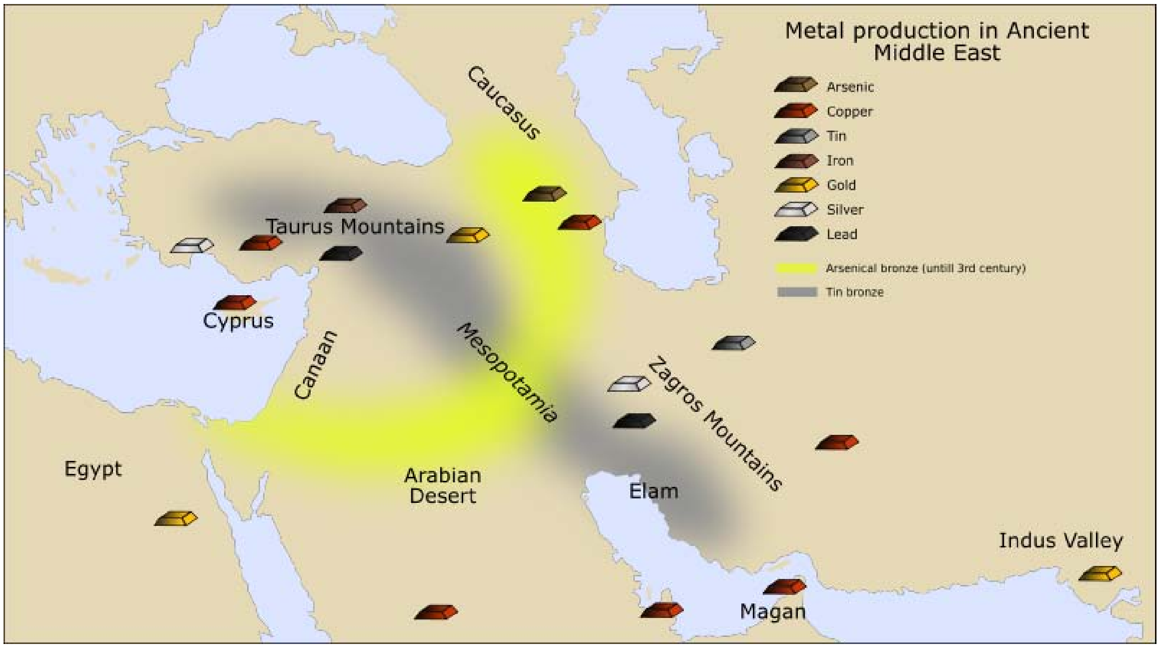
## *Etymology*

The word was originally (1593) an alchemist's term for the extraction of metals from minerals: the ending *-urgy* signifying a process, especially manufacturing: it was in this sense it was used by the 1797 Encyclopaedia Britannica. In the late 19th century it was extended to the more general scientific study of metals and alloys and related processes.

## *History*

Gold headband from Thebes 750-700 BC

The first evidence of human metallurgy dates from the 5th and 6th millennium BC, and was found in the archaeological sites of Majdanpek, Yarmovac and Plocnik, Serbia. To date, the earliest copper smelting is found at the Belovode site, these examples include a copper axe from 5,500BC belonging to the Vincha culture. Other signs of human metallurgy are found from the third millennium BC in places like Palmela (Portugal), Cortes de Navarra (Spain), and Stonehenge (United Kingdom). However, as often happens with the study of prehistoric times, the ultimate beginnings cannot be clearly defined and new discoveries are continuous and ongoing.



Mining areas of the ancient Middle East. Boxes colors: arsenic is in brown, copper in red, tin in grey, iron in reddish brown, gold in yellow, silver in white and lead in black. Yellow area stands for arsenic bronze, while grey area stands for tin bronze.

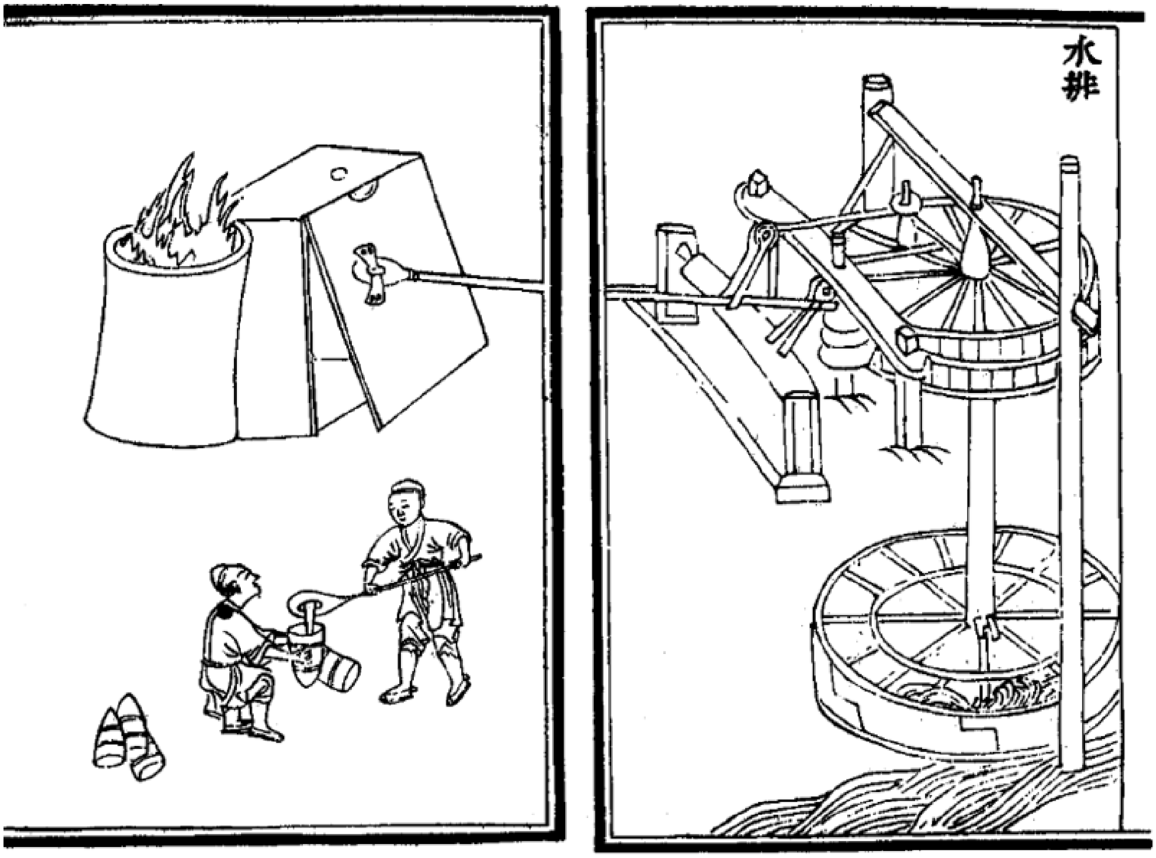
Silver, copper, tin and meteoric iron can also be found native, allowing a limited amount of metalworking in early cultures. Egyptian weapons made from meteoric iron in about 3000 B.C. were highly prized as "Daggers from Heaven". However, by learning to get copper and tin by heating rocks and combining those two metals to make an alloy called bronze, the technology of metallurgy began about 3500 B.C. with the Bronze Age.

The extraction of iron from its ore into a workable metal is much more difficult. It appears to have been invented by the Hittites in about 1200 B.C., beginning the Iron Age. The secret of extracting and working iron was a key factor in the success of the Philistines.

Historical developments in ferrous metallurgy can be found in a wide variety of past cultures and civilizations. This includes the ancient and medieval kingdoms and empires of the Middle East and Near East, ancient Iran, ancient Egypt, ancient Nubia, and Anatolia (Turkey), Ancient Nok, Carthage, the Greeks and Romans of ancient Europe, medieval Europe, ancient and medieval China, ancient and medieval India, ancient and medieval Japan, etc. Of interest to note is that many applications, practices, and devices associated or involved in metallurgy were possibly established in ancient China before Europeans mastered these crafts (such as the innovation of the blast furnace, cast iron, steel).

A 16th century book by Georg Agricola called De re metallica describes the highly developed and complex processes of mining metal ores, metal extraction and metallurgy of the time. Agricola has been described as the "father of metallurgy".

## *Extraction*



Furnace bellows operated by waterwheels, Yuan Dynasty, China.

Extractive metallurgy is the practice of removing valuable metals from an ore and refining the extracted raw metals into a purer form. In order to convert a metal oxide or sulfide to a purer metal, the ore must be reduced physically, chemically, or electrolytically.

Extractive metallurgists are interested in three primary streams: feed, concentrate (valuable metal oxide/sulfide), and tailings (waste). After mining, large pieces of the ore feed are broken through crushing and/or grinding in order to obtain particles small enough where each particle is either mostly valuable or mostly waste. Concentrating the particles of value in a form supporting separation enables the desired metal to be removed from waste products.

Mining may not be necessary if the ore body and physical environment are conducive to leaching. Leaching dissolves minerals in an ore body and results in an enriched solution. The solution is collected and processed to extract valuable metals.

Ore bodies often contain more than one valuable metal. Tailings of a previous process may be used as a feed in another process to extract a secondary product from the original ore. Additionally, a concentrate may contain more than one valuable metal. That concentrate would then be processed to separate the valuable metals into individual constituents.

## *Alloys*

Casting bronze

Common engineering metals include aluminium, chromium, copper, iron, magnesium, nickel, titanium and zinc. These are most often used as alloys. Much effort has been placed on understanding the iron-carbon alloy system, which includes steels and cast irons. Plain carbon steels are used in low cost, high strength applications where weight and corrosion are not a problem. Cast irons, including ductile iron are also part of the iron-carbon system.

Stainless steel or galvanized steel are used where resistance to corrosion is important. Aluminium alloys and magnesium alloys are used for applications where strength and lightness are required.

Copper-nickel alloys (such as Monel) are used in highly corrosive environments and for non-magnetic applications. Nickel-based superalloys like Inconel are used in high temperature applications such as turbochargers, pressure vessel, and heat exchangers. For extremely high temperatures, single crystal alloys are used to minimize creep.

## *Production*

In production engineering, metallurgy is concerned with the production of metallic components for use in consumer or engineering products. This involves the production of alloys, the shaping, the heat treatment and the surface treatment of the product. The task of the metallurgist is to achieve balance between material properties such as cost, weight, strength, toughness, hardness, corrosion and fatigue resistance, and performance in temperature extremes. To achieve this goal, the operating environment must be carefully considered. In a saltwater environment, ferrous metals and some aluminium alloys corrode quickly. Metals exposed to cold or cryogenic conditions may endure a ductile to brittle transition and lose their toughness, becoming more brittle and prone to cracking. Metals under continual cyclic loading can suffer from metal fatigue. Metals under constant stress at elevated temperatures can creep.

### Metalworking processes

Metals are shaped by processes such as:

- casting - molten metal is poured into a shaped mould.
- forging - a red-hot billet is hammered into shape.
- flow forming
- rolling - a billet is passed through successively narrower rollers to create a sheet.
- extrusion - a hot and malleable metal is forced under pressure through a die, which shapes it before it cools.
- sintering - a powdered metal is heated in a non-oxidizing environment after being compressed into a die.
- metalworking
- machining - lathes, milling machines, and drills cut the cold metal to shape.
- fabrication - sheets of metal are cut with guillotines or gas cutters and bent into shape.

Cold working processes, where the product’s shape is altered by rolling, fabrication or other processes while the product is cold, can increase the strength of the product by a process called work hardening. Work hardening creates microscopic defects in the metal, which resist further changes of shape.

Various forms of casting exist in industry and academia. These include sand casting, investment casting (also called the “lost wax process”), die casting and continuous casting.

## Heat treatment

Metals can be heat treated to alter the properties of strength, ductility, toughness, hardness or resistance to corrosion. Common heat treatment processes include annealing, precipitation strengthening, quenching, and tempering. The **annealing** process softens the metal by heating it and then allowing it to cool very slowly, which gets rid of stresses in the metal and makes the grain structure large and soft-edged so that when the metal is hit or stressed it dents or perhaps bends, rather than breaking; it is also easier to sand, grind, or cut annealed metal. **Quenching** is the process of cooling a high-carbon steel very quickly after you have heated it, thus "freezing" the steel's molecules in the very hard martensite form, which makes the metal harder. There is a balance between hardness and toughness in any steel, where the harder it is, the less tough or impact-resistant it is, and the more impact-resistant it is, the less hard it is. **Tempering** relieves stresses in the metal that were caused by the hardening process; tempering makes the metal less hard while making it better able to sustain impacts without breaking.

Often, mechanical and thermal treatments are combined in what is known as thermo-mechanical treatments for better properties and more efficient processing of materials. These processes are common to high alloy special steels, super alloys and titanium alloys.

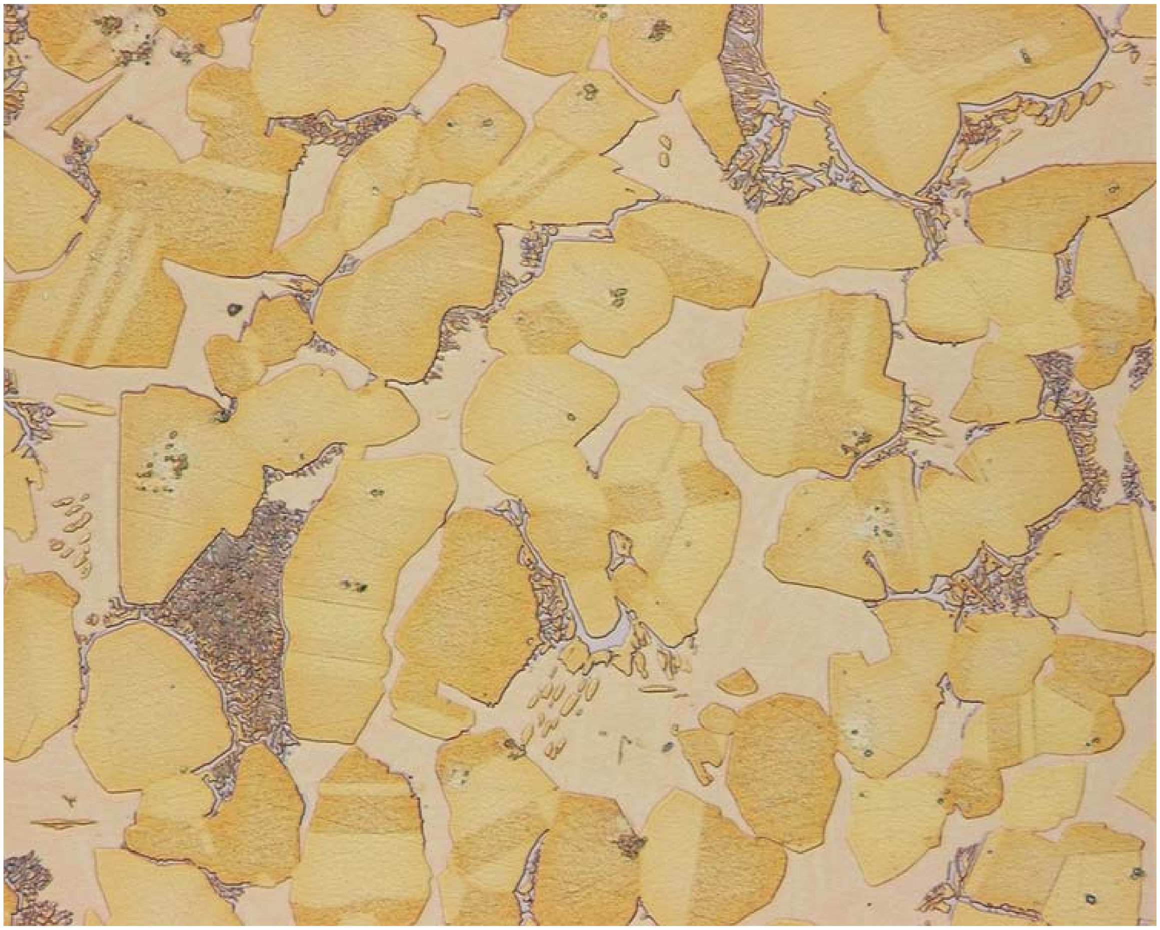
## Plating

Electroplating is a common surface-treatment technique. It involves bonding a thin layer of another metal such as gold, silver, chromium or zinc to the surface of the product. It is used to reduce corrosion as well as to improve the product's aesthetic appearance.

## Thermal spraying

Thermal spraying techniques are another popular finishing option, and often have better high temperature properties than electroplated coatings.

## *Microstructure*



Metallography allows the metallurgist to study the microstructure of metals.

Metallurgists study the microscopic and macroscopic properties using metallography, a technique invented by Henry Clifton Sorby. In metallography, an alloy of interest is ground flat and polished to a mirror finish. The sample can then be etched to reveal the microstructure and macrostructure of the metal. The sample is then examined in an optical or electron microscope, and the image contrast provides details on the composition, mechanical properties, and processing history.

Crystallography, often using diffraction of x-rays or electrons, is another valuable tool available to the modern metallurgist. Crystallography allows identification of unknown materials and reveals the crystal structure of the sample. Quantitative crystallography can be used to calculate the amount of phases present as well as the degree of strain to which a sample has been subjected.

## Chapter 2

# Corrosion

**Corrosion** is the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings. In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Formation of an oxide of iron due to oxidation of the iron atoms in solid solution is a well-known example of electrochemical corrosion, commonly known as rusting. This type of damage typically produces oxide(s) and/or salt(s) of the original metal. Corrosion can also refer to other materials than metals, such as ceramics or polymers, although in this context, the term degradation is more common.

In other words, corrosion is the wearing away of metals due to a chemical reaction.

Many structural alloys corrode merely from exposure to moisture in the air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate-conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

Rust, the most familiar example of corrosion.

Volcanic gases have sped the corrosion of this abandoned mining machinery.

Corrosion on exposed metal.

## *Galvanic corrosion*

Galvanic corrosion occurs when two different metals electrically contact each other and are immersed in an electrolyte. In order for galvanic corrosion to occur, an electrically conductive path and an ionically conductive path are necessary. This effects a galvanic couple where the more active metal corrodes at an accelerated rate and the more noble metal corrodes at a retarded rate. When immersed, neither metal would normally corrode as quickly without the electrically conductive connection (usually via a wire or direct contact). Galvanic corrosion is often utilized in sacrificial anodes. What type of metal(s) to use is readily determined by following the galvanic series. For example, zinc is often used as a sacrificial anode for steel structures, such as pipelines or docked naval ships. Galvanic corrosion is of major interest to the marine industry and also anywhere water can contact pipes or metal structures.

Factors such as relative size of anode (smaller is generally less desirable), types of metal, and operating conditions (temperature, humidity, salinity, etc.) will affect galvanic corrosion. The surface area ratio of the anode and cathode will directly affect the corrosion rates of the materials.

### Galvanic series

In a given sea environment (one standard medium is aerated, room-temperature seawater), one metal will be either more *noble* or more *active* than the next, based on how strongly its ions are bound to the surface. Two metals in electrical contact share the same electrons, so that the tug-of-war at each surface is translated into a competition for free electrons between the two materials. The noble metal will tend to take electrons from the active one, while the electrolyte hosts a flow of ions in the same direction. The resulting mass flow or electrical current can be measured to establish a hierarchy of materials in the medium of interest. This hierarchy is called a *galvanic series*, and can be a very useful in predicting and understanding corrosion.

## *Resistance to corrosion*

Some metals are more intrinsically resistant to corrosion than others, either due to the fundamental nature of the electrochemical processes involved or due to the details of how reaction products form. If a more susceptible material is used, many techniques can be applied during an item's manufacture and use to protect its materials from damage.

### Intrinsic chemistry

Gold nuggets do not naturally corrode, even on a geological time scale.

The materials most resistant to corrosion are those for which corrosion is thermodynamically unfavorable. Any corrosion products of gold or platinum tend to decompose spontaneously into pure metal, which is why these elements can be found in metallic form on Earth, and is a large part of their intrinsic value. More common "base" metals can only be protected by more temporary means.

Some metals have naturally slow reaction kinetics, even though their corrosion is thermodynamically favorable. These include such metals as zinc, magnesium, and cadmium. While corrosion of these metals is continuous and ongoing, it happens at an acceptably slow rate. An extreme example is graphite, which releases large amounts of energy upon oxidation, but has such slow kinetics that it is effectively immune to electrochemical corrosion under normal conditions.

## Passivation

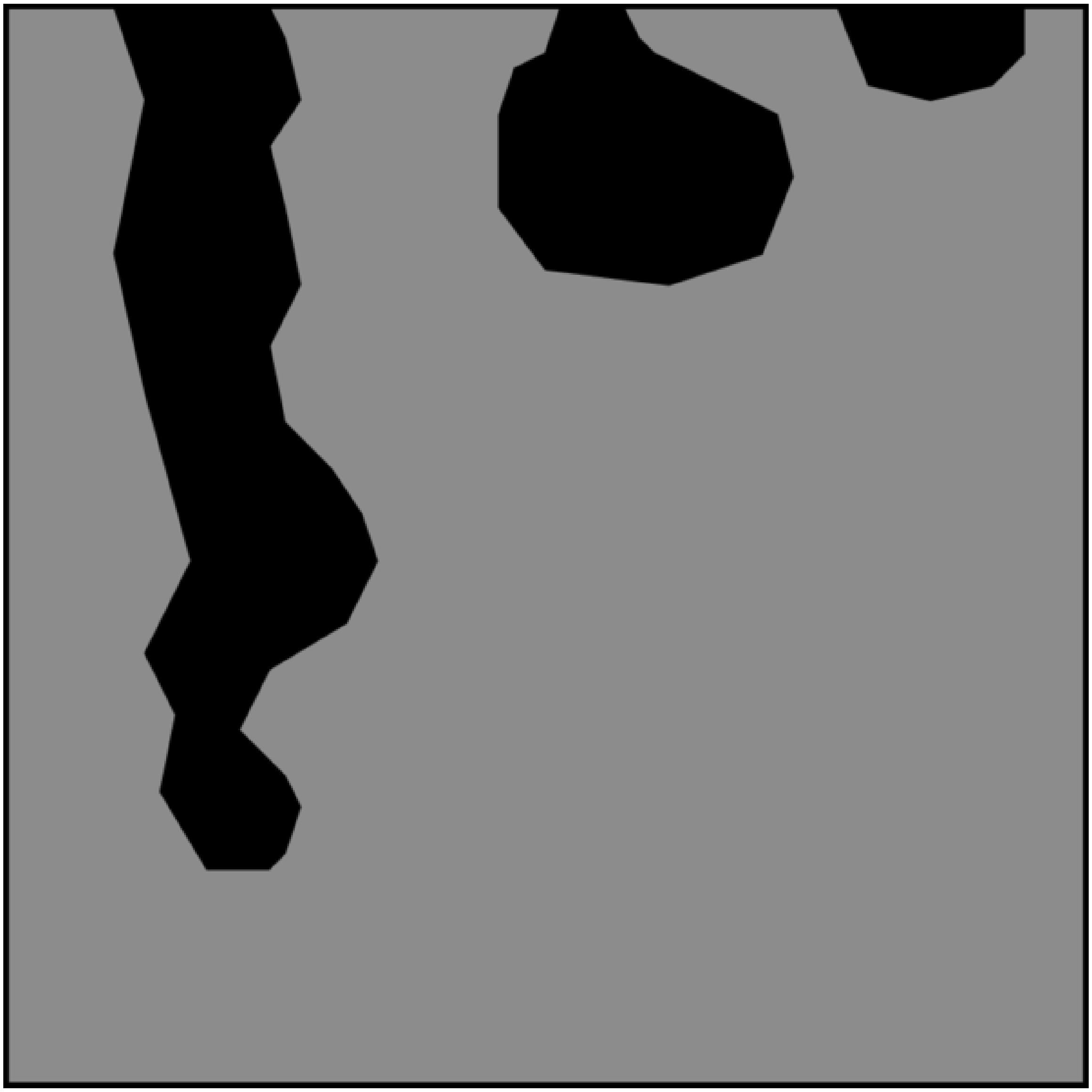
Given the right conditions, a thin film of corrosion products can form on a metal's surface spontaneously, acting as a barrier to further oxidation. When this layer stops growing at less than a micrometre thick under the conditions that a material will be used in, the phenomenon is known as passivation (rust, for example, usually grows to be much thicker, and so is not considered passivation, because this mixed oxidized layer is not protective). While this effect is in some sense a property of the material, it serves as an indirect kinetic barrier: the reaction is often quite rapid unless and until an impermeable layer forms. Passivation in air and water at moderate pH is seen in such materials as aluminium, stainless steel, titanium, and silicon.

These conditions required for passivation are specific to the material. The effect of pH is recorded using Pourbaix diagrams, but many other factors are influential. Some conditions that inhibit passivation include: high pH for aluminium, low pH or the presence of chloride ions for stainless steel, high temperature for titanium (in which case the oxide dissolves into the metal, rather than the electrolyte) and fluoride ions for silicon. On the other hand, sometimes unusual conditions can bring on passivation in materials that are normally unprotected, as the alkaline environment of concrete does for steel rebar. Exposure to a liquid metal such as mercury or hot solder can often circumvent passivation mechanisms.

### *Corrosion in passivated materials*

Passivation is extremely useful in alleviating corrosion damage, but care must be taken not to trust it too thoroughly. Even a high-quality alloy will corrode if its ability to form a passivating film is hindered. Because the resulting modes of corrosion are more exotic and their immediate results are less visible than rust and other bulk corrosion, they often escape notice and cause problems among those who are not familiar with them.

## Pitting corrosion



The scheme of pitting corrosion

Certain conditions, such as low concentrations of oxygen or high concentrations of species such as chloride which compete as anions, can interfere with a given alloy's ability to re-form a passivating film. In the worst case, almost all of the surface will remain protected, but tiny local fluctuations will degrade the oxide film in a few critical points. Corrosion at these points will be greatly amplified, and can cause *corrosion pits* of several types, depending upon conditions. While the corrosion pits only nucleate under fairly extreme circumstances, they can continue to grow even when conditions return to normal, since the interior of a pit is naturally deprived of oxygen and locally the pH decreases to very low values and the corrosion rate increases due to an auto-catalytic process. In extreme cases, the sharp tips of extremely long and narrow corrosion pits can cause stress concentration to the point that otherwise tough alloys can shatter; a thin film pierced by an invisibly small hole can hide a thumb sized pit from view. These problems are especially dangerous because they are difficult to detect before a part or structure fails. Pitting remains among the most common and damaging forms of corrosion in passivated alloys, but it can be prevented by control of the alloy's environment.

### Weld decay and knifeline attack

Stainless steel can pose special corrosion challenges, since its passivating behavior relies on the presence of a minor alloying component (Chromium, typically only 18%). Due to the elevated temperatures of welding or during improper heat treatment, chromium carbides can form in the grain boundaries of stainless alloys. This chemical reaction robs the material of chromium in the zone near the grain boundary, making those areas much less resistant to corrosion. This creates a galvanic couple with the well-protected alloy nearby, which leads to *weld decay* (corrosion of the grain boundaries near welds) in highly corrosive environments. Special alloys, either with low carbon content or with added carbon "getters" such as titanium and niobium (in types 321 and 347, respectively), can prevent this effect, but the latter require special heat treatment after welding to prevent the similar phenomenon of *knifeline attack*. As its name applies, this is limited to a small zone, often only a few micrometres across, which causes it to proceed more rapidly. This zone is very near the weld, making it even less noticeable[1].

### Crevice corrosion

Crevice corrosion is a localized form of corrosion occurring in spaces to which the access of the working fluid from the environment is limited and a concentration cell, areas with different oxygen concentration, will take place with consequent high corrosion rate . These spaces are generally called crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles.

## *Microbial corrosion*

Microbial corrosion, or bacterial corrosion, is a corrosion caused or promoted by microorganisms, usually chemoautotrophs. It can apply to both metals and non-metallic materials, in both the presence and lack of oxygen. Sulfate-reducing bacteria are common in lack of oxygen; they produce hydrogen sulfide, causing sulfide stress cracking. In presence of oxygen, some bacteria directly oxidize iron to iron oxides and hydroxides, other bacteria oxidize sulfur and produce sulfuric acid causing biogenic sulfide corrosion. Concentration cells can form in the deposits of corrosion products, causing and enhancing galvanic corrosion.

Accelerated Low Water Corrosion (ALWC) is a particularly aggressive form of MIC that affects steel piles in seawater near the low water tide mark. It is characterised by an orange sludge, which smells of Hydrogen Sulphide when treated with acid. Corrosion rates can be very high and design corrosion allowances can soon be exceeded leading to premature failure of the steel pile. Piles that have been coating and have cathodic protection installed at the time of construction are not susceptible to ALWC. For unprotected piles, sacrificial anodes can be installed local to the affected areas to inhibit the corrosion or a complete retrofitted sacrificial anode system can be installed. Affected areas can also be treated electrochemically by using an electrode to first produce chlorine to kill the bacteria, and then to produced a calcareous deposit, which will help shield the metal from further attack.

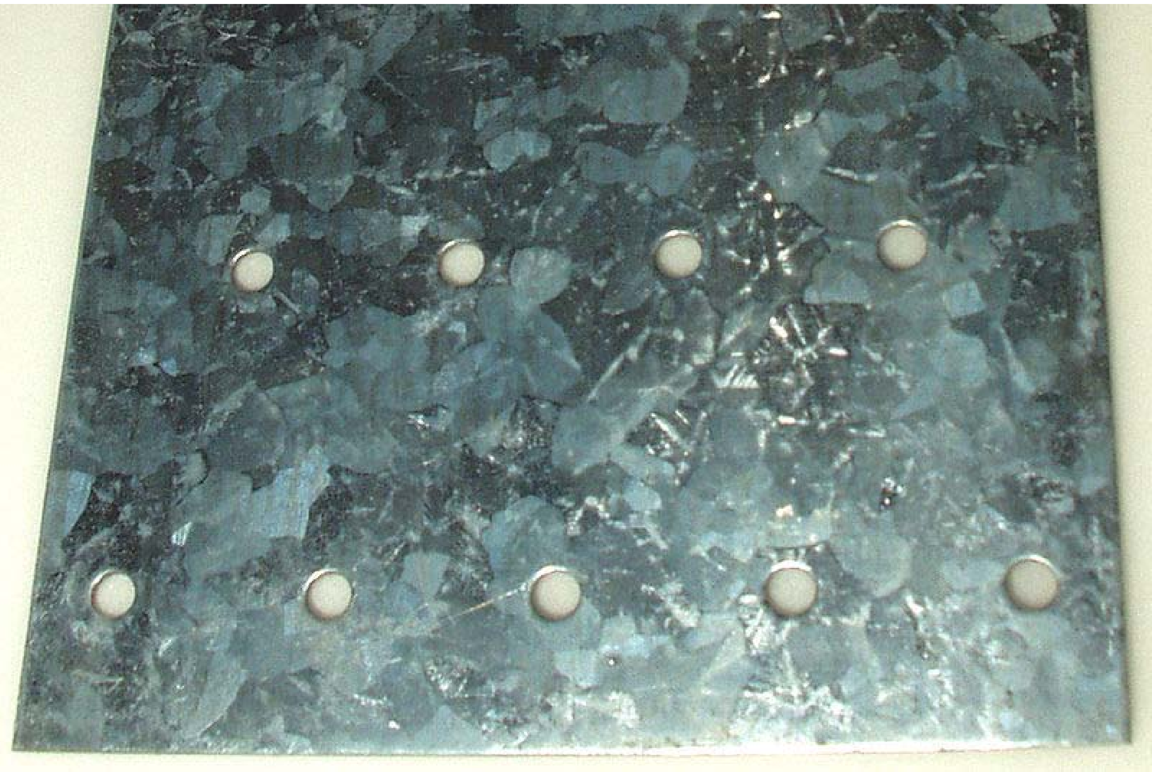
## *High temperature corrosion*

High temperature corrosion is chemical deterioration of a material (typically a metal) under very high temperature conditions. This non-galvanic form of corrosion can occur when a metal is subject to a high temperature atmosphere containing oxygen, sulfur or other compounds capable of oxidising (or assisting the oxidation of) the material concerned. For example, materials used in aerospace, power generation and even in car engines have to resist sustained periods at high temperature in which they may be exposed to an atmosphere containing potentially highly corrosive products of combustion.

The products of high temperature corrosion can potentially be turned to the advantage of the engineer. The formation of oxides on stainless steels, for example, can provide a protective layer preventing further atmospheric attack, allowing for a material to be used for sustained periods at both room and high temperature in hostile conditions. Such high temperature corrosion products in the form of compacted oxide layer glazes have also been shown to prevent or reduce wear during high temperature sliding contact of metallic (or metallic and ceramic) surfaces.

## *Methods of protection from corrosion*

### Surface treatments



Galvanized surface

**Applied coatings**

Plating, painting, and the application of enamel are the most common anti-corrosion treatments. They work by providing a barrier of corrosion-resistant material between the damaging environment and the (often cheaper, tougher, and/or easier-to-process) structural material. Aside from cosmetic and manufacturing issues, there are tradeoffs in mechanical flexibility versus resistance to abrasion and high temperature. Platings usually fail only in small sections, and if the plating is more noble than the substrate (for example, chromium on steel), a galvanic couple will cause any exposed area to corrode much more rapidly than an unplated surface would. For this reason, it is often wise to plate with a more active metal such as zinc or cadmium. Painting either by roller or brush is more desirable for tight spaces; spray would be better for larger coating areas such as steel decks and waterfront applications. Flexible polyurethane coatings, like Durabak-M26 for example, can provide an anti-corrosive seal with a highly durable slip resistant membrane. Painted coatings are relatively easy to apply and have fast drying times although temperature and humidity may cause dry times to vary.

### Reactive coatings

If the environment is controlled (especially in recirculating systems), corrosion inhibitors can often be added to it. These form an electrically insulating and/or chemically impermeable coating on exposed metal surfaces, to suppress electrochemical reactions. Such methods obviously make the system less sensitive to scratches or defects in the coating, since extra inhibitors can be made available wherever metal becomes exposed. Chemicals that inhibit corrosion include some of the salts in hard water (Roman water systems are famous for their mineral deposits), chromates, phosphates, polyaniline, other conducting polymers and a wide range of specially-designed chemicals that resemble surfactants (i.e. long-chain organic molecules with ionic end groups).

This figure-8 descender is annodized with a yellow finish. Climbing equipment is available in a wide range of anodized colors.

### Anodization

Aluminium alloys often undergo a surface treatment. Electrochemical conditions in the bath are carefully adjusted so that uniform pores several nanometers wide appear in the metal's oxide film. These pores allow the oxide to grow much thicker than passivating conditions would allow. At the end of the treatment, the pores are allowed to seal, forming a harder-than-usual surface layer. If this coating is scratched, normal passivation processes take over to protect the damaged area. Anodizing is very resilient to weathering and corrosion, so it is commonly used for building facades and other areas that the surface will come into regular contact with the elements. Whilst being resilient, it must be cleaned frequently. If left without cleaning Panel Edge Staining will naturally occur.

## Controlled permeability formwork

Controlled permeability formwork (CPF) is a method of preventing the corrosion of reinforcement by naturally enhancing the durability of the cover during concrete placement, . CPF has been used in environments to combat the effects of carbonation, chlorides, frost and abrasion.

## Cathodic protection

Cathodic protection (CP) is a technique to control the corrosion of a metal surface by making that surface the cathode of an electrochemical cell. Cathodic protection systems are most commonly used to protect steel, water, and fuel pipelines and tanks; steel pier piles, ships, and offshore oil platforms.

### Sacrificial anode protection

Sacrificial anode in the hull of a ship.

For effective CP, the potential of the steel surface is polarized (pushed) more negative until the metal surface has a uniform potential. With a uniform potential, the driving force for the corrosion reaction is halted. For galvanic CP systems, the anode material corrodes under the influence of the steel, and eventually it must be replaced. The polarization is caused by the current flow from the anode to the cathode, driven by the difference in electrochemical potential between the anode and the cathode.

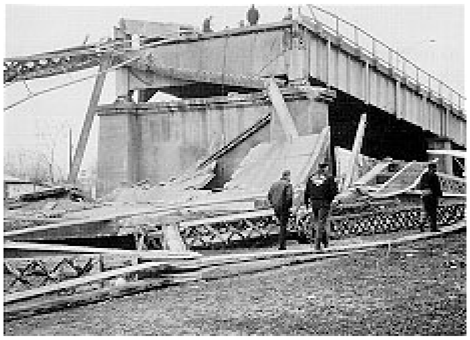
### Impressed current cathodic protection

For larger structures, galvanic anodes cannot economically deliver enough current to provide complete protection. Impressed Current Cathodic Protection (ICCP) systems use anodes connected to a DC power source (such as a cathodic protection rectifier). Anodes for ICCP systems are tubular and solid rod shapes of various specialized materials. These include high silicon cast iron, graphite, mixed metal oxide or platinum coated titanium or niobium coated rod and wires.

## Anodic protection

Anodic protection impresses anodic current on the structure to be protected (opposite to the cathodic protection). It is appropriate for metals that exhibit passivity (e.g., stainless steel) and suitably small passive current over a wide range of potentials. It is used in aggressive environments, e.g., solutions of sulfuric acid.

## *Economic impact*



The collapsed Silver Bridge, as seen from the Ohio side

The US Federal Highway Administration released a study, entitled *Corrosion Costs and Preventive Strategies in the United States,* in 2002 on the direct costs associated with metallic corrosion in nearly every U.S. industry sector. The study showed that for 1998 the total annual estimated direct cost of corrosion in the U.S. was approximately $276 billion (approximately 3.2% of the US gross domestic product).

Rust is one of the most common causes of bridge accidents. As rust has a much higher volume than the originating mass of iron, its build-up can also cause failure by forcing apart adjacent parts. It was the cause of the collapse of the Mianus river bridge in 1983, when the bearings rusted internally and pushed one corner of the road slab off its support.

Three drivers on the roadway at the time died as the slab fell into the river below. The following NTSB investigation showed that a drain in the road had been blocked for road re-surfacing, and had not been unblocked so that runoff water penetrated the support hangers. It was also difficult for maintenance engineers to see the bearings from the inspection walkway. Rust was also an important factor in the Silver Bridge disaster of 1967 in West Virginia, when a steel suspension bridge collapsed in less than a minute, killing 46 drivers and passengers on the bridge at the time.

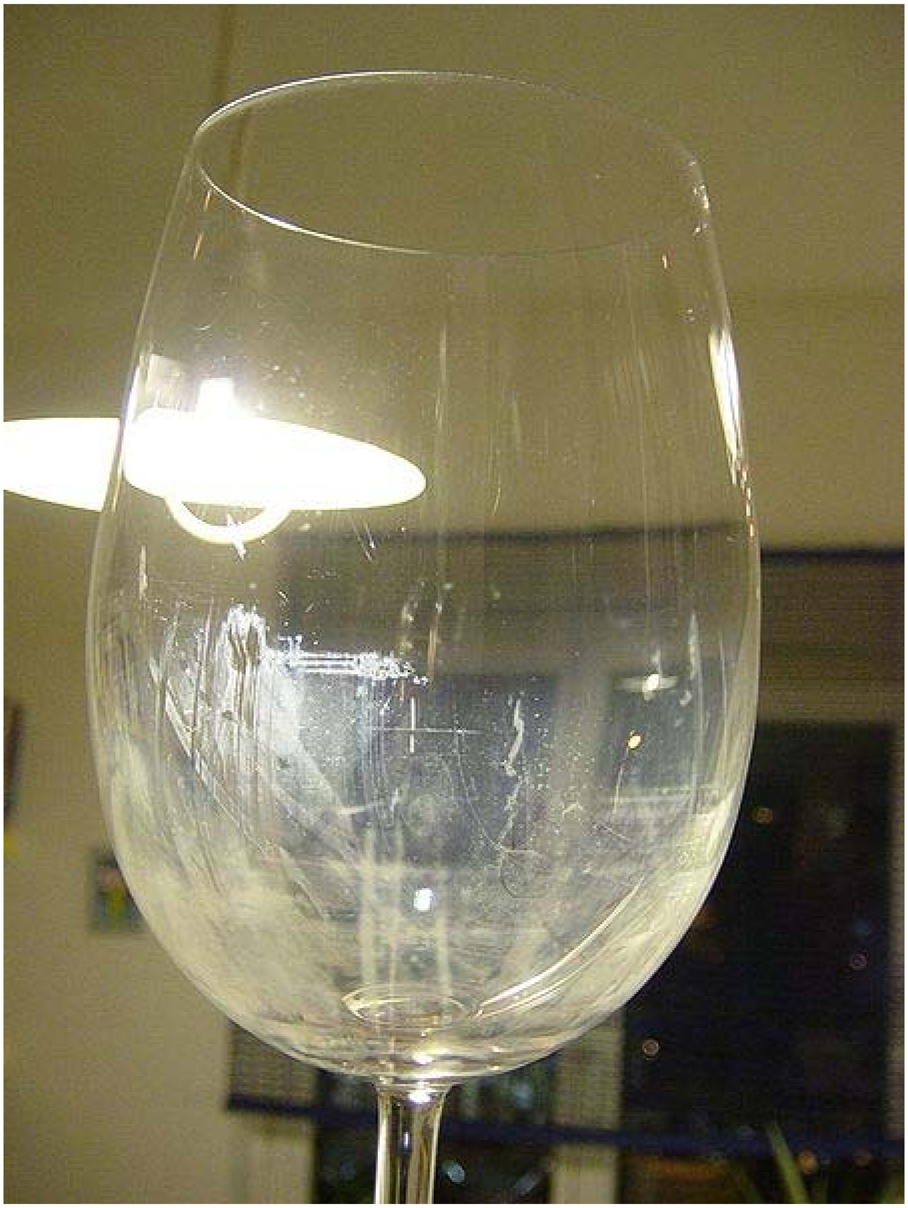
Similarly corrosion of concrete-covered steel and iron can cause the concrete to spall, creating severe structural problems. It is one of the most common failure modes of reinforced concrete bridges. Measuring instruments based on the half-cell potential are able to detect the potential corrosion spots before total failure of the concrete structure is reached.

## *Corrosion in nonmetals*

Most ceramic materials are almost entirely immune to corrosion. The strong ionic and/or covalent bonds that hold them together leave very little free chemical energy in the structure; they can be thought of as already corroded. When corrosion does occur, it is almost always a simple dissolution of the material or chemical reaction, rather than an electrochemical process. A common example of corrosion protection in ceramics is the lime added to soda-lime glass to reduce its solubility in water; though it is not nearly as soluble as pure sodium silicate, normal glass does form sub-microscopic flaws when exposed to moisture. Due to its brittleness, such flaws cause a dramatic reduction in the strength of a glass object during its first few hours at room temperature.

Polymer degradation is due to a wide array of complex and often poorly-understood physiochemical processes. These are strikingly different from the other processes discussed here, and so the term "corrosion" is only applied to them in a loose sense of the word. Because of their large molecular weight, very little entropy can be gained by mixing a given mass of polymer with another substance, making them generally quite difficult to dissolve. While dissolution is a problem in some polymer applications, it is relatively simple to design against. A more common and related problem is *swelling*, where small molecules infiltrate the structure, reducing strength and stiffness and causing a volume change. Conversely, many polymers (notably flexible vinyl) are intentionally swelled with plasticizers, which can be leached out of the structure, causing brittleness or other undesirable changes. The most common form of degradation, however, is a decrease in polymer chain length. Mechanisms which break polymer chains are familiar to biologists because of their effect on DNA: ionizing radiation (most commonly ultraviolet light), free radicals, and oxidizers such as oxygen, ozone, and chlorine. Additives can slow these process very effectively, and can be as simple as a UV-absorbing pigment (i.e., titanium dioxide or carbon black). Plastic shopping bags often do not include these additives so that they break down more easily as litter.

## Corrosion of glasses



Glass corrosion

**Glass disease** is the corrosion of silicate glasses in aqueous solutions. It is governed by two mechanisms: diffusion-controlled leaching (ion exchange) and glass network hydrolytic dissolution. Both corrosion mechanisms strongly depend on the pH of contacting solution: the rate of ion exchange decreases with pH as $10^{-0.5pH}$ whereas the rate of hydrolytic dissolution increases with pH as $10^{0.5pH}$

Mathematically, corrosion rates of glasses are characterised by normalised corrosion rates of elements $NR_i$ (g/cm$^2$ d) which are determined as the ratio of total amount of released species into the water $M_i$ (g) to the water-contacting surface area S (cm$^2$), time of contact t (days) and weight fraction content of the element in the glass $f_i$:

$$NR_i = \frac{M_i}{Sf_i t}.$$

The overall corrosion rate is a sum of contributions from both mechanisms (leaching + dissolution) $NR_i$=$Nrx_i$+NRh. Diffusion-controlled leaching (ion exchange) is characteristic of the initial phase of corrosion and involves replacement of alkali ions in the glass by a hydronium ($H_3O^+$) ion from the solution. It causes an ion-selective depletion of near surface layers of glasses and gives an inverse square root dependence of corrosion rate with exposure time. The diffusion controlled normalised leaching rate of cations from glasses ($g/cm^2$ d) is given by:

$$NRx_i = 2\rho\sqrt{\frac{D_i}{\pi t}},$$

where t is time, $D_i$ is the i-th cation effective diffusion coefficient ($cm^2/d$), which depends on pH of contacting water as $D_i = D_{i0} \cdot 10^{-pH}$, and ρ is the density of the glass ($g/cm^3$).

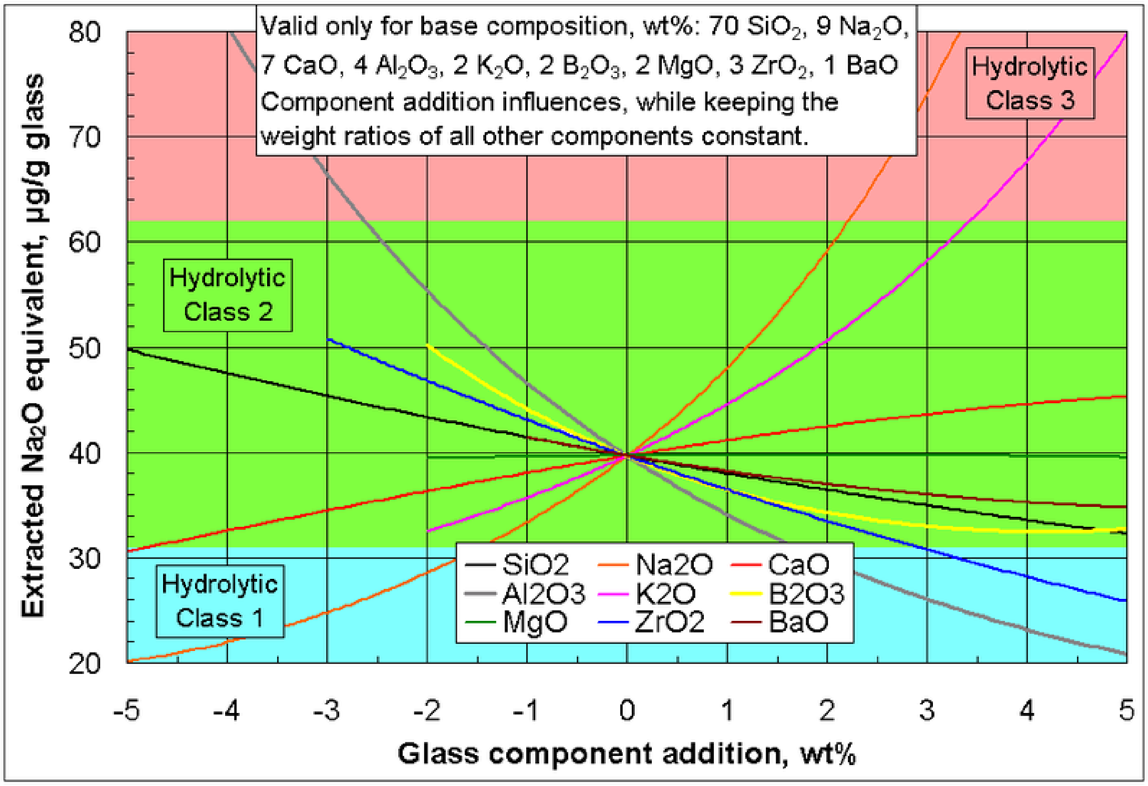
Glass network dissolution is characteristic of the later phases of corrosion and causes a congruent release of ions into the water solution at a time-independent rate in dilute solutions ($g/cm^2$ d):

$$NRh = \rho r_h,$$

where $r_h$ is the stationary hydrolysis (dissolution) rate of the glass (cm/d). In closed systems the consumption of protons from the aqueous phase increases the pH and causes a fast transition to hydrolysis. However further silica saturation of solution impedes hydrolysis and causes the glass to return to an ion-exchange, e.g. diffusion-controlled regime of corrosion.

In typical natural conditions normalised corrosion rates of silicate glasses are very low and are of the order of $10^{-7}$ - $10^{-5}$ $g/cm^2$ d. The very high durability of silicate glasses in water makes them suitable for hazardous and nuclear waste immobilisation.

## Glass corrosion tests



Influences of selected glass component additions on the chemical durability against water corrosion of a specific base glass (corrosion test ISO 719).

There exist numerous standardized procedures for measuring the corrosion (also called **chemical durability**) of glasses in neutral, basic, and acidic environments, under simulated environmental conditions, in simulated body fluid, at high temperature and pressure, and under other conditions.

In the standard procedure ISO 719 a test of the extraction of water soluble basic compounds under neutral conditions is described: 2 g glass, particle size 300-500 µm, is kept for 60 min in 50 ml de-ionized water of grade 2 at 98°C. 25 ml of the obtained solution is titrated against 0.01 mol/l HCl solution. The volume of HCl needed for neutralization is recorded and classified following the values in the table below.

| **0.01M HCl needed to neutralize extracted basic oxides, ml** | **Extracted $Na_2O$ equivalent, µg** | **Hydrolytic class** |
|---|---|---|
| to 0.1 | to 31 | 1 |
| above 0.1 to 0.2 | above 31 to 62 | 2 |
| above 0.2 to 0.85 | above 62 to 264 | 3 |
| above 0.85 to 2.0 | above 264 to 620 | 4 |
| above 2.0 to 3.5 | above 620 to 1085 | 5 |

| | | |
|---|---|---|
| above 3.5 | above 1085 | >5 |

## Chapter 3

# Steel

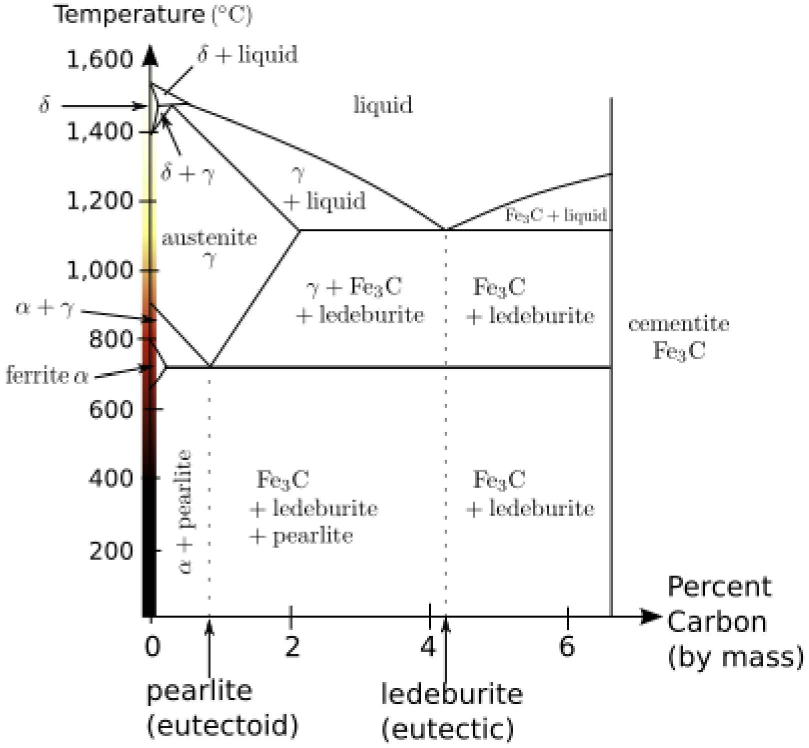
The steel cable of a colliery winding tower

**Steel** is an alloy that consists mostly of iron and has a carbon content between 0.2% and 2.1% by weight, depending on the grade. Carbon is the most common alloying material for iron, but various other alloying elements are used, such as manganese, chromium, vanadium, and tungsten. Carbon and other elements act as a hardening agent, preventing dislocations in the iron atom crystal lattice from sliding past one another. Varying the amount of alloying elements and the form of their presence in the steel (solute elements, precipitated phase) controls qualities such as the hardness, ductility, and tensile strength of the resulting steel. Steel with increased carbon content can be made harder and stronger than iron, but such steel is also less ductile than iron.

Alloys with a higher than 2.1% carbon content are known as cast iron because of their lower melting point and castability. Steel is also distinguishable from wrought iron, which can contain a small amount of carbon, but it is included in the form of slag inclusions. Two distinguishing factors are steel's increased rust resistance and better weldability.

Though steel had been produced by various inefficient methods long before the Renaissance, its use became more common after more-efficient production methods were devised in the 17th century. With the invention of the Bessemer process in the mid-19th century, steel became an inexpensive mass-produced material. Further refinements in the process, such as basic oxygen steelmaking (BOS), lowered the cost of production while increasing the quality of the metal. Today, steel is one of the most common materials in the world, with more than 1.3 billion tons produced annually. It is a major component in buildings, infrastructure, tools, ships, automobiles, machines, appliances, and weapons. Modern steel is generally identified by various grades defined by assorted standards organizations.

## *Material properties*



Iron-carbon phase diagram, showing the conditions necessary to form different phases

Iron is found in the Earth's crust only in the form of an ore, i.e., combined with other elements such as oxygen or sulfur. Typical iron-containing minerals include $Fe_2O_3$—the form of iron oxide found as the mineral hematite, and $FeS_2$—pyrite (fool's gold). Iron is extracted from ore by removing oxygen and combining the ore with a preferred chemical partner such as carbon. This process, known as smelting, was first applied to metals with lower melting points, such as tin, which melts at approximately 250 °C (482 °F) and copper, which melts at approximately 1,100 °C (2,010 °F). In comparison, cast iron melts at approximately 1,375 °C (2,507 °F). All of these temperatures could be reached with ancient methods that have been used since the Bronze Age. Since the oxidation rate itself increases rapidly beyond 800 °C (1,470 °F), it is important that smelting take place in a low-oxygen environment. Unlike copper and tin, liquid iron dissolves carbon quite readily. Smelting results in an alloy (pig iron) containing too much carbon to be called steel. The excess carbon and other impurities are removed in a subsequent step.

Other materials are often added to the iron/carbon mixture to produce steel with desired properties. Nickel and manganese in steel add to its tensile strength and make austenite more chemically stable, chromium increases hardness and melting temperature, and vanadium also increases hardness while reducing the effects of metal fatigue. To prevent corrosion, at least 11% chromium is added to steel so that a hard oxide forms on the metal surface; this is known as stainless steel. Tungsten interferes with the formation of cementite, allowing martensite to form with slower quench rates, resulting in high speed steel. On the other hand, sulfur, nitrogen, and phosphorus make steel more brittle, so these commonly found elements must be removed from the ore during processing.

The density of steel varies based on the alloying constituents, but usually ranges between 7,750 and 8,050 kg/m$^3$ (484 and 503 lb/cu ft), or 7.75 and 8.05 g/cm$^3$ (4.48 and 4.65 oz/cu in).

Even in the narrow range of concentrations which make up steel, mixtures of carbon and iron can form a number of different structures, with very different properties. Understanding such properties is essential to making quality steel. At room temperature, the most stable form of iron is the body-centered cubic (BCC) structure α-ferrite. It is a fairly soft metallic material that can dissolve only a small concentration of carbon, no more than 0.021 wt% at 723 °C (1,333 °F), and only 0.005% at 0 °C (32 °F). If steel contains more than 0.021% carbon at steelmaking temperatures then it transforms into a face-centered cubic (FCC) structure, called austenite or γ-iron. It is also soft and metallic but can dissolve considerably more carbon, as much as 2.1% carbon at 1,148 °C (2,098 °F), which reflects the upper carbon content of steel.

When steels with less than 0.8% carbon, known as a hypoeutectoid steel, are cooled from an austenitic phase the mixture attempts to revert to the ferrite phase, resulting in an excess of carbon. One way for carbon to leave the austenite is for cementite to precipitate out of the mix, leaving behind iron that is pure enough to take the form of ferrite, resulting in a cementite-ferrite mixture. Cementite is a hard and brittle intermetallic compound with the chemical formula of $Fe_3C$. At the eutectoid, 0.8% carbon, the cooled structure takes the form of pearlite, named after its resemblance to mother of pearl. For steels that have more than 0.8% carbon the cooled structure takes the form of pearlite and cementite.

Perhaps the most important polymorphic form is martensite, a metastable phase which is significantly stronger than other steel phases. When the steel is in an austenitic phase and then quenched it forms into martensite, because the atoms "freeze" in place when the cell structure changes from FCC to BCC. Depending on the carbon content the martensitic phase takes different forms. Below approximately 0.2% carbon it takes an α ferrite BCC crystal form, but higher carbon contents take a body-centered tetragonal (BCT) structure. There is no thermal activation energy for the transformation from austenite to martensite. Moreover, there is no compositional change so the atoms generally retain their same neighbors.

Martensite has a lower density than austenite does, so that transformation between them results in a change of volume. In this case, expansion occurs. Internal stresses from this expansion generally take the form of compression on the crystals of martensite and tension on the remaining ferrite, with a fair amount of shear on both constituents. If quenching is done improperly, the internal stresses can cause a part to shatter as it cools. At the very least, they cause internal work hardening and other microscopic imperfections. It is common for quench cracks to form when water quenched, although they may not always be visible.

## Heat treatment

There are many types of heat treating processes available to steel. The most common are annealing and quenching and tempering. Annealing is the process of heating the steel to a sufficiently high temperature to soften it. This process occurs through three phases: recovery, recrystallization, and grain growth. The temperature required to anneal steel depends on the type of annealing and the constituents of the alloy.

Quenching and tempering first involves heating the steel to the austenite phase, then quenching it in water or oil. This rapid cooling results in a hard and brittle martensitic structure. The steel is then tempered, which is just a specialized type of annealing. In this application the annealing (tempering) process transforms some of the martensite into cementite, or spheroidite to reduce internal stresses and defects, which ultimately results in a more ductile and fracture-resistant metal.

## *Steel production*

Iron ore pellets for the production of steel

When iron is smelted from its ore by commercial processes, it contains more carbon than is desirable. To become steel, it must be melted and reprocessed to reduce the carbon to the correct amount, at which point other elements can be added. This liquid is then continuously cast into long slabs or cast into ingots. Approximately 96% of steel is continuously cast, while only 4% is produced as cast steel ingots. The ingots are then heated in a soaking pit and hot rolled into slabs, blooms, or billets. Slabs are hot or cold rolled into sheet metal or plates. Billets are hot or cold rolled into bars, rods, and wire. Blooms are hot or cold rolled into structural steel, such as I-beams and rails. In modern foundries these processes often occur in one assembly line, with ore coming in and finished steel coming out. Sometimes after a steel's final rolling it is heat treated for strength, however this is relatively rare.

## *History of steelmaking*

Bloomery smelting during the Middle Ages

### Ancient steel

Steel was known in antiquity, and may have been produced by managing bloomeries, iron-smelting facilities, where the bloom contained carbon.

The earliest known production of steel is a piece of ironware excavated from an archaeological site in Anatolia (Kaman-Kalehoyuk) and is about 4,000 years old. Other ancient steel comes from East Africa, dating back to 1400 BC. In the 4th century BC steel weapons like the Falcata were produced in the Iberian Peninsula, while Noric steel was used by the Roman military. The Chinese of the Warring States (403–221 BC) had quench-hardened steel, while Chinese of the Han Dynasty (202 BC – 220 AD) created steel by melting together wrought iron with cast iron, gaining an ultimate product of a carbon-intermediate steel by the 1st century AD. The Haya people of East Africa discovered a type of high-heat blast furnace which allowed them to forge carbon steel at 1,802 °C (3,276 °F) nearly 2,000 years ago. This ability was not duplicated until centuries later in Europe during the Industrial Revolution.

## Wootz steel and Damascus steel

Evidence of the earliest production of high carbon steel in the Indian Subcontinent was found in Samanalawewa area in Sri Lanka. Wootz steel was produced in India by about 300 BC. Along with their original methods of forging steel, the Chinese had also adopted the production methods of creating Wootz steel, an idea imported into China from India by the 5th century AD. In Sri Lanka, this early steel-making method employed the unique use of a wind furnace, blown by the monsoon winds, that was capable of producing high-carbon steel. Also known as Damascus steel, wootz is famous for its durability and ability to hold an edge. It was originally created from a number of different materials including various trace elements. It was essentially a complicated alloy with iron as its main component. Recent studies have suggested that carbon nanotubes were included in its structure, which might explain some of its legendary qualities, though given the technology available at that time, they were produced by chance rather than by design. Natural wind was used where the soil containing iron was heated up with the use of wood. The ancient Sinhalese managed to extract a ton of steel for every 2 tons of soil, a remarkable feat at the time. One such furnace was found in Samanalawewa and archaeologists were able to produce steel as the ancients did long ago.

Crucible steel, formed by slowly heating and cooling pure iron and carbon (typically in the form of charcoal) in a crucible, was produced in Merv by the 9th to 10th century AD. In the 11th century, there is evidence of the production of steel in Song China using two techniques: a "berganesque" method that produced inferior, inhomogeneous steel and a precursor to the modern Bessemer process that utilized partial decarbonization via repeated forging under a cold blast.

## Modern steelmaking

A Bessemer converter in Sheffield, England

Since the 17th century the first step in European steel production has been the smelting of iron ore into pig iron in a blast furnace. Originally using charcoal, modern methods use coke, which has proven to be a great deal cheaper.

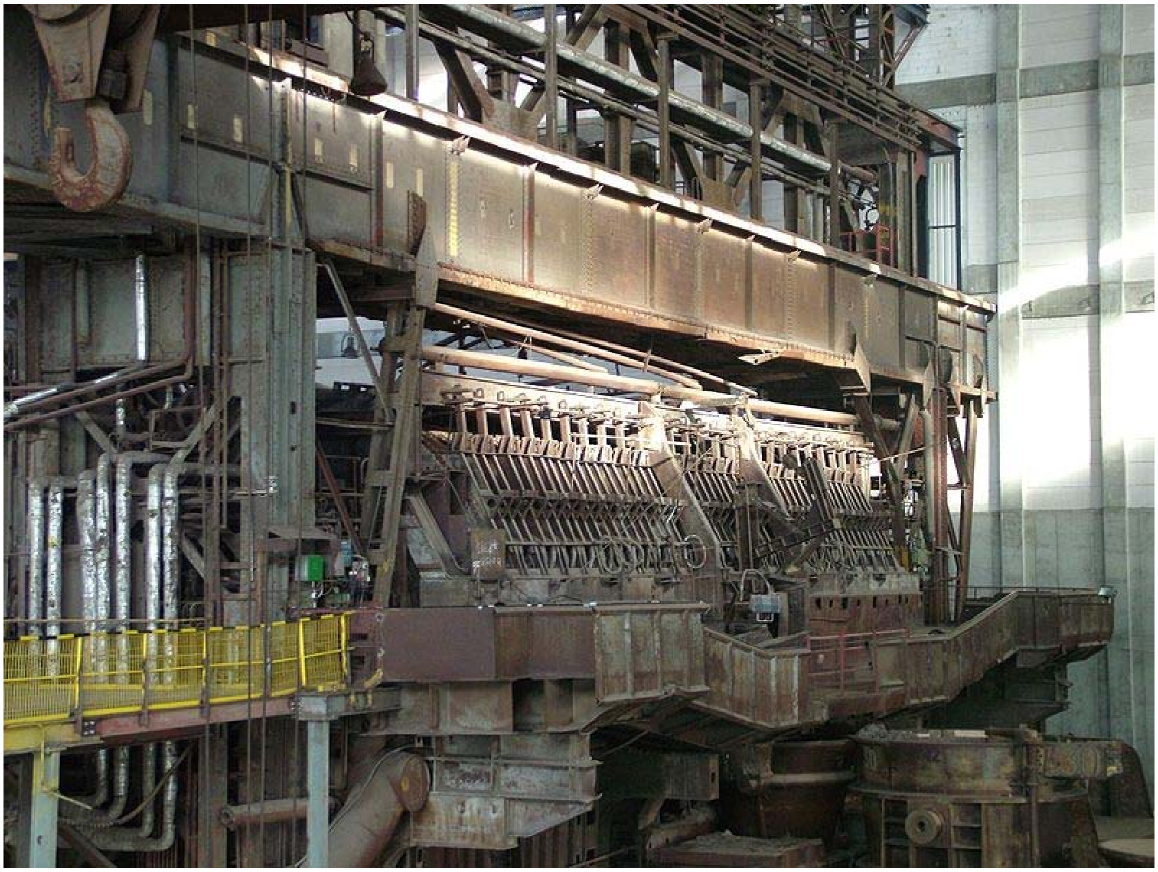
### Processes starting from bar iron

In these processes pig iron was "fined" in a finery forge to produce bar iron (wrought iron), which was then used in steel-making.

The production of steel by the cementation process was described in a treatise published in Prague in 1574 and was in use in Nuremberg from 1601. A similar process for case hardening armour and files was described in a book published in Naples in 1589. The process was introduced to England in about 1614. It was produced by Sir Basil Brooke at Coalbrookdale during the 1610s. The raw material for this were bars of wrought iron. During the 17th century it was realised that the best steel came from oregrounds iron from a region of Sweden, north of Stockholm. This was still the usual raw material in the 19th century, almost as long as the process was used.

Crucible steel is steel that has been melted in a crucible rather than being forged, with the result that it is more homogeneous. Most previous furnaces could not reach high enough temperatures to melt the steel. The early modern crucible steel industry resulted from the invention of Benjamin Huntsman in the 1740s. Blister steel (made as above) was melted in a crucible or in a furnace, and cast (usually) into ingots.

**Processes starting from pig iron**



A Siemens-Martin steel oven from the Brandenburg Museum of Industry

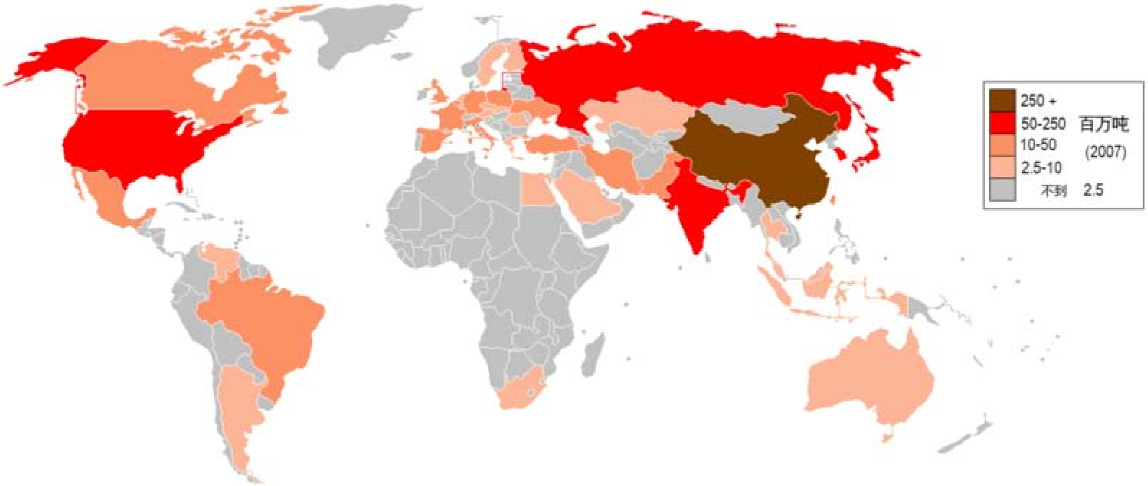
White-hot steel pouring out of an electric arc furnace

The modern era in steelmaking began with the introduction of Henry Bessemer's Bessemer process in 1858. His raw material was pig iron. This enabled steel to be produced in large quantities cheaply, thus mild steel is now used for most purposes for which wrought iron was formerly used. The Gilchrist-Thomas process (or *basic Bessemer process*) was an improvement to the Bessemer process, lining the converter with a basic material to remove phosphorus. Another improvement in steelmaking was the Siemens-Martin process, which complemented the Bessemer process.

These were rendered obsolete by the Linz-Donawitz process of basic oxygen steelmaking (BOS), developed in the 1950s, and other oxygen steelmaking processes. Basic oxygen steelmaking is superior to previous steelmaking methods because the oxygen pumped into the furnace limits impurities. Now, electric arc furnaces (EAF) are a common method of reprocessing scrap metal to create new steel. They can also be used for converting pig iron to steel, but they use a great deal of electricity (about 440 kWh per metric ton), and are thus generally only economical when there is a plentiful supply of cheap electricity.

### *Steel industry*

A steel plant in the United Kingdom



Steel production by country in 2007

It is common today to talk about "the iron and steel industry" as if it were a single entity, but historically they were separate products. The steel industry is often considered to be an indicator of economic progress, because of the critical role played by steel in infrastructural and overall economic development.

The economic boom in China and India has caused a massive increase in the demand for steel in recent years. Between 2000 and 2005, world steel demand increased by 6%. Since 2000, several Indian and Chinese steel firms have risen to prominence like Tata Steel (which bought Corus Group in 2007), Shanghai Baosteel Group Corporation and Shagang Group. ArcelorMittal is however the world's largest steel producer.

In 2005, the British Geological Survey stated China was the top steel producer with about one-third of the world share; Japan, Russia, and the US followed respectively.

In 2008, steel started to be traded as a commodity in the London Metal Exchange. At the end of 2008, the steel industry faced a sharp downturn that led to many cut-backs.

## Contemporary steel

Bethlehem Steel in Bethlehem, Pennsylvania was one of the world's largest manufacturers of steel before its 2003 closure.

Modern steels are made with varying combinations of alloy metals to fulfill many purposes. Carbon steel, composed simply of iron and carbon, accounts for 90% of steel production. High strength low alloy steel has small additions (usually < 2% by weight) of other elements, typically 1.5% manganese, to provide additional strength for a modest price increase. Low alloy steel is alloyed with other elements, usually molybdenum, manganese, chromium, or nickel, in amounts of up to 10% by weight to improve the hardenability of thick sections. Stainless steels and surgical stainless steels contain a minimum of 11% chromium, often combined with nickel, to resist corrosion (rust). Some stainless steels are magnetic, while others are nonmagnetic.

Some more modern steels include tool steels, which are alloyed with large amounts of tungsten and cobalt or other elements to maximize solution hardening. This also allows the use of precipitation hardening and improves the alloy's temperature resistance. Tool steel is generally used in axes, drills, and other devices that need a sharp, long-lasting cutting edge. Other special-purpose alloys include weathering steels such as Cor-ten, which weather by acquiring a stable, rusted surface, and so can be used un-painted.

Many other high-strength alloys exist, such as dual-phase steel, which is heat treated to contain both a ferritic and martensitic microstructure for extra strength. Transformation Induced Plasticity (TRIP) steel involves special alloying and heat treatments to stabilize amounts of austentite at room temperature in normally austentite-free low-alloy ferritic steels. By applying strain to the metal, the austentite undergoes a phase transition to martensite without the addition of heat. Maraging steel is alloyed with nickel and other elements, but unlike most steel contains almost no carbon at all. This creates a very strong but still malleable metal. Twinning Induced Plasticity (TWIP) steel uses a specific type of strain to increase the effectiveness of work hardening on the alloy. Eglin Steel uses a combination of over a dozen different elements in varying amounts to create a relatively low-cost metal for use in bunker buster weapons. Hadfield steel (after Sir Robert Hadfield) or manganese steel contains 12–14% manganese which when abraded forms an incredibly hard skin which resists wearing. Examples include tank tracks, bulldozer blade edges and cutting blades on the jaws of life.

Most of the more commonly used steel alloys are categorized into various grades by standards organizations. For example, the Society of Automotive Engineers has a series of grades defining many types of steel. The American Society for Testing and Materials has a separate set of standards, which define alloys such as A36 steel, the most commonly used structural steel in the United States.

Though not an alloy, galvanized steel is a commonly used variety of steel which has been hot-dipped or electroplated in zinc for protection against rust.

### *Uses*

A roll of steel wool

Iron and steel are used widely in the construction of roads, railways, other infrastructure, applicances, and buildings. Most large modern structures, such as stadiums and skyscrapers, bridges, and airports, are supported by a steel skeleton. Even those with a concrete structure will employ steel for reinforcing. In addition to widespread use in major appliances and cars. Despite growth in usage of aluminium, it is still the main material for car bodies. Steel is used in a variety of other construction materials, such as bolts, nails, and screws. Other common applications include shipbuilding, pipeline transport, mining, offshore construction, aerospace, white goods (e.g. washing machines), heavy equipment such as bulldozers, office furniture, steel wool, tools, and armour in the form of personal vests or vehicle armour (better known as rolled homogeneous armour in this role).

## Historical

A carbon steel knife

Before the introduction of the Bessemer process and other modern production techniques, steel was expensive and was only used where no cheaper alternative existed, particularly for the cutting edge of knives, razors, swords, and other items where a hard, sharp edge was needed. It was also used for springs, including those used in clocks and watches. With the advent of speedier and thriftier production methods, steel has been easier to obtain and much cheaper. It has replaced wrought iron for a multitude of purposes. However, the availability of plastics in the latter part of the 20th century allowed these materials to replace steel due to their lower cost and weight.

## Long steel

A steel pylon suspending overhead powerlines

- As reinforcing bars and mesh in reinforced concrete
- Railroad tracks
- Structural steel in modern buildings and bridges
- Wires

## Flat carbon steel

- Major appliances
- Magnetic cores
- The inside and outside body of automobiles, trains, and ships.

## Stainless steel

A stainless steel gravy boat

- Cutlery
- Rulers
- Surgical equipment
- Wrist watches

## Low-background steel

Steel manufactured after World War II became contaminated with radionuclides due to nuclear weapons testing. Low-background steel, steel manufactured prior to 1945, is used for certain radiation-sensitive applications such as Geiger counters and radiation shielding.

## Chapter 4

# Intermetallics

**Intermetallics** or **intermetallic compounds** is a term that is used in a number of different ways. Most commonly it refers to solid-state phases involving metals. There is a "research definition" adhered to generally in scientific publications, and a wider "common use" term. There is also a completely different use in coordination chemistry, where it has been used to refer to complexes containing two or more different metals.

Although the term *intermetallic compounds*, as it applies to solid phases, has been in use for many years, its introduction was regretted, for example by Hume-Rothery in 1955.

Note that many intermetallic compounds are often simply called alloys, even though strictly speaking they are not. For example, complex metallic alloys are intermetallic compounds with large unit cells.

## *Definitions*

### Research definition

This was stated by Schulze in 1967, and defines intermetallic compounds as solid phases containing two or more metallic elements, with optionally one or more non-metallic elements, whose crystal structure differs from that of the other constituents. Under this definition the following are included

- Electron (or Hume-Rothery) compounds
- Size packing phases. e.g. Laves phases, Frank-Kaspar phases and Nowotny phases
- Zintl phases

The definition of a metal is taken to include:

- the so-called poor metals, i.e. aluminium, gallium, indium, thallium, tin and lead
- some, if not all, of the metalloids, e.g. silicon, germanium, arsenic, antimony and tellurium.

Alloys, which are a homogeneous mixture of metals, and interstitial compounds such as the carbides and nitrides are excluded under this definition. However, interstitial intermetallic compounds are included as are alloys of intermetallic compounds with a metal.

## Common use

In common use of the research definition, including poor metals and metalloids, is extended to include compounds such as cementite, $Fe_3C$. These compounds, sometimes termed interstitial compounds can be stoichiometric, and share similar properties to the intermetallic compounds defined above.

## Complexes

The term intermetallic is used  to describe compounds involving two or more metals such as the cyclopentadienyl complex $Cp_6Ni_2Zn_4$.

## *Intermetallics involving two or more metallic elements*

Intermetallic compounds are generally brittle and high melting. They often offer a compromise between ceramic and metallic properties when hardness and/or resistance to high temperatures is important enough to sacrifice some toughness and ease of processing. They can also display desirable magnetic, superconducting and chemical properties, due to their strong internal order and mixed (metallic and covalent/ionic) bonding, respectively. Intermetallics have given rise to various novel materials developments. Some examples include alnico and the hydrogen storage materials in nickel metal hydride batteries. $Ni_3Al$, which is the hardening phase in the familiar nickel-base superalloys, and the various titanium aluminides have also attracted interest for turbine blade applications, while the latter is also used in very small quantities for grain refinement of titanium alloys.

## Properties and examples

- magnetic materials e.g. alnico; sendust; Permendur, FeCo
- superconductors e.g. A15 phases; niobium-tin
- hydrogen storage e.g. $AB_5$ compounds (nickel metal hydride batteries)
- shape memory alloys e.g. Cu-Al-Ni (alloys of $Cu_3Al$ and nickel); Nitinol (NiTi)
- coating materials e.g. NiAl
- high temperature structural materials e.g. nickel aluminide, $Ni_3Al$
- dental amalgams which are alloys of intermetallics $Ag_3Sn$ and $Cu_3Sn$

The formation of intermetallics can cause problems. Intermetallics of gold and aluminium are a significant cause of wire bond failures in semiconductor devices and other microelectronics devices. There are 5 of them. $AuAl_2$ is known as "purple plague". $Au_5Al_2$ is known as "white plague".

## History

Examples of intermetallics through history include:

- Roman yellow brass, CuZn
- Chinese high tin bronze, $Cu_{31}Sn_8$
- type metal SbSn

German type metal is described as breaking like glass, not bending, softer than copper but more fusible than lead. The chemical formula does not agree with the one above; however, the properties match with an intermetallic compound or an alloy of one.

## Chapter 5

# Metalworking

**Metalworking** is the process of working with metals to create individual parts, assemblies, or large scale structures. The term covers a wide range of work from large ships and bridges to precise engine parts and delicate jewelry. It therefore includes a correspondingly wide range of skills, processes, and tools.

Metalworking is a science, art, hobby, industry and trade. Its historical roots span cultures, civilizations, and millennia. Metalworking has evolved from the discovery of smelting various ores, producing malleable and ductile metal useful for tools and adornments. Modern metalworking processes, though diverse and specialized, can be categorized as forming, cutting or joining processes. Today's machine shop includes a number of machine tools capable of creating a precise, useful workpiece.

### *Prehistory*

Metalworking predates history. No one knows with any certainty where or when metalworking began. The earliest technologies were impermanent and were unlikely to leave evidence for long. The advance that brought metal into focus was the connection of fire and metals. Who accomplished this is as unknown as the when and where, but the Egyptians are thought to have been one of the first civilizations to work gold.

Not all metal required fire to obtain it or work it. Isaac Asimov speculated that gold was the "first metal." His reasoning is that gold by its chemistry is found in nature as nuggets of pure gold. In other words, gold, as rare as it is, is always found in nature as the metal that it is. There are a few other metals that sometimes occur natively, and as a result of meteors. Almost all other metals are found in ores, a mineral bearing rock, that require heat or some other process to liberate the metal. Another feature of gold is that it is workable as it is found, meaning that no technology beyond eyes to find a nugget and a hammer and an anvil to work the metal is needed. Stone hammer and stone anvil will suffice for technology. This is the result of gold's properties of malleability and ductility. The earliest tools were stone, bone, wood, and sinew. They sufficed to work gold.

At some unknown point the connection between heat and the liberation of metals from rock became clear, rocks rich in copper, tin, and lead came into demand. These ores were mined wherever they were recognized. Remnants of such ancient mines have been found all over what is today the Middle East. Metalworking was being carried out by the South Asian inhabitants of Mehrgarh between 7000–3300 BCE. The end of the beginning of metalworking occurs sometime around 6000 BCE when copper smelting became common in the Middle East.

The ancients knew of seven metals. Here they are arranged in order of their oxidation potential:

- Iron +0.44,
- Tin +0.14
- Lead +0.13
- Copper -0.34
- Mercury -0.79
- Silver -0.80
- Gold -1.50

The oxidation potential is important because it is one indicator of how tightly bound to the ore the metal is likely to be. As can be seen, iron is significantly higher than the other six metals while gold is dramatically lower than the six above it. Gold's low oxidation is one of the main reasons that gold is found in nuggets. These nuggets are relatively pure gold and are workable as they are found.

Copper ore, being relatively abundant, and tin ore became the next important players in the story of metalworking. Using heat to smelt copper from ore, a great deal of copper was produced. It was used for both jewelry and simple tools. However, copper by itself was too soft for tools requiring edges and stiffness. At some point tin was added into the molten copper and bronze was born. Bronze is an alloy of copper and tin. Bronze was an important advance because it had the edge-durability and stiffness that pure copper lacked. Until the advent of iron, bronze was the most advanced metal for tools and weapons in common use.

Looking beyond the Middle East, these same advances and materials were being discovered and used the world around. China and Britain jumped into the use of bronze with little time being devoted to copper. Japan began the use of bronze and iron almost simultaneously. In the Americas things were different. Although the peoples of the Americas knew of metals, it wasn't until the arrival of Europeans that metal for tools and weapons took off. Jewelry and art were the principal uses of metals in the Americas prior to European influence.

Around the date 2700 BCE, production of bronze was common in locales where the necessary materials could be assembled for smelting, heating, and working the metal. Iron was beginning to be smelted. Iron began its emergence as an important metal for tools and weapons. The Iron Age was dawning.

## *History*

A turret lathe operator machining parts for transport planes at the Consolidated Aircraft Corporation plant, Fort Worth, Texas, USA in the 1940s.

By the historical periods of the Pharaohs in Egypt, the Vedic Kings in India, the Tribes of Israel, and the Mayan Civilization in North America, among other ancient populations, precious metals began to have value attached to them. In some cases rules for ownership, distribution, and trade were created, enforced, and agreed upon by the respective peoples. By the above periods metalworkers were very skilled at creating objects of adornment, religious artifacts, and trade instruments of precious metals (non-ferrous), as well as weaponry usually of ferrous metals and/or alloys. These skills were finely honed and well executed. The techniques were practiced by artisans, blacksmiths, atharvavedic practitioners, alchemists, and other categories of metalworkers around the globe. For example, the ancient technique of granulation is found around the world in numerous ancient cultures before the historic record shows people traveled seas or overland to far regions of the earth to share this process that still being used by metalsmiths today.

As time progressed metal objects became more common, and ever more complex. The need to further acquire and work metals grew in importance. Skills related to extracting metal ores from the earth began to evolve, and metalsmiths became more knowledgeable. Metalsmiths became important members of society. Fates and economies of entire civilizations were greatly affected by the availability of metals and metalsmiths. The metalworker depends on the extraction of precious metals to make jewelry, build more efficient electronics, and for industrial and technological applications from construction to shipping containers to rail, and air transport. Without metals, goods and services would cease to move around the globe on the scale we know today.

More individuals than ever before are learning metalworking as a creative outlet in the forms of jewelry making, hobby restoration of aircraft and cars, blacksmithing, tinsmithing, tinkering, and in other art and craft pursuits. Trade schools continue to teach welding in all of its forms, and there is a proliferation of schools of Lapidary and Jewelers arts and sciences at this- the beginning of the 21st Century AD.

## *General metalworking processes*

A combination square used for transferring designs.

A caliper is used to precisely measure a short length.

Metalworking generally is divided into the following categories, *forming*, *cutting*, and, *joining*. Each of these categories contain various processes.

Compatibility chart of materials versus processes

| | **Material** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Process** | **Iron** | **Steel** | **Aluminium** | **Copper** | **Magnesium** | **Nickel** | **Refractory metals** | **Titanium** | **Zinc** |
| **Sand casting** | X | X | X | X | X | X | | | 0 |
| **Permanent mold casting** | X | 0 | X | 0 | X | 0 | | | 0 |
| **Die casting** | | | X | 0 | X | | | | X |
| **Investment casting** | | X | X | X | 0 | 0 | | | |
| **Closed-die forging** | | X | 0 | 0 | 0 | 0 | 0 | 0 | |
| **Extrusion** | | 0 | X | X | X | 0 | 0 | 0 | |
| **Cold heading** | | X | X | X | | 0 | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Stamping & deep drawing** | | X | X | X | 0 | X | | 0 | 0 |
| **Screw machine** | 0 | X | X | X | 0 | X | 0 | 0 | 0 |
| **Powder metallurgy** | X | X | 0 | X | | 0 | X | 0 | |
| Key: **X** = Routinely performed, **0** = Performed with difficulty, caution, or some sacrifice, **blank** = Not recommended | | | | | | | | | |

Prior to most operations, the metal must be marked out and/or measured, depending on the desired finished product.

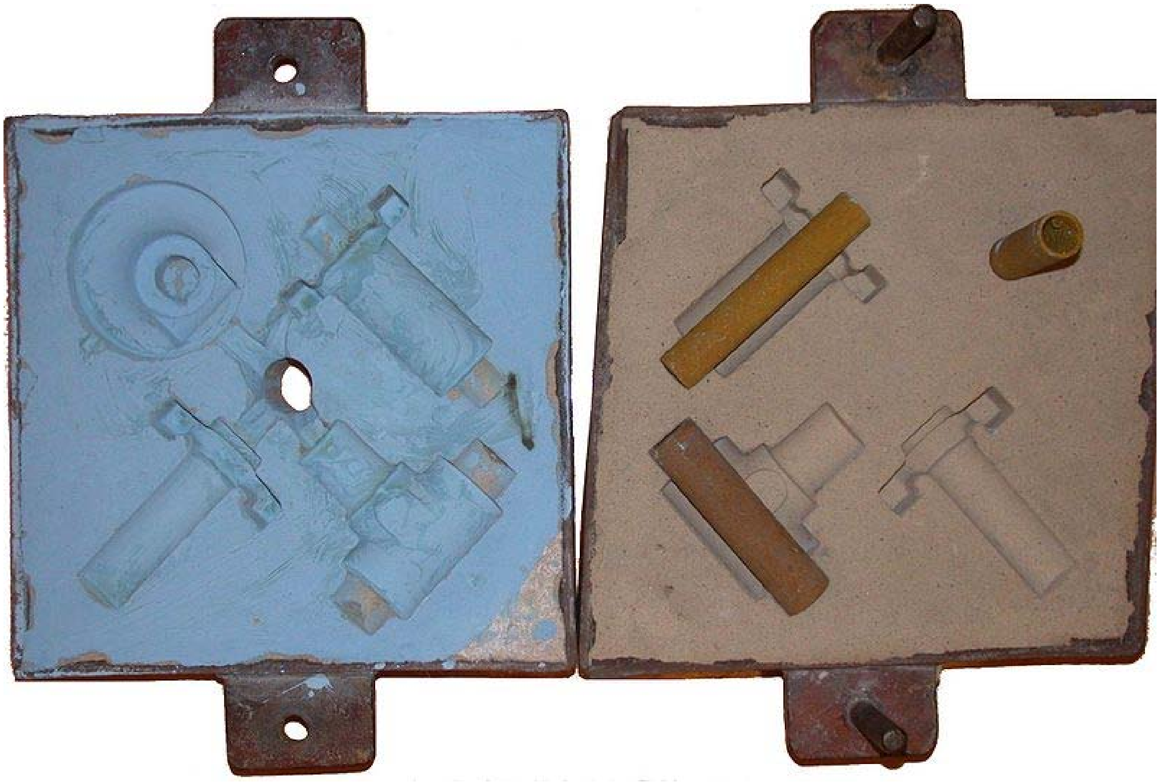
*Marking out* (also known as layout) is the process of transferring a design or pattern to a workpiece and is the first step in the handcraft of metalworking. It is performed in many industries or hobbies, although in the repetition industries the need to mark out every individual piece is eliminated. In the metal trades area, marking out consists of transferring the engineer's plan to the workpiece in preparation for the next step, machining or manufacture.

*Calipers* are hand tools designed to precisely measure the distance between two points. Most calipers have two sets of flat, perpendicular edges used for inner or outer diameter. These calipers can be accurate to within one-thousandth of an inch (25.4μm). Different types of calipers have different mechanisms for displaying the distance measured. Where larger objects need to be measured with less precision, a tape measure is often used.

## Forming processes

These *forming* processes modify metal or workpiece by deforming the object, that is, without removing any material. Forming is done with heat and pressure, or with mechanical force, or both.

### Casting



A sand casting mold

Casting achieves a specific form by pouring molten metal into a mold and allowing it to cool, with no mechanical force. Forms of casting include:

- Investment casting (called lost wax casting in art)
- Centrifugal casting
- Die casting
- Sand casting
- Shell casting
- Spin casting

### Plastic deforming

A red-hot metal workpiece is inserted into a forging press.

Plastic deformation involves using heat or pressure to make a workpiece more conductive to mechanical force. Historically, this and casting were done by blacksmiths, though today the process has been industrialized.

- Cold sizing
- Extrusion
- Forging
- Hot metal gas forming
- Powder metallurgy
- Friction drilling

**Sheet metal forming**

A metal spun brass vase

These types of forming process involve the application of mechanical force at room temperature.

- Bending
- Coining
- Decambering
- Deep drawing
- Drawing
- Spinning

- Flow turning
- Raising
- Roll forming
- Roll bending
- Repoussé and chasing
- Rolling
- Rubber pad forming
- Shearing
- Stamping
- Wheeling using an English wheel (wheeling machine)

### *Cutting processes*

A CNC plasma cutting machining

*Cutting* is a collection of processes wherein material is brought to a specified geometry by removing excess material using various kinds of tooling to leave a finished part that meets specifications. The net result of cutting is two products, the waste or excess material, and the finished part. If this were a discussion of woodworking, the waste would be sawdust and excess wood. In cutting metals the waste is chips or swarf and excess metal. These processes can be divided into chip producing cutting, generally known as machining. Burning or cutting with an oxyfuel torch is a welding process not machining. There are also miscellaneous specialty processes such as chemical milling.

Cutting is nearly fully represented by:

- Chip producing processes most commonly known as machining
- Burning, a set of processes which cut by oxidizing a kerf to separate pieces of metal
- Specialty processes

Drilling a hole in a metal part is the most common example of a chip producing process. Using an oxy-fuel cutting torch to separate a plate of steel into smaller pieces is an example of burning. Chemical milling is an example of a specialty process that removes excess material by the use of etching chemicals and masking chemicals.

There are many technologies available to cut metal, including:

- Manual technologies: saw, chisel, shear or snips
- Machine technologies: turning, milling, drilling, grinding, sawing
- Welding/burning technologies: burning by laser, oxy-fuel burning, and plasma
- Erosion technologies:by water jet or electric discharge.

Cutting fluid or coolant is used where there is significant friction and heat at the cutting interface between a cutter such as a drill or an end mill and the workpiece. Coolant is generally introduced by a spray across the face of the tool and workpiece to decrease friction and temperature at the cutting tool/workpiece interface to prevent excessive tool wear. In practice there are many methods of delivering coolant.

## Machining

A milling machine in operation, including coolant hoses.

*Milling* is the complex shaping of metal or other materials by removing material to form the final shape. It is generally done on a milling machine, a power-driven machine that in its basic form consists of a milling cutter that rotates about the spindle axis (like a drill), and a worktable that can move in multiple directions (usually two dimensions [x and y axis] relative to the workpiece). The spindle usually moves in the z axis. It is possible to raise the table (where the workpiece rests). Milling machines may be operated manually or under computer numerical control (CNC), and can perform a vast number of complex operations, such as slot cutting, planing, drilling and threading, rabbeting, routing, etc. Two common types of mills are the horizontal mill and vertical mill.

The pieces produced are usually complex 3D objects that are converted into x, y, and z coordinates that are then fed into the CNC machine and allow it to complete the tasks required. The milling machine can produce most parts in 3D, but some require the objects to be rotated around the x, y, or z coordinate axis (depending on the need). Tolerances are usually in the thousandths of an inch (Unit known as Thou), depending on the specific machine.

In order to keep both the bit and material cool, a high temperature coolant is used. In most cases the coolant is sprayed from a hose directly onto the bit and material. This coolant can either be machine or user controlled, depending on the machine.

Materials that can be milled range from aluminum to stainless steel and most everything in between. Each material requires a different speed on the milling tool and varies in the amount of material that can be removed in one pass of the tool. Harder materials are usually milled at slower speeds with small amounts of material removed. Softer materials vary, but usually are milled with a high bit speed.

The use of a milling machine adds costs that are factored into the manufacturing process. Each time the machine is used coolant is also used, which must be periodically added in order to prevent breaking bits. A milling bit must also be changed as needed in order to prevent damage to the material. Time is the biggest factor for costs. Complex parts can require hours to complete, while very simple parts take only minutes. This in turn varies the production time as well, as each part will require different amounts of time.

Safety is key with these machines. The bits are traveling at high speeds and removing pieces of usually scalding hot metal. The advantage of having a CNC milling machine is that it protects the machine operator.

## Turning

A lathe cutting material from a workpiece.

Turning is a metal cutting process for producing a cylindrical surface with a single point tool. The workpiece is rotated on a spindle and the cutting tool is fed into it radially, axially or both. Producing surfaces perpendicular to the workpiece axis is called facing. Producing surfaces using both radial and axial feeds is called profiling.

A *lathe* is a machine tool which spins a block or cylinder of material so that when abrasive, cutting, or deformation tools are applied to the workpiece, it can be shaped to produce an object which has rotational symmetry about an axis of rotation. Examples of objects that can be produced on a lathe include candlestick holders, table legs, bowls, baseball bats, crankshafts, camshafts, and bearing mounts.

Lathes have three main components: the headstock, the carriage, and the tailstock. The headstock's spindle secures the workpiece with a chuck, whose jaws (usually three or four) are tightened around the piece. The spindle rotates at high speed, providing the energy to cut the material. While historic lathes were powered by belts from the ceiling, modern examples uses electric motors. The workpiece extends out of the spindle along the axis of rotation above the flat bed. The carriage is a platform that can be moved, precisely and independently, horizontally parallel and perpendicular to the axis of rotation. A hardened cutting tool is held at the desired height (usually the middle of the workpiece) by the toolpost. The carriage is then moved around the rotating workpiece, and the cutting tool gradually shaves material from the workpiece. The tailstock can be slid along the axis of rotation and then locked in place as necessary. It may hold centers to further secure the workpiece, or cutting tools driven into the end of the workpiece.

Other operation that can be performed with a single point tool on a lathe are:

Chamfering: Cutting an angle on the comer of a cylinder.
Parting: The tool is fed radially into the workpiece to cut off the end of a part.
Threading: A tool is fed along and across the outside or inside surface of rotating parts to produce external or internal threads.
Boring: A single-point tool is fed linearly and parallel to the axis of rotation.
Drilling: Feeding the drill into the workpiece axially.
Knurling: Produces a regular cross-hatched pattern in work surfaces intended to be gripped by hand.

Modern computer numerical control (CNC) lathes and (CNC) machining centres can do secondary operations like milling by using driven tools. When driven tools are used the work piece stops rotating and the driven tool executes the machining operation with a rotating cutting tool. The CNC machines use x, y, and z coordinates in order to control the turning tools and produce the product. Most modern day CNC lathes are able to produce most turned objects in 3D.

Materials appropriate for turning used are softer metals, although harder metals can be turned with a bit more time and effort.

The turning tool material must be harder than the material being turned in order for the process to work. Production rates for this process depend on the object being turned and the speed at which it can be done. More complex materials, therefore, will take more time.

## Threading

Three different types and sizes of taps.

There are many threading processes including: cutting threads with a tap or die, thread milling, single-point thread cutting, thread rolling and forming, and thread grinding. A *tap* is used to cut a female thread on the inside surface of a pre-drilled hole, while a *die* cuts a male thread on a preformed cylindrical rod.

## Grinding

A surface grinder

*Grinding* uses an abrasive process to remove material from the workpiece. A **grinding machine** is a machine tool used for producing very fine finishes, making very light cuts, or high precision forms using a abrasive wheel as the cutting device. This wheel can be made up of various sizes and types of stones, diamonds or inorganic materials.

The simplest grinder is a bench grinder or a hand-held angle grinder, for deburring parts or cutting metal with a zip-disc.

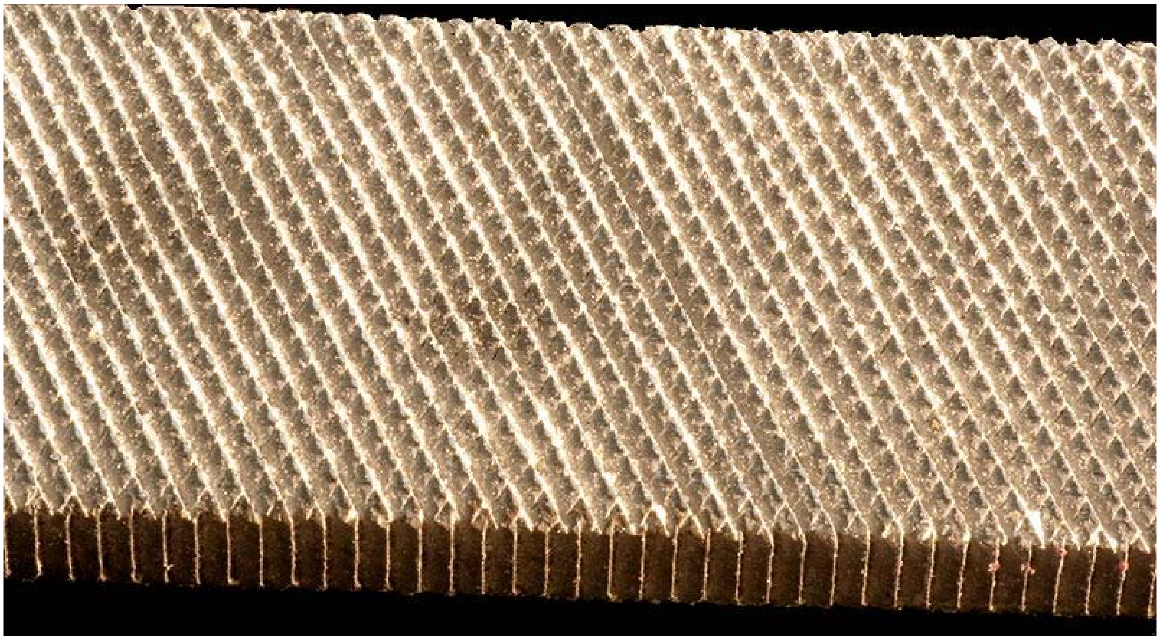
Grinders have increased in size and complexity with advances in time and technology. From the old days of a manual toolroom grinder sharpening endmills for a production shop, to today's 30000 RPM CNC auto-loading manufacturing cell producing jet turbines, grinding processes vary greatly.

Grinders need to be very rigid machines to produce the required finish. Some grinders are even used to produce glass scales for positioning CNC machine axis. The common rule is the machines used to produce scales be 10 times more accurate than the machines the parts are produced for.

In the past grinders were used for finishing operations only because of limitations of tooling. Modern grinding wheel materials and the use of industrial diamonds or other man-made coatings (cubic boron nitride) on wheel forms have allowed grinders to achieve excellent results in production environments instead of being relegated to the back of the shop.

Modern technology has advanced grinding operations to include CNC controls, high material removal rates with high precision, lending itself well to aerospace applications and high volume production runs of precision components.

## Filing



A file is an abrasive surface like this one that allows machinists to remove small, imprecise amounts of metal.

*Filing* is combination of grinding and saw tooth cutting using a file. Prior to the development of modern machining equipment it provided a relatively accurate means for the production of small parts, especially those with flat surfaces. The skilled use of a file allowed a machinist to work to fine tolerances and was the hallmark of the craft. Today filing is rarely used as a production technique in industry, though it remains as a common method of deburring.

## Other

Broaching is a machining operation used to cut keyways into shafts. Electron beam machining (EBM) is a machining process where high-velocity electrons are directed toward a work piece, creating heat and vaporizing the material. Ultrasonic machining uses ultrasonic vibrations to machine very hard or brittle materials.

## *Joining processes*

Mig welding

### Welding

*Welding* is a fabrication process that joins materials, usually metals or thermoplastics, by causing coalescence. This is often done by melting the workpieces and adding a filler material to form a pool of molten material that cools to become a strong joint, but sometimes pressure is used in conjunction with heat, or by itself, to produce the weld.

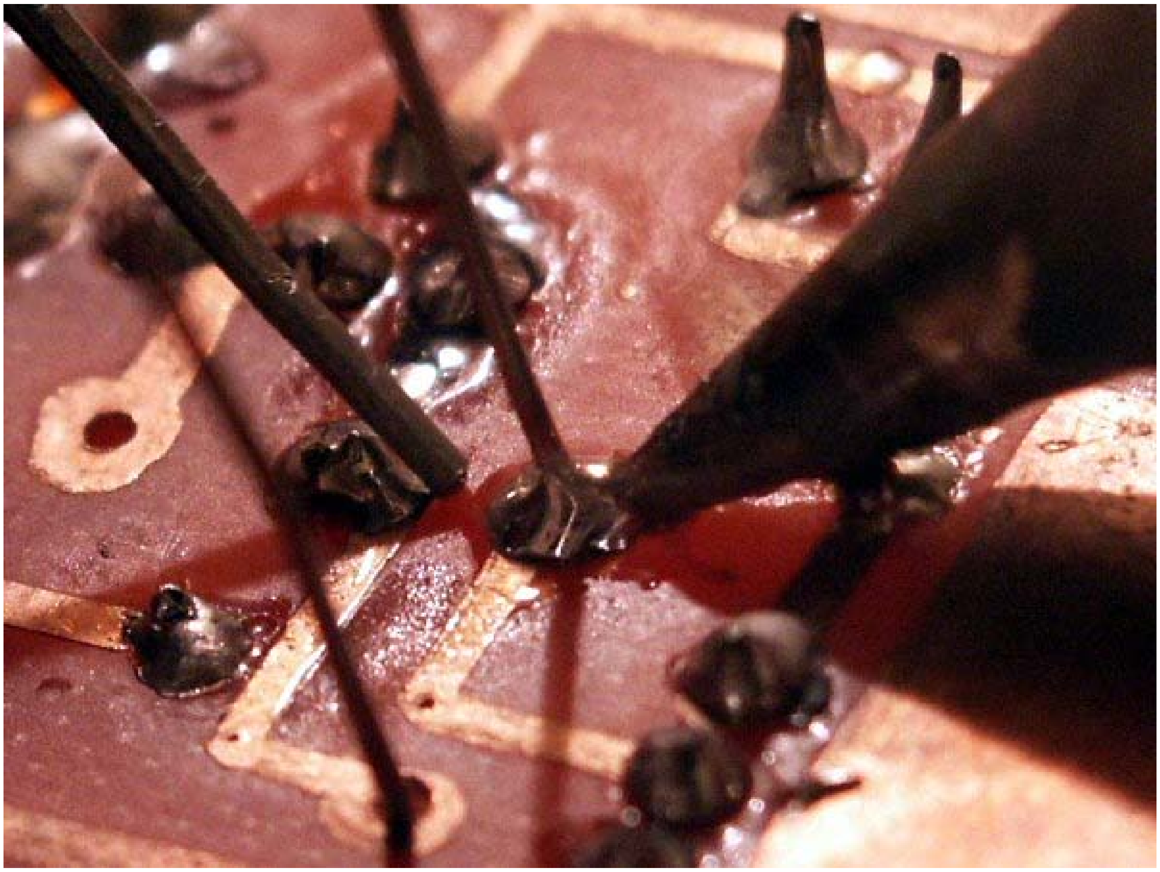
Many different energy sources can be used for welding, including a gas flame, an electric arc, a laser, an electron beam, friction, and ultrasound. While often an industrial process, welding can be done in many different environments, including open air, underwater and in space. Regardless of location, however, welding remains dangerous, and precautions must be taken to avoid burns, electric shock, poisonous fumes, and overexposure to ultraviolet light.

## Brazing

*Brazing* is a joining process in which a filler metal is melted and drawn into a capillary formed by the assembly of two or more work pieces. The filler metal reacts metallurgically with the workpiece(s) and solidifies in the capillary, forming a strong joint. Unlike welding, the work piece is not melted. Brazing is similar to soldering, but occurs at temperatures in excess of 450 °C (842 °F). Brazing has the advantage of producing less thermal stresses than welding, and brazed assemblies tend to be more ductile than weldments because alloying elements can not segregate and precipitate.

Brazing techniques include, flame brazing, resistance brazing, furnace brazing, diffusion brazing, and inductive brazing.

## Soldering



Soldering a printed circuit board.

*Soldering* is a joining process that occurs at temperatures below 450 °C (842 °F). It is similar to brazing in the fact that a filler is melted and drawn into a capillary to form a join, although at a lower temperature. Because of this lower temperature and different alloys used as fillers, the metallurgical reaction between filler and work piece is minimal, resulting in a weaker joint.

### Riveting

*Riveting* is one of the most ancient metalwork joining processes. Its use has declined markedly during the second half of the 20th century, but it still retains important uses in industry and construction into the 21st century. The earlier use of rivets is being superseded by improvements in welding and component fabrication techniques.

A rivet is essentially a two-headed and unthreaded bolt which holds two other pieces of metal together. Holes are drilled or punched through the two pieces of metal to be joined. The holes being aligned, a rivet is passed through the holes and permanent heads are formed onto the ends of the rivet utilizing hammers and forming dies (by either coldworking or hotworking). Rivets are commonly purchased with one head already formed.

When it is necessary to remove rivets, one of the rivet's heads is sheared off with a cold chisel. The rivet is then driven out with a hammer and punch.

## *Associated processes*

While these processes are not primary metalworking processes, they are often performed before or after metalworking processes.

### Heat treatment

Metals can be heat treated to alter the properties of strength, ductility, toughness, hardness or resistance to corrosion. Common heat treatment processes include annealing, precipitation strengthening, quenching, and tempering. The **annealing** process softens the metal by allowing recovery of cold work and grain growth. **Quenching** can be used to harden alloy steels, or in precipitation hardenable alloys, to trap dissolved solute atoms in solution. **Tempering** will cause the dissolved alloying elements to precipitate, or in the case of quenched steels, improve impact strength and ductile properties.

Often, mechanical and thermal treatments are combined in what is known as thermo-mechanical treatments for better properties and more efficient processing of materials. These processes are common to high alloy special steels, super alloys and titanium alloys.

## Plating

Electroplating is a common surface-treatment technique. It involves bonding a thin layer of another metal such as gold, silver, chromium or zinc to the surface of the product. It is used to reduce corrosion as well as to improve the product's aesthetic appearance.

## Thermal spraying

Thermal spraying techniques are another popular finishing option, and often have better high temperature properties than electroplated coatings.

## Chapter 6

# Casting (Metalworking)


Casting iron in a sand mold

In metalworking, **casting** involves pouring a liquid metal into a mold, which contains a hollow cavity of the desired shape, and then is allowed to solidify. The solidified part is also known as a casting, which is ejected or broken out of the mold to complete the process. Casting is most often used for making complex shapes that would be difficult or uneconomical to make by other methods.

The casting process is subdivided into two main categories: expendable and non-expendable casting. It is further broken down by the mold material, such as sand or metal, and pouring method, such as gravity, vacuum, or low pressure.

## *Terminology*

Metal casting processes uses the following terminology:

- Pattern: An approximate duplicate of the final casting used to form the mold cavity.
- Molding material: The material that is packed around the pattern and then the pattern is removed to leave the cavity where the casting material will be poured.
- Flask: The rigid wood or metal frame that holds the molding material.
  - Cope: The top half of the pattern, flask, mold, or core.
  - Drag: The bottom half of the pattern, flask, mold, or core.
- Core: An insert in the mold that produces internal features in the casting, such as holes.
  - Core print: The region added to the pattern, core, or mold used to locate and support the core.
- Mold cavity: The combined open area of the molding material and core, there the metal is poured to produce the casting.
- Riser: An extra void in the mold that fills with molten material to compensate for shrinkage during solidification.
- Gating system: The network of connected channels that deliver the molten material to the mold cavities.
  - Pouring cup or pouring basin: The part of the gating system that receives the molten material from the pouring vessel.
  - Sprue: The pouring cup attaches to the sprue, which is the vertical part of the gating system. The other end of the sprue attaches to the runners.
  - Runners: The horizontal portion of the gating system that connects the sprues to the gates.
  - Gates: The controlled entrances from the runners into the mold cavities.
- Vents: Additional channels that provide an escape for gases generated during the pour.
- Parting line or parting surface: The interface between the cope and drag halves of the mold, flask, or pattern.
- Draft: The taper on the casting or pattern that allow it to be withdrawn from the mold
- Core box: The mold or die used to produce the cores.

Some specialized processes, such as die casting, use additional terminology.

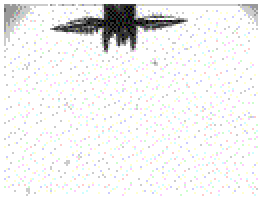
## *Theory*

Casting is a solidification process, which means the solidification phenomenon controls most of the properties of the casting. Moreover, most of the casting defects occur during solidification, such as *gas porosity* and *solidification shrinkage*.

Solidification occurs in two steps: *nucleation* and *crystal growth*. In the nucleation stage solid particles form within the liquid. When these particles form their internal energy is lower than the surrounded liquid, which creates an energy interface between the two. The formation of the surface at this interface requires energy, so as nucleation occurs the material actually undercools, that is it cools below its freezing temperature, because of the extra energy required to form the interface surfaces. It then recalescences, or heats back up to its freezing temperature, for the crystal growth stage. Note that nucleation occurs on a pre-existing solid surface, because not as much energy is required for a partial interface surface, as is for a complete spherical interface surface. This can be advantageous because fine-grained castings possess better properties than coarse-grained castings. A fine grain structure can be induced by *grain refinement* or *inoculation*, which is the process of adding impurities to induce nucleation.

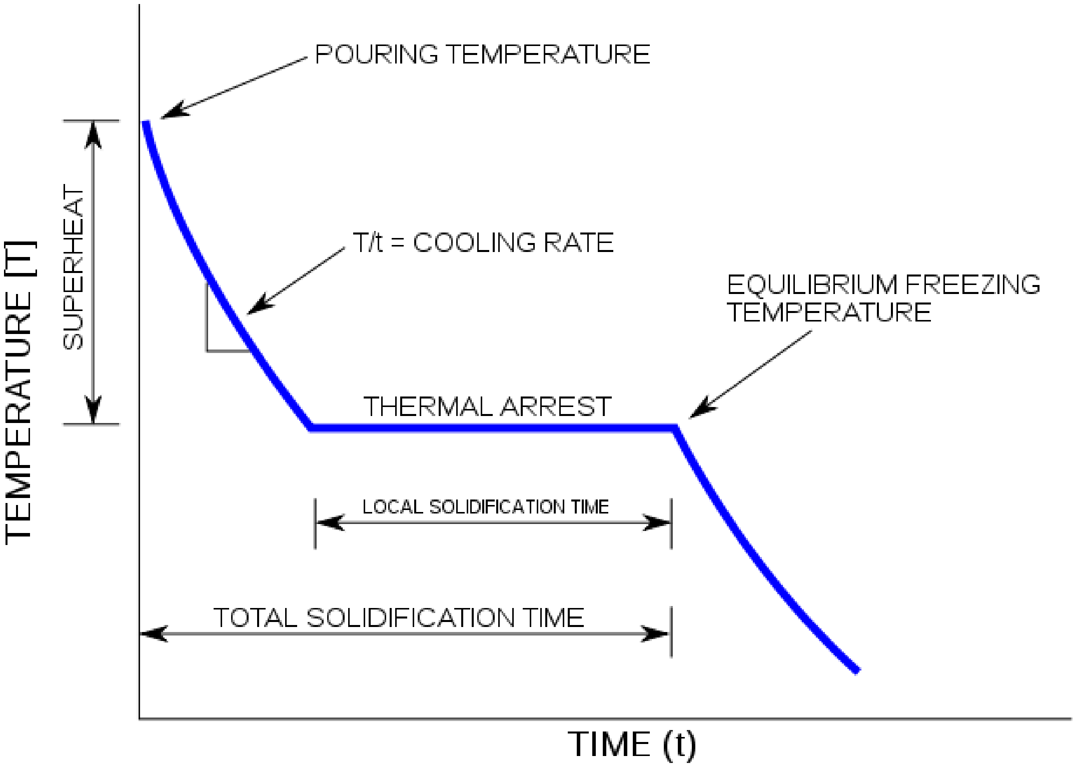
All of the nucleations represent a crystal, which grows as the heat of fusion is extracted from the liquid until there is no liquid left. The direction, rate, and type of growth can be controlled to maximize the properties of the casting. Directional solidification is when the material solidifies at one end and proceeds to solidify to the other end; this is the most ideal type of grain growth because it allows liquid material to compensate for shrinkage.

### Cooling curves



Intermediate cooling rates from melt result in a dendritic microstructure. Primary and secondary dendrites can be seen in this image.

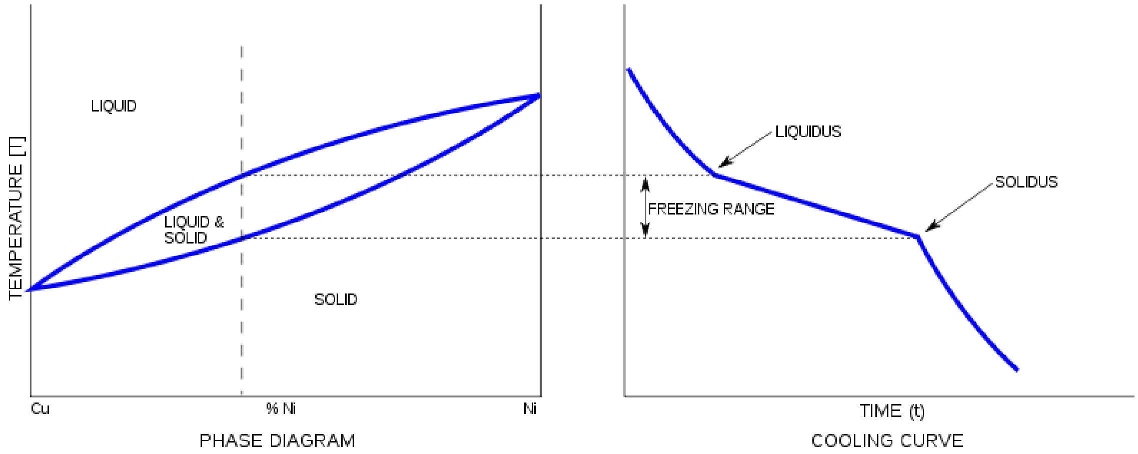
Cooling curves are important in controlling the quality of a casting. The most important part of the cooling curve is the *cooling rate* which affects the microstructure and properties. Generally speaking, an area of the casting which is cooled quickly will have a fine grain structure and an area which cools slowly will have a coarse grain structure. Below is an example cooling curve of a pure metal or eutectic alloy, with defining terminology.



Note that before the thermal arrest the material is a liquid and after it the material is a solid; during the thermal arrest the material is converting from a liquid to a solid. Also, note that the greater the superheat the more time there is for the liquid material to flow into intricate details.

The cooling rate is largely controlled by the mold material. When the liquid material is poured into the mold, the cooling begins. This happens because the heat within the molten metal flows into the relatively cooler parts of the mold. Molding materials transfer heat from the casting into the mold at different rates. For example, some molds made of plaster may transfer heat very slowly, while steel would transfer the heat quickly. Where heat should be removed quickly, the engineer will plan the mold to include special heat sinks to the mold, called chills. Fins may also be designed on a casting to extract heat, which are later removed in the cleaning (also called fettling) process. Both methods may be used at local spots in a mold where the heat will be extracted quickly. Where heat should be removed slowly, a riser or some padding may be added to a casting.

The above cooling curve depicts a basic situation with a pure alloy, however, most castings are of alloys, which have a cooling curve shaped as shown below.



Note that there is no longer a thermal arrest, instead there is a freezing range. The freezing range corresponds directly to the liquidus and solidus found on the phase diagram for the specific alloy.

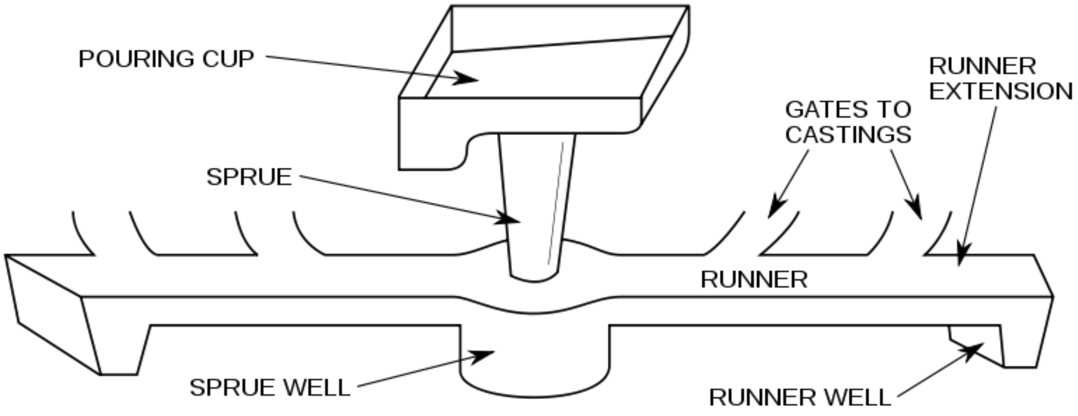
## Chvorinov's rule

The local solidification time can be calculated using Chvorinov's rule, which is:

$$t = B\left(\frac{V}{A}\right)^n$$

Where *t* is the solidification time, *V* is the volume of the casting, *A* is the surface area of the casting that contacts the mold, *n* is a constant, and *B* is the mold constant. It is most useful in determining if a riser will solidify before the casting, because if the riser does solidify first then it is worthless.

## The gating system



A simple gating system for a horizontal parting mold.

The gating system serves many purposes, the most important being conveying the liquid material to the mold, but also controlling shrinkage, the speed of the liquid, turbulence, and trapping dross. The gates are usually attached to the thickest part of the casting to assist in controlling shrinkage. In especially large castings multiple gates or runners may be required to introduce metal to more than one point in the mold cavity. The speed of the material is important because if the material is traveling too slowly it can cool before completely filling, leading to misruns and cold shuts. If the material is moving too fast then the liquid material can erode the mold and contaminate the final casting. The shape and length of the gating system can also control how quickly the material cools; short round or square channels minimize heat loss.

The gating system may be designed to minimize turbulence, depending on the material being cast. For example, steel, cast iron, and most copper alloys are turbulent insensitive, but aluminium and magnesium alloys are turbulent sensitive. The turbulent insensitive materials usually have a short and open gating system to fill the mold as quickly as possible. However, for turbulent sensitive materials short sprues are used to minimize the distance the material must fall when entering the mold. Rectangular pouring cups and tapered sprues are used to prevent the formation of a vortex as the material flows into the mold; these vortices tend to suck gas and oxides into the mold. A large sprue well is used to dissipate the kinetic energy of the liquid material as it falls down the sprue, decreasing turbulence. The *choke*, which is the smallest cross-sectional area in the gating system used to control flow, can be placed near the sprue well to slow down and smooth out the flow. Note that on some molds the choke is still placed on the gates to make separation of the part easier, but induces extreme turbulence. The gates are usually attached to the bottom of the casting to minimize turbulence and splashing.

The gating system may also be designed to trap dross. One method is to take advantage of the fact that some dross has a lower density than the base material so it floats to the top of the gating system. Therefore long flat runners with gates that exit from the bottom of the runners can trap dross in the runners; note that long flat runners will cool the material more rapidly than round or square runners. For materials where the dross is a similar density to the base material, such as aluminium, *runner extensions* and *runner wells* can be advantageous. These take advantage of the fact that the dross is usually located at the beginning of the pour, therefore the runner is extended past the last gate(s) and the contaminates are contained in the wells. Screens or filters may also be used to trap contaminates.

It is important to keep the size of the gating system small, because it all must be cut from the casting and remelted to be reused. The efficiency, or *yield*, of a casting system can be calculated by dividing the weight of the casting by the weight of the metal poured. Therefore, the higher the number the more efficient the gating system/risers.

## Shrinkage

There are three types of shrinkage: *shrinkage of the liquid*, *solidification shrinkage* and *patternmaker's shrinkage*. The shrinkage of the liquid is rarely a problem because more material is flowing into the mold behind it. Solidification shrinkage occurs because metals are less dense as a liquid than a solid, so during solidification the metal density dramatically increases. Patternmaker's shrinkage refers to the shrinkage that occurs when the material is cooled from the solidification temperature to room temperature, which occurs due to thermal contraction.

### Solidification shrinkage

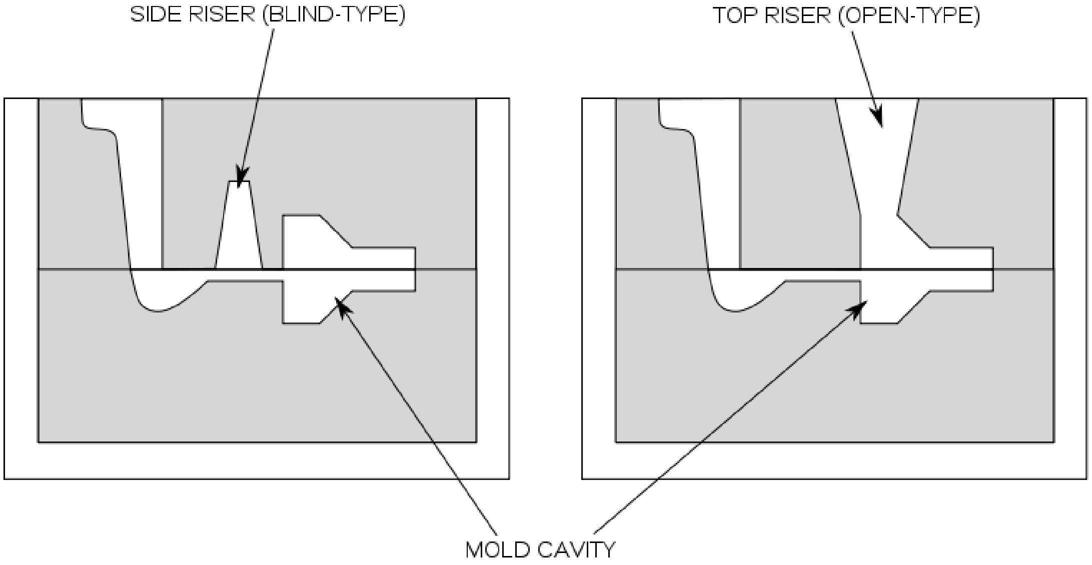
Solidification shrinkage of various metals

| Metal | Percentage |
|---|---|
| Aluminium | 6.6 |
| Copper | 4.9 |
| Magnesium | 4.0 or 4.2 |
| Zinc | 3.7 or 6.5 |
| Low carbon steel | 2.5–3.0 |
| High carbon steel | 4.0 |
| White cast iron | 4.0–5.5 |
| Gray cast iron | −2.5–1.6 |
| Ductile cast iron | −4.5–2.7 |

Most materials shrink as they solidify, but, as the table to the right shows, a few materials do not, such as gray cast iron. For the materials that do shrink upon solidification the type of shrinkage depends on how wide the freezing range is for the material. For materials with a narrow freezing range, less than 50 °C (122 °F), a cavity, known as a *pipe*, forms in the center of the casting, because the outer shell freezes first and progressively solidifies to the center. Pure and eutectic metals usually have narrow solidification ranges. These materials tend to form a *skin* in open air molds, therefore they are known as *skin forming alloys*. For materials with a wide freezing range, greater than 110 °C (230 °F), much more of the casting occupies the *mushy* or *slushy* zone (the temperature range between the solidus and the liquidus), which leads to small pockets of liquid trapped throughout and ultimately porosity. These castings tend to have poor ductility, toughness, and fatigue resistance. Moreover, for these types of materials to be fluid-tight a secondary operation is required to impregnate the casting with a lower melting point metal or resin.

For the materials that have narrow solidification ranges pipes can be overcome by designing the casting to promote directional solidification, which means the casting freezes first at the point farthest from the gate, then progressively solidifies towards the gate. This allows a continuous feed of liquid material to be present at the point of solidification to compensate for the shrinkage. Note that there is still a shrinkage void where the final material solidifies, but if designed properly this will be in the gating system or riser.

## Risers and riser aids



Different types of risers

Risers, also known as *feeders*, are the most common way of providing directional solidification. It supplies liquid metal to the solidifying casting to compensate for solidification shrinkage. For a riser to work properly the riser must solidify after the casting, otherwise it cannot supply liquid metal to shrinkage within the casting. Risers add cost to the casting because it lowers the *yield* of each casting; i.e. more metal is lost as scrap for each casting. Another way to promote directional solidification is by adding chills to the mold. A chill is any material which will conduct heat away from the casting more rapidly that the material used for molding.

Risers are classified by three criteria. The first is if the riser is open to the atmosphere, if it is then its called an *open* riser, otherwise its known as a *blind* type. The second criterion is where the riser is located; if it is located on the casting then it is known as a *top riser* and if it is located next to the casting it is known as a *side riser*. Finally, if riser is located on the gating system so that it fills after the molding cavity, it is known as a *live riser* or *hot riser*, but if the riser fills with materials that's already flowed through the molding cavity it is known as a *dead riser* or *cold riser*.

Riser aids are items used to assist risers in creating directional solidification or reducing the number of risers required. One of these items are *chills* which accelerate cooling in a certain part of the mold. There are two types: external and internal chills. External chills are masses of high-heat-capacity and high-thermal-conductivity material that are placed on an edge of the molding cavity. Internal chills are pieces of the same metal that is being poured, which are placed inside the mold cavity and become part of the casting. Insulating sleeves and toppings may also be installed around the riser cavity to slow the solidification of the riser. Heater coils may also be installed around or above the riser cavity to slow solidification.

**Patternmaker's shrink**

Typical patternmaker's shrinkage of various metals

| Metal | Percentage | in/ft |
|---|---|---|
| Aluminium | 1.0–1.3 | $\frac{1}{8}$–$\frac{5}{32}$ |
| Brass | 1.5 | $\frac{3}{16}$ |
| Magnesium | 1.0–1.3 | $\frac{1}{8}$–$\frac{5}{32}$ |
| Cast iron | 0.8–1.0 | $\frac{1}{10}$–$\frac{1}{8}$ |
| Steel | 2.5–3.0 | $\frac{3}{16}$–$\frac{1}{4}$ |

Shrinkage after solidification can be dealt with by using an oversized pattern designed specifically for the alloy used. *Contraction rules*, or *shrink rules*, are used to make the patterns oversized to compensate for this type of shrinkage. These rulers are up to 2% oversize, depending on the material being cast. These rulers are mainly referred to by their percentage change. A pattern made to match an existing part would be made as follows: First, the existing part would be measured using a standard ruler, then when constructing the pattern, the pattern maker would use a contraction rule, ensuring that the casting would contract to the correct size.

Note that patternmaker's shrinkage does not take phase change transformations into account. For example, eutectic reactions, martensitic reactions, and graphitization can cause expansions or contractions.

## Mold cavity

The mold cavity of a casting does not reflect the exact dimensions of the finished part due to a number of reasons. These modifications to the mold cavity are known as *allowances* and account for patternmaker's shrinkage, draft, machining, and distortion. In non-expendable processes, these allowances are imparted directly into the permanent mold, but in expendable mold processes they are imparted into the patterns, which later form the mold cavity. Note that for non-expendable molds an allowance is required for the dimensional change of the mold due to heating to operating temperatures.

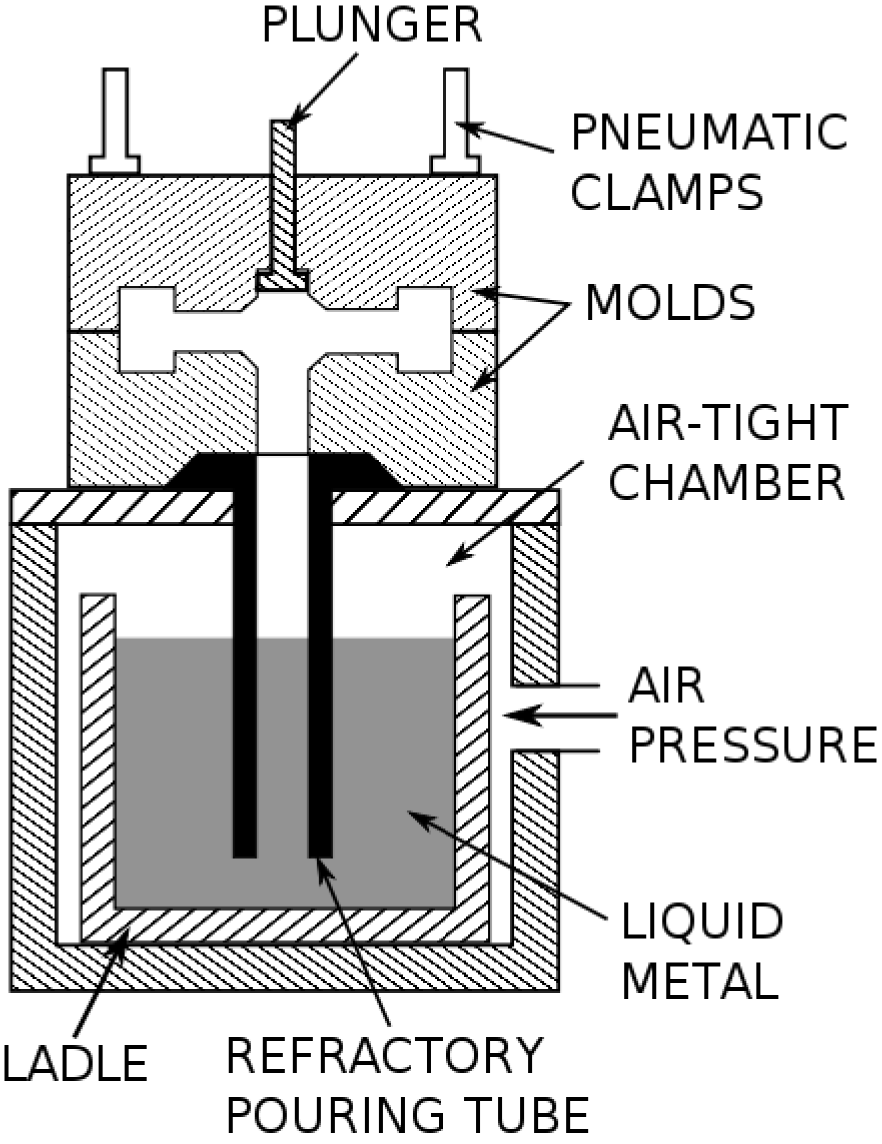
For surfaces of the casting that are perpendicular to the parting line of the mold a draft must be included. This is so that the casting can be released in non-expendable processes or the pattern can be released from the mold without destroying the mold in expendable processes. The required draft angle depends on the size and shape of the feature, the depth of the mold cavity, how the part or pattern is being removed from the mold, the pattern or part material, the mold material, and the process type. Usually the draft is not less than 1%.

The machining allowance varies drastically from one process to another. Sand castings generally have a rough surface finish, therefore need a greater machining allowance, whereas die casting has a very fine surface finish, which may not need any machining tolerance. Also, the draft may provide enough of a machining allowance to begin with.

The distortion allowance is only necessary for certain geometries. For instance, U-shaped castings will tend to distort with the legs splaying outward, because the base of the shape can contract while the legs are constrained by the mold. This can be overcome by designing the mold cavity to slope the leg inward to begin with. Also, long horizontal sections tend to sag in the middle if ribs are not incorporated, so a distortion allowance may be required.

Cores may be used in expendable mold processes to produce internal features. The core can be of metal but it is usually done in sand.

## Filling



Schematic of the low-pressure permanent mold casting process

There are a few common methods for filling the mold cavity: *gravity*, *low-pressure*, *high-pressure*, and *vacuum*.

Vacuum filling, also known as *counter-gravity* filling, is more metal efficient than gravity pouring because less material solidifies in the gating system. Gravity pouring only has a 15 to 50% metal yield as compared to 60 to 95% for vacuum pouring. There is also less turbulence, so the gating system can be simplified since it does not have to control turbulence. Plus, because the metal is drawn from below the top of the pool the metal is free from dross and slag, as these are lower density (lighter) and float to the top of the pool. The pressure differential helps the metal flow into every intricacy of the mold. Finally, lower temperatures can be used, which improves the grain structure. The first patented vacuum casting machine and process dates to 1879.

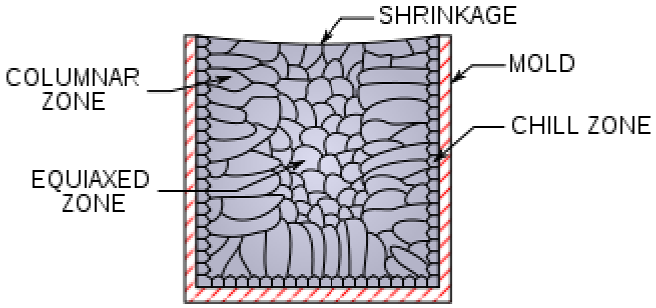
Low-pressure filling uses 5 to 15 psig (35 to 100 kPag) of air pressure to force liquid metal up a feed tube into the mold cavity. This eliminates turbulence found in gravity casting and increases density, repeatability, tolerances, and grain uniformity. After the casting has solidified the pressure is released and any remaining liquid returns to the crucible, which increases yield.

**Tilt filling**

*Tilt filling*, also known as *tilt casting*, is an uncommon filling technique where the crucible is attached to the gating system and both are slowly rotated so that the metal enters the mold cavity with little turbulence. The goal is to reduce porosity and inclusions by limiting turbulence. For most uses tilt filling is not feasible because the following inherent problem: if the system is rotated slow enough to not induce turbulence, the front of the metal stream begins to solidify, which results in mis-runs. If the system is rotated faster then it induces turbulence, which defeats the purpose. Durville of France was the first to try tilt casting, in the 1800s. He tried to use it to reduce surface defects when casting coinage from aluminum bronze.

## Macrostructure

The grain macrostructure in ingots and most castings have three distinct regions or zones: the chill zone, columnar zone, and equiaxed zone. The image below depicts these zones.



The chill zone is named so because it occurs at the walls of the mold where the wall *chills* the material. Here is where the nucleation phase of the solidification process takes place. As more heat is removed the grains grow towards the center of the casting. These are thin, long *columns* that are perpendicular to the casting surface, which are undesirable because they have anisotropic properties. Finally, in the center the equiaxed zone contains spherical, randomly oriented crystals. These are desirable because they have isotropic properties. The creation of this zone can be promoted by using a low pouring temperature, alloy inclusions, or inoculants.

## Inspection

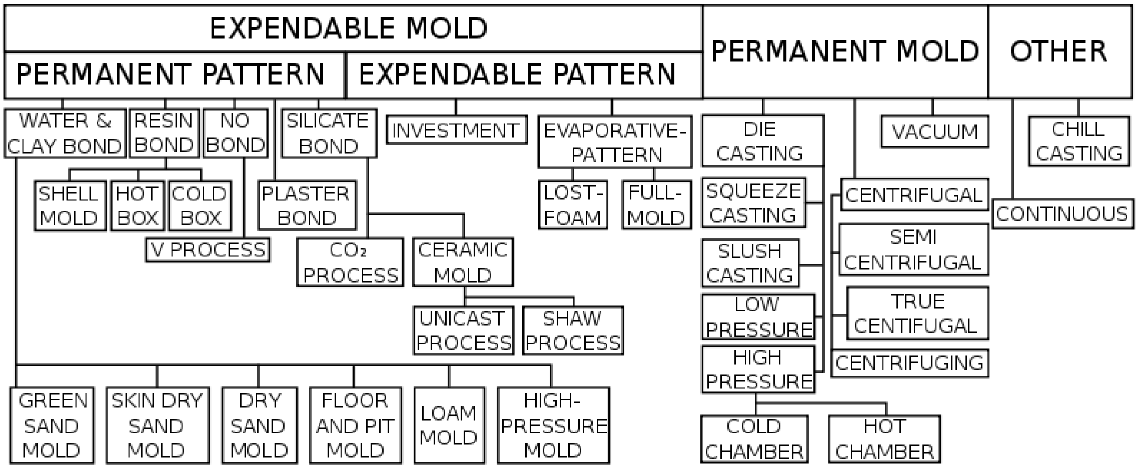
Common inspection methods for steel castings are *magnetic particle* and *liquid penetrant*. Common inspection methods for aluminum castings are *radiography*, *ultrasonic*, and *liquid penetrant*.

### Defects

There are a number of problems that can be encountered during the casting process. The main types are: *gas porosity*, *shrinkage defects*, *mold material defects*, *pouring metal defects*, and *metallurgical defects*.

## *Expendable mold casting*

Expendable mold casting is a generic classification that includes sand, plastic, shell, plaster, and investment (lost-wax technique) moldings. This method of mold casting involves the use of temporary, non-reusable molds.



## Waste molding of plaster

A durable plaster intermediate is often used as a stage toward the production of a bronze sculpture or as a pointing guide for the creation of a carved stone. With the completion of a plaster, the work is more durable (if stored indoors) than a clay original which must be kept moist to avoid cracking. With the low cost plaster at hand, the expensive work of bronze casting or stone carving may be deferred until a patron is found, and as such work is considered to be a technical, rather than artistic process, it may even be deferred beyond the lifetime of the artist.

In waste molding a simple and thin plaster mold, reinforced by sisal or burlap, is cast over the original clay mixture. When cured, it is then removed from the damp clay, incidentally destroying the fine details in undercuts present in the clay, but which are now captured in the mold. The mold may then at any later time (but only once) be used to cast a plaster positive image, identical to the original clay. The surface of this plaster may be further refined and may be painted and waxed to resemble a finished bronze casting.

## Sand casting

Sand casting is one of the most popular and simplest types of casting that has been used for centuries. Sand casting allows for smaller batches to be made compared to permanent mold casting and at a very reasonable cost. Not only does this method allow manufacturers to create products at a low cost, but there are other benefits to sand casting, such as very small size operations. From castings that fit in the palm of your hand to train beds (one casting can create the entire bed for one rail car), it can all be done with sand casting. Sand casting also allows most metals to be cast depending on the type of sand used for the molds.

Sand casting requires a lead time of days for production at high output rates (1–20 pieces/hr-mold) and is unsurpassed for large-part production. Green (moist) sand has almost no part weight limit, whereas dry sand has a practical part mass limit of 2,300–2,700 kg (5,100–6,000 lb). Minimum part weight ranges from 0.075–0.1 kg (0.17–0.22 lb). The sand is bonded together using clays, chemical binders, or polymerized oils (such as motor oil). Sand can be recycled many times in most operations and requires little maintenance.

## Plaster mold casting

Plaster casting is similar to sand casting except that plaster of paris is substituted for sand as a mold material. Generally, the form takes less than a week to prepare, after which a production rate of 1–10 units/hr-mold is achieved, with items as massive as 45 kg (99 lb) and as small as 30 g (1 oz) with very good surface finish and close tolerances. Plaster casting is an inexpensive alternative to other molding processes for complex parts due to the low cost of the plaster and its ability to produce near net shape castings. The biggest disadvantage is that it can only be used with low melting point non-ferrous materials, such as aluminium, copper, magnesium, and zinc.

## Shell molding

Shell molding is similar to sand casting, but the molding cavity is formed by a hardened "shell" of sand instead of flask filled with sand. The sand is finer than sand casting sand and is mixed with a resin so that it can be heated by the pattern and harden into a shell around the pattern. Because of the resin it gives a much finer surface finish. The process is easily automated and more precise than sand casting. Common metals that are cast include cast iron, aluminium, magnesium, and copper alloys. This process is ideal for complex items that are small to medium sized.

## Investment casting

An investment-cast valve cover

Investment casting (known as lost-wax casting in art) is a process that has been practised for thousands of years, with the lost-wax process being one of the oldest known metal forming techniques. From 5000 years ago, when beeswax formed the pattern, to today's high technology waxes, refractory materials and specialist alloys, the castings ensure high-quality components are produced with the key benefits of accuracy, repeatability, versatility and integrity.

Investment casting derives its name from the fact that the pattern is invested, or surrounded, with a refractory material. The wax patterns require extreme care for they are not strong enough to withstand forces encountered during the mold making. One advantage of investment casting is that the wax can be reused.

The process is suitable for repeatable production of net shape components from a variety of different metals and high performance alloys. Although generally used for small castings, this process has been used to produce complete aircraft door frames, with steel castings of up to 300 kg and aluminium castings of up to 30 kg. Compared to other casting processes such as die casting or sand casting, it can be an expensive process, however the components that can be produced using investment casting can incorporate intricate contours, and in most cases the components are cast near net shape, so requiring little or no rework once cast.

## Evaporative-pattern casting

This is a class of casting processes that use pattern materials that evaporate during the pour, which means there is no need to remove the pattern material from the mold before casting. The two main processes are lost-foam casting and full-mold casting.

### Lost-foam casting

Lost-foam casting is a type of evaporative-pattern casting process that is similar to investment casting except foam is used for the pattern instead of wax. This process takes advantage of the low boiling point of foam to simplify the investment casting process by removing the need to melt the wax out of the mold.

### Full-mold casting

Full-mold casting is an evaporative-pattern casting process which is a combination of sand casting and lost-foam casting. It uses a expanded polystyrene foam pattern which is then surrounded by sand, much like sand casting. The metal is then poured directly into the mold, which vaporizes the foam upon contact.

## *Non-expendable mold casting*

The permanent molding process

Non-expendable mold casting differs from expendable processes in that the mold need not be reformed after each production cycle. This technique includes at least four different methods: permanent, die, centrifugal, and continuous casting. This form of casting also results in improved repeatability in parts produced and delivers Near Net Shape results.

## Permanent mold casting

Permanent mold casting is metal casting process that employs reusable molds ("permanent molds"), usually made from metal. The most common process uses gravity to fill the mold, however gas pressure or a vacuum are also used. A variation on the typical gravity casting process, called slush casting, produces hollow castings. Common casting metals are aluminum, magnesium, and copper alloys. Other materials include tin, zinc, and lead alloys and iron and steel are also cast in graphite molds. Permanent molds, while lasting more than one casting still have a limited life before wearing out.

## Die casting

The die casting process forces molten metal under high pressure into mold cavities (which are machined into dies). Most die castings are made from nonferrous metals, specifically zinc, copper, and aluminium based alloys, but ferrous metal die castings are possible. The die casting method is especially suited for applications where many small to medium sized parts are needed with good detail, a fine surface quality and dimensional consistency.

## Semi-solid metal casting

Semi-solid metal (SSM) casting is a modified die casting process that reduces or eliminates the residual porosity present in most die castings. Rather than using liquid metal as the feed material, SSM casting uses a higher viscosity feed material that is partially solid and partially liquid. A modified die casting machine is used to inject the semi-solid slurry into re-usable hardened steel dies. The high viscosity of the semi-solid metal, along with the use of controlled die filling conditions, ensures that the semi-solid metal fills the die in a non-turbulent manner so that harmful porosity can be essentially eliminated.

Used commercially mainly for aluminium and magnesium alloys, SSM castings can be heat treated to the T4, T5 or T6 tempers. The combination of heat treatment, fast cooling rates (from using un-coated steel dies) and minimal porosity provides excellent combinations of strength and ductility. Other advantages of SSM casting include the ability to produce complex shaped parts net shape, pressure tightness, tight dimensional tolerances and the ability to cast thin walls.

## Centrifugal casting

Centrifugal casting is both gravity- and pressure-independent since it creates its own force feed using a temporary sand mold held in a spinning chamber at up to 900 N. Lead time varies with the application. Semi- and true-centrifugal processing permit 30-50 pieces/hr-mold to be produced, with a practical limit for batch processing of approximately 9000 kg total mass with a typical per-item limit of 2.3-4.5 kg.

Industrially, the centrifugal casting of railway wheels was an early application of the method developed by German industrial company Krupp and this capability enabled the rapid growth of the enterprise.

Small art pieces such as jewelry are often cast by this method using the lost wax process, as the forces enable the rather viscous liquid metals to flow through very small passages and into fine details such as leaves and petals. This effect is similar to the benefits from vacuum casting, also applied to jewelry casting.

## Continuous casting

Continuous casting is a refinement of the casting process for the continuous, high-volume production of metal sections with a constant cross-section. Molten metal is poured into an open-ended, water-cooled copper mold, which allows a 'skin' of solid metal to form over the still-liquid centre. The strand, as it is now called, is withdrawn from the mold and passed into a chamber of rollers and water sprays; the rollers support the thin skin of the strand while the sprays remove heat from the strand, gradually solidifying the strand from the outside in. After solidification, predetermined lengths of the strand are cut off by either mechanical shears or travelling oxyacetylene torches and transferred to further forming processes, or to a stockpile. Cast sizes can range from strip (a few millimetres thick by about five metres wide) to billets (90 to 160 mm square) to slabs (1.25 m wide by 230 mm thick). Sometimes, the strand may undergo an initial hot rolling process before being cut.

Continuous casting is used due to the lower costs associated with continuous production of a standard product, and also increases the quality of the final product. Metals such as steel, copper and aluminium are continuously cast, with steel being the metal with the greatest tonnages cast using this method.

## Chapter 7

# Blast Furnace

Blast furnace in Sestao, Spain. The actual furnace itself is inside the central girderwork.

A **blast furnace** is a type of metallurgical furnace used for smelting to produce industrial metals, generally iron.

In a blast furnace, fuel and ore are continuously supplied through the top of the furnace, while air (sometimes with oxygen enrichment) is blown into the bottom of the chamber, so that the chemical reactions take place throughout the furnace as the material moves downward. The end products are usually molten metal and slag phases tapped from the bottom, and flue gases exiting from the top of the furnace.

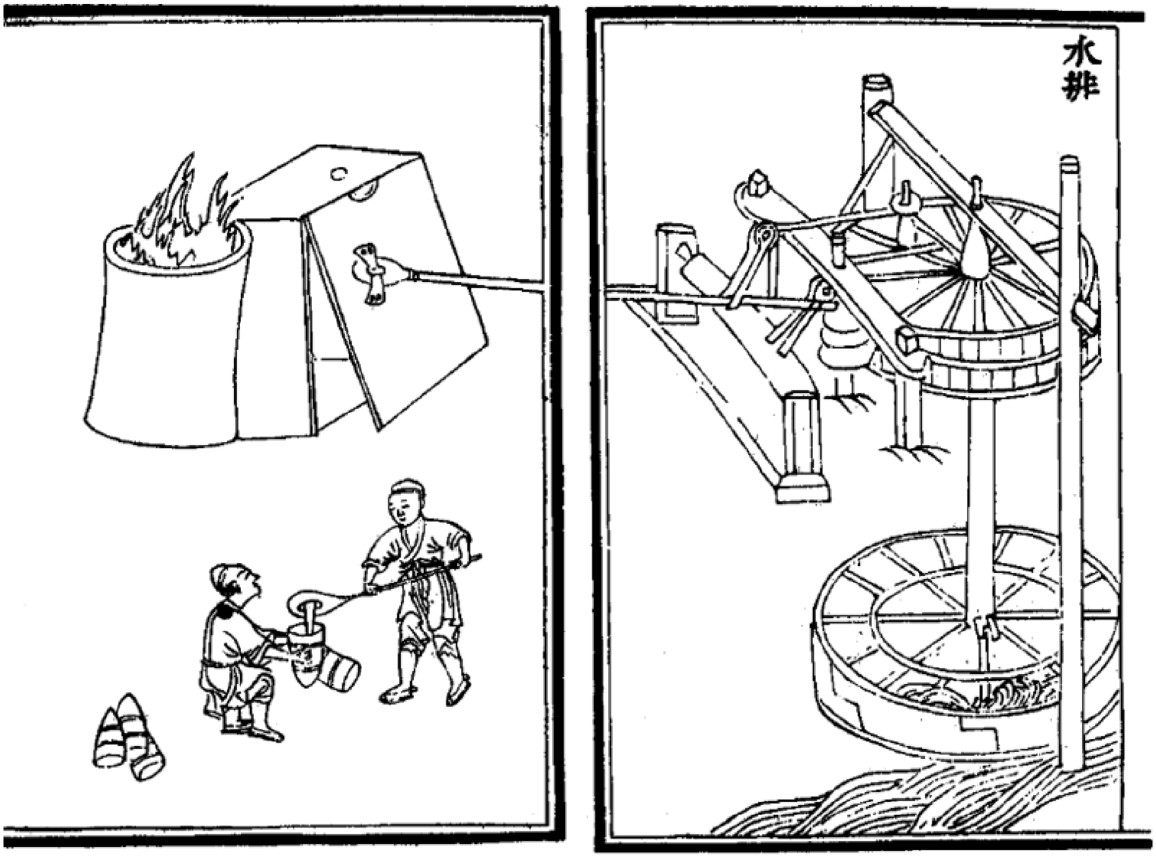
Blast furnaces are to be contrasted with air furnaces (such as reverberatory furnaces), which were naturally aspirated, usually by the convection of hot gases in a chimney flue. According to this broad definition, bloomeries for iron, blowing houses for tin, and smelt mills for lead, would be classified as blast furnaces. However, the term has usually been limited to those used for smelting iron ore to produce pig iron, an intermediate material used in the production of commercial iron and steel.

## *History*

Blast furnaces existed in China from about the 5th century BC, and in the West from the High Middle Ages. They spread from the region around Namur in Wallonia (Belgium) in the late 15th century, being introduced to England in 1491. The fuel used in these was invariably charcoal. The successful substitution of coke for charcoal is widely attributed to Abraham Darby in 1709. The efficiency of the process was further enhanced by the practice of preheating the blast, patented by James Beaumont Neilson in 1828.

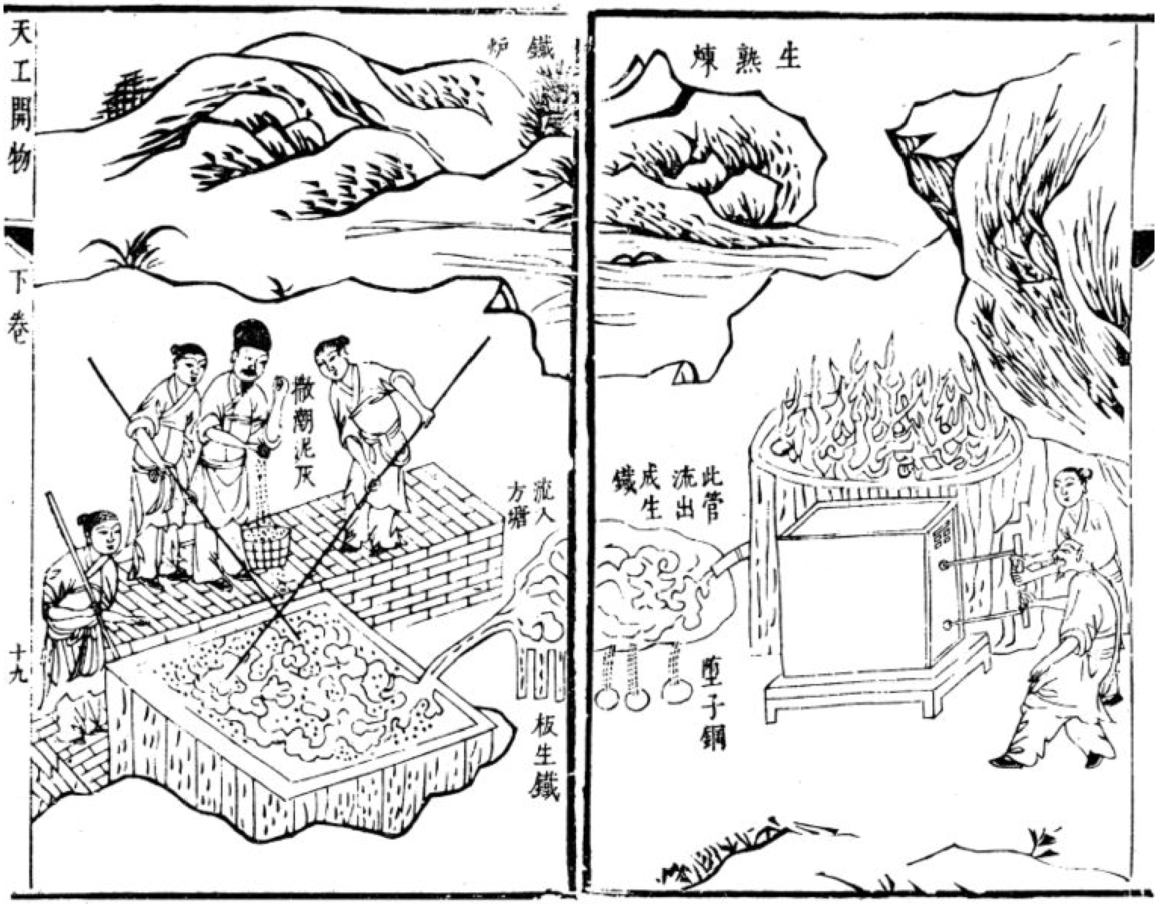
The blast furnace is distinguished from the bloomery in that the object of the blast furnace is to produce molten metal that can be tapped from the furnace, whereas the intention in the bloomery is to avoid it melting so that carbon does not become dissolved in the iron. Bloomeries were also artificially blown using bellows, but the term "blast furnace" is normally reserved for furnaces where iron (or another metal) is refined from ore.

## China



An illustration of furnace bellows operated by waterwheels, from the *Nong Shu*, by Wang Zhen, 1313 AD, during the Yuan Dynasty of China.

The oldest extant blast furnaces were built during the Han Dynasty of China in the 1st century BC. However, cast iron farm tools and weapons were widespread in China by the 5th century BC, while 3rd century BC iron smelters employed an average workforce of over two hundred men. These early furnaces had clay walls and used phosphorus-containing minerals as a flux. The effectiveness of the Chinese blast furnace was enhanced during this period by the engineer Du Shi (c. 31 AD), who applied the power of waterwheels to piston-bellows in forging cast iron.



The left picture illustrates the fining process to make wrought iron from pig iron, with the right illustration displaying men working a blast furnace, of smelting iron ore producing pig iron, from the *Tiangong Kaiwu* encyclopedia, 1637.

While it was long thought that the Chinese had developed the blast furnace and cast iron as their first method of iron production, Donald Wagner (the author of the above referenced study) has published a more recent paper that supersedes some of the statements in the earlier work; the newer paper still places the date of the first cast iron artifacts at the 4th and 5th century BC, but also provides evidence of earlier bloomery furnace use, which migrated in from the west during the beginning of the Chinese Bronze Age of the late Longshan culture (2000 BC). He suggests that early blast furnace and cast iron production evolved from furnaces used to melt bronze. Certainly, though, iron was essential to military success by the time the State of Qin had unified China (221 BC). By the 11th century, the Song Dynasty Chinese iron industry made a remarkable switch of resources from charcoal to bituminous coal in casting iron and steel, sparing thousands of acres of woodland from felling. This may have happened as early as the 4th century AD.

## Ancient World elsewhere

Other than in China, there is no evidence of the use of the blast furnace (proper). Instead iron was made by direct reduction in bloomeries. These are not correctly described as blast furnaces, though the term is occasionally misused in referring to them.

In Europe, the Greeks, Celts, Romans, and Carthaginians all used this process. Several examples have been found in France, and materials found in Tunisia suggest they were used there as well as in Antioch during the Hellenistic Period. Though little is known of it during the Dark Ages, the process probably continued in use. Similarly, smelting in bloomery-type furnaces in West Africa and forging for tools, appears in the Nok culture in Africa by 500 BC. The earliest records of bloomery-type furnaces in East Africa are discoveries of smelted iron and carbon in Nubia and Axum which date back between 1,000-500 BCE. Particularly in Meroe, there are known to have been ancient blast furnaces which produced metal tools for the Nubians/Kushites and produced surplus for their economy.

## Medieval Europe

The first blast furnace of Germany as depicted in a miniature in the Deutsches Museum

An improved bloomery, named the Catalan forge, was invented in Catalonia, Spain during the 8th century. Instead of using natural draught, air was pumped in by bellows, resulting in better quality iron and an increased capacity. This pumping of airstream in with bellows is known as *cold blast*, and it increases the fuel efficiency of the bloomery and improves yield. The Catalan forges can also be built bigger than natural draught bloomeries.

Modern experimental archaeology and history re-enactment has shown there is only a very short step from Catalan forge to the true blast furnace, where the iron is gained as pig iron in liquid phase. Usually obtaining the iron in liquid phase is actually undesired and the temperature is intentionally kept below the melting point of iron, since while removing the solid bloom mechanically is tedious and means batch process instead of continuous process, it is almost pure iron and can be worked immediately. On the other hand, pig iron is the eutectic mixture of carbon and iron, and needs to be decarburized to produce steel or wrought iron, which was extremely tedious in the Middle Ages.

The oldest known blast furnaces in the West were built in Dürstel in Switzerland, the Märkische Sauerland in Germany, and at Lapphyttan in Sweden where the complex was active between 1150 and 1350. At Noraskog in the Swedish county of Järnboås there have also been found traces of blast furnaces dated even earlier, possibly to around 1100. These early blast furnaces, like the Chinese examples, were very inefficient compared to those used today. The iron from the Lapphyttan complex was used to produce balls of wrought iron known as osmonds, and these were traded internationally – a possible reference occurs in a treaty with Novgorod from 1203 and several certain references in accounts of English customs from the 1250s and 1320s. Other furnaces of the 13th to 15th centuries have been identified in Westphalia.

Knowledge of certain technological advances was transmitted as a result of the General Chapter of the Cistercian monks. This may have included the blast furnace, as the Cistercians are known to have been skilled metallurgists. According to Jean Gimpel, their high level of industrial technology facilitated the diffusion of new techniques: "Every monastery had a model factory, often as large as the church and only several feet away, and waterpower drove the machinery of the various industries located on its floor." Iron ore deposits were often donated to the monks along with forges to extract the iron, and within time surpluses were being offered for sale. The Cistercians became the leading iron producers in Champagne, France, from the mid-13th century to the 17th century, also using the phosphate-rich slag from their furnaces as an agricultural fertilizer.

Archaeologists are still discovering the extent of Cistercian technology. At Laskill, an outstation of Rievaulx Abbey and the only medieval blast furnace so far identified in Britain, the slag produced was low in iron content. Slag from other furnaces of the time contained a substantial concentration of iron, whereas Laskill is believed to have produced cast iron quite efficiently. Its date is not yet clear, but it probably did not survive until Henry VIII's Dissolution of the Monasteries in the late 1530s, as an agreement (immediately after that) concerning the "smythes" with the Earl of Rutland in 1541 refers to blooms. Nevertheless, the means by which the blast furnace spread in medieval Europe has not finally been determined.

## Early modern blast furnaces: origin and spread

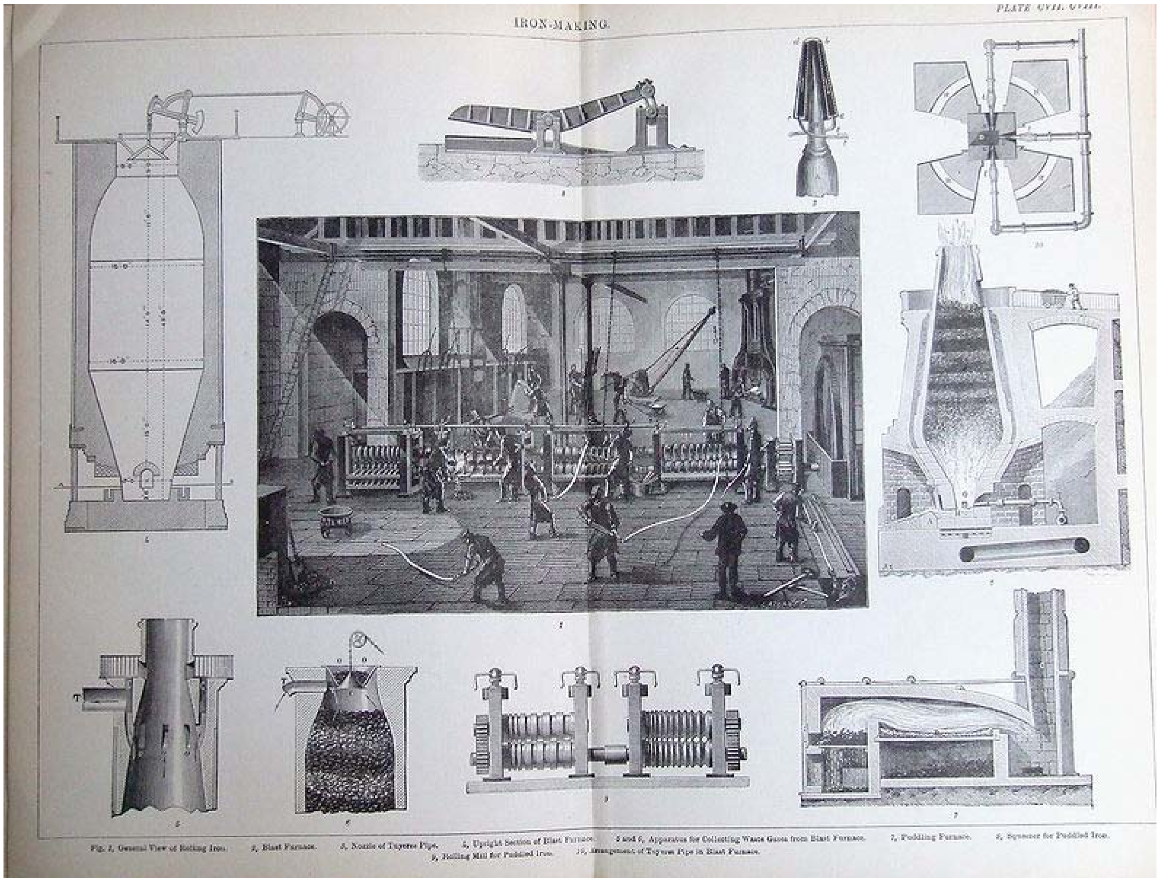
*Luisenhuette* at Balve

The direct ancestor of these used in France and England was in the Namur region in what is now Wallonia (Belgium). From there, they spread first to the Pays de Bray on the eastern boundary of Normandy and from there to the Weald of Sussex, where the first furnace (called Queenstock) in Buxted was built in about 1491, followed by one at Newbridge in Ashdown Forest in 1496. They remained few in number until about 1530 but many were built in the following decades in the Weald, where the iron industry perhaps reached its peak about 1590. Most of the pig iron from these furnaces was taken to finery forges for the production of bar iron.

The first British furnaces outside the Weald appeared during the 1550s, and many were built in the remainder of that century and the following ones. The output of the industry probably peaked about 1620, and was followed by a slow decline until the early 18th century. This was apparently because it was more economic to import iron from Sweden and elsewhere than to make it in some more remote British locations. Charcoal that was economically available to the industry was probably being consumed as fast as the wood to make it grew. The Backbarrow blast furnace built in Cumbria in 1711 has been described as the first efficient example.

The first blast furnace in Russia opened in 1637 near Tula and was called the Gorodishche Works. The blast furnace spread from here to the central Russia and then finally to the Urals.

Blast furnaces have also been discovered and recorded to have been created in medieval West Africa with some of the metalworking Bantu civilizations such as the Bunyoro Empire and the Nyoro people.



Representation of blast furnaces and other ironmaking processes from the 19th century

## Coke blast furnaces

In 1709, at Coalbrookdale in Shropshire, England, Abraham Darby began to fuel a blast furnace with coke instead of charcoal. Coke iron was initially only used for foundry work, making pots and other cast iron goods. Foundry work was a minor branch of the industry, but Darby's son built a new furnace at nearby Horsehay, and began to supply the owners of finery forges with coke pig iron for the production of bar iron. Coke pig iron was by this time cheaper to produce than charcoal pig iron. The use of a coal-derived fuel in the iron industry was a key factor in the British Industrial Revolution. Darby's old blast furnace has been archaeologically excavated and can be seen in situ at Coalbrookdale, part of the Ironbridge Gorge Museums. Cast iron from the furnace was used to make girders for the world's first iron bridge in 1779. The Iron Bridge crosses the River Severn at Coalbrookdale and remains in use for pedestrians.

A further important development was the change to hot blast, patented by James Beaumont Neilson at Wilsontown Ironworks in Scotland in 1828. This further reduced production costs. Within a few decades, the practice was to have a "stove" as large as the furnace next to it into which the waste gas (containing CO) from the furnace was directed and burnt. The resultant heat was used to preheat the air blown into the furnace.

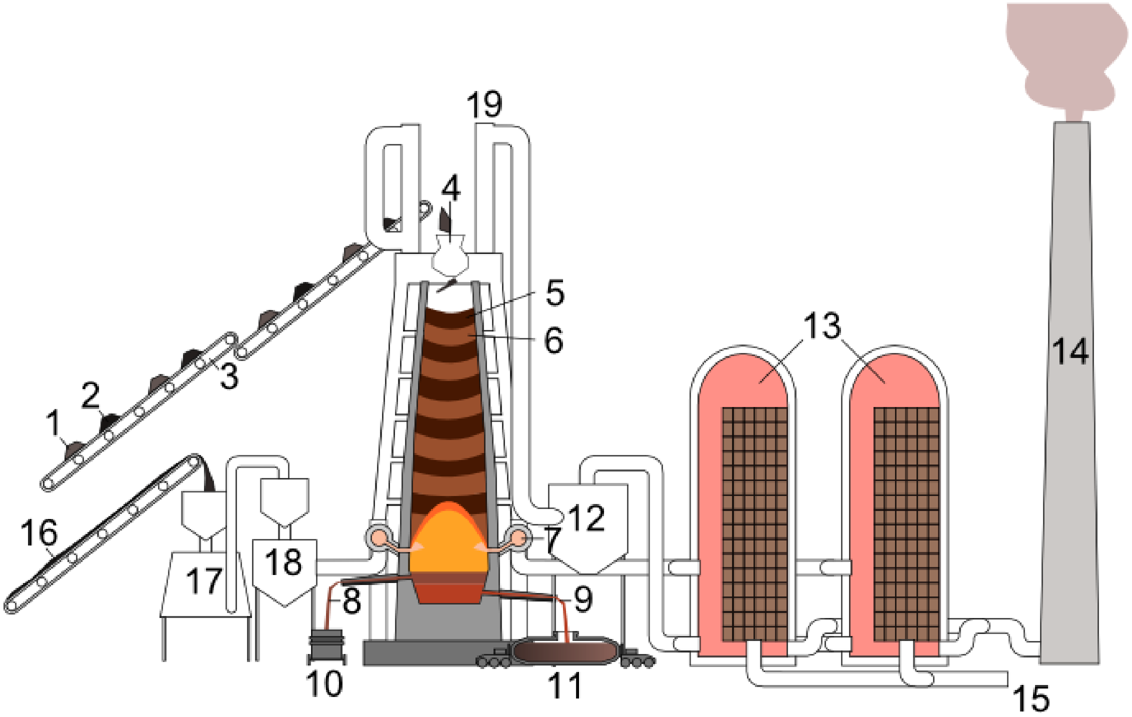
A further significant development was the application of raw anthracite coal to the blast furnace, first tried successfully by George Crane at Ynyscedwyn ironworks in south Wales in 1837. It was taken up in America by the Lehigh Crane Iron Company at Catasauqua, Pennsylvania in 1839.

## Modern furnaces

The blast furnace remains an important part of modern iron production. Modern furnaces are highly efficient, including Cowper stoves to pre-heat the blast air and employ recovery systems to extract the heat from the hot gases exiting the furnace. Competition in industry drives higher production rates. The largest blast furnaces have a volume around 5580 $m^3$ (190,000 cu ft) and can produce around 80,000 tonnes (88,000 short tons) of iron per week.

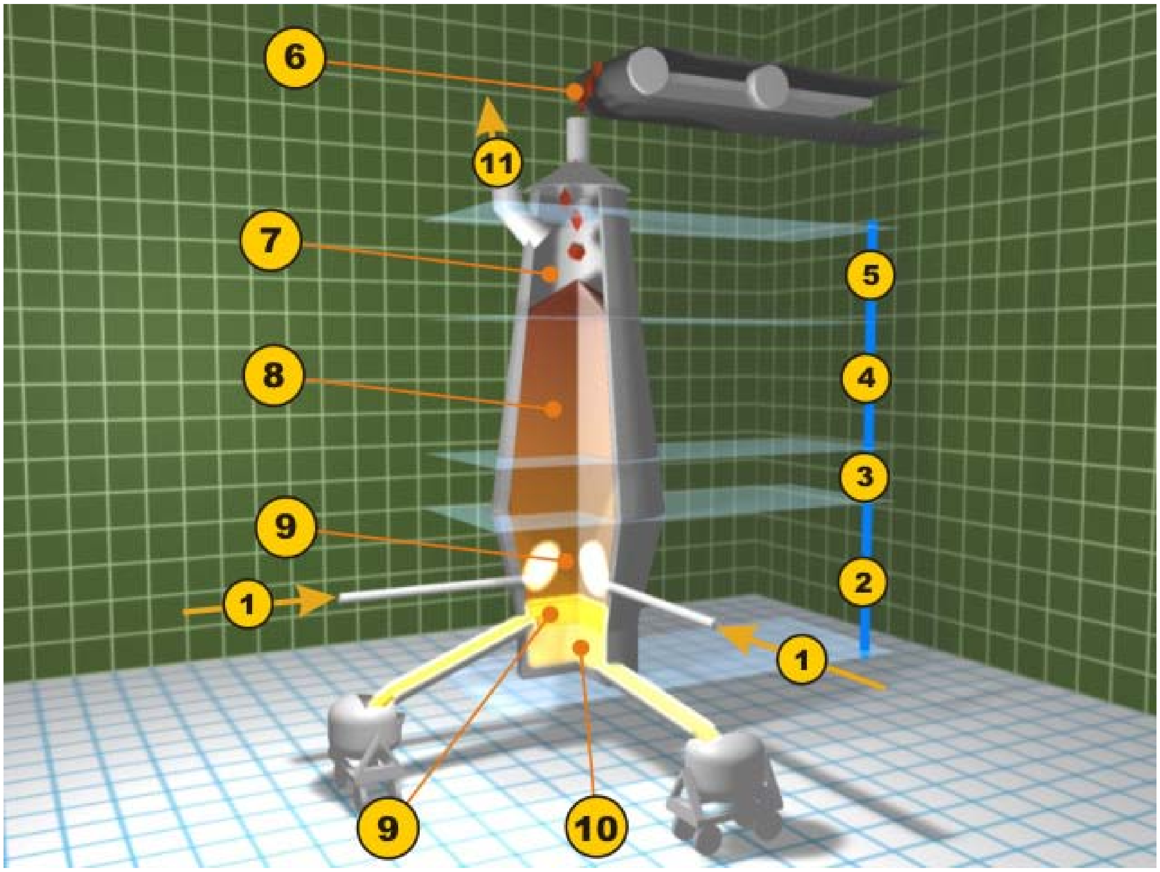
This is a great increase from the typical 18th-century furnaces, which averaged about 360 tonnes (400 short tons) per year. Variations of the blast furnace, such as the Swedish electric blast furnace, have been developed in countries which have no native coal resources.

## *Modern process*



**Blast furnace placed in an installation**

1. Iron ore + limestone sinter
2. Coke
3. Elevator
4. Feedstock inlet
5. Layer of coke
6. Layer of sinter pellets of ore and limestone
7. Hot blast (around 1200°C)
8. Removal of slag
9. Tapping of molten pig iron
10. Slag pot
11. Torpedo car for pig iron
12. Dust cyclone for separation of solid particles
13. Cowper stoves for hot blast
14. Smoke outlet (can be redirected to carbon capture & storage (CCS) tank)
15: Feed air for Cowper stoves (air pre-heaters)
16. Powdered coal
17. Coke oven
18. Coke
19. Blast furnace gas downcomer



**Blast furnace diagram**

1. Hot blast from Cowper stoves
2. Melting zone (*bosh*)
3. Reduction zone of ferrous oxide (*barrel*)
4. Reduction zone of ferric oxide (*stack*)
5. Pre-heating zone (*throat*)
6. Feed of ore, limestone, and coke
7. Exhaust gases
8. Column of ore, coke and limestone
9. Removal of slag
10. Tapping of molten pig iron
11. Collection of waste gases

Modern furnaces are equipped with an array of supporting facilities to increase efficiency, such as ore storage yards where barges are unloaded. The raw materials are transferred to the stockhouse complex by ore bridges, or rail hoppers and ore transfer cars. Rail-mounted scale cars or computer controlled weight hoppers weigh out the various raw materials to yield the desired hot metal and slag chemistry. The raw materials are brought to the top of the blast furnace via a skip car powered by winches or conveyor belts.

There are different ways in which the raw materials are charged into the blast furnace. Some blast furnaces use a "double bell" system where two "bells" are used to control the entry of the raw material into the blast furnace. The purpose of the two bells is to minimize the loss of hot gases in the blast furnace. First the raw materials are emptied into the upper or small bell. The bell is then rotated a predetermined amount in order to distribute the charge more accurately. The small bell then opens to empty the charge into the large bell. The small bell then closes, to seal the blast furnace, while the large bell dispenses the charge into the blast furnace. A more recent design is to use a "bell-less" system. These systems use multiple hoppers to contain each raw material, which is then discharged into the blast furnace through valves. These valves are more accurate at controlling how much of each constituent is added, as compared to the skip or conveyor system, thereby increasing the efficiency of the furnace. Some of these bell-less systems also implement a chute in order to precisely control where the charge is placed.

The iron making blast furnace itself is built in the form of a tall chimney-like structure lined with refractory brick. Coke, limestone flux, and iron ore (iron oxide) are charged into the top of the furnace in a precise filling order which helps control gas flow and the chemical reactions inside the furnace. Four "uptakes" allow the hot, dirty gas to exit the furnace dome, while "bleeder valves" protect the top of the furnace from sudden gas pressure surges. When plugged, bleeder valves need to be cleaned with a bleeder cleaner. The coarse particles in the gas settle in the "dust catcher" and are dumped into a railroad car or truck for disposal, while the gas itself flows through a venturi scrubber and a gas cooler to reduce the temperature of the cleaned gas.

The "casthouse" at the bottom half of the furnace contains the bustle pipe, tuyeres and the equipment for casting the liquid iron and slag. Once a "taphole" is drilled through the refractory clay plug, liquid iron and slag flow down a trough through a "skimmer" opening, separating the iron and slag. Modern, larger blast furnaces may have as many as four tapholes and two casthouses. Once the pig iron and slag has been tapped, the taphole is again plugged with refractory clay.

The tuyeres are used to implement a hot blast, which is used to increase the efficiency of the blast furnace. The hot blast is directed into the furnace through water-cooled copper nozzles called tuyeres near the base. The hot blast temperature can be from 900 °C to 1300 °C (1600 °F to 2300 °F) depending on the stove design and condition. The temperatures they deal with may be 2000 °C to 2300 °C (3600 °F to 4200 °F). Oil, tar, natural gas, powdered coal and oxygen can also be injected into the furnace at tuyere level to combine with the coke to release additional energy which is necessary to increase productivity.

Blast furnaces of Třinec Iron and Steel Works

The main chemical reaction producing the molten iron is:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

This reaction might be divided into multiple steps, with the first being that preheated blast air blown into the furnace reacts with the carbon in the form of coke to produce carbon monoxide and heat:

$$2\ C(s) + O_2(g) \rightarrow 2\ CO(g)$$

The hot carbon monoxide is the reducing agent for the iron ore and reacts with the iron oxide to produce molten iron and carbon dioxide. Depending on the temperature in the different parts of the furnace (warmest at the bottom) the iron is reduced in several steps. At the top, where the temperature usually is in the range between 200 °C and 700 °C, the iron(III) oxide is reduced to iron(II) iron(III) oxide, $Fe_3O_4$.

$$3\ Fe_2O_3(s) + CO(g) \rightarrow 2\ Fe_3O_4(s) + CO_2(g)$$

At temperatures around 850 °C, further down in the furnace, the iron(II) iron(III) is reduced to iron(II) oxide:

$Fe_3O_4(s) + CO(g) \rightarrow 3\ FeO(s) + CO_2(g)$

Hot carbon dioxide, unreacted carbon monoxide, and nitrogen from the air pass up through the furnace as fresh feed material travels down into the reaction zone. As the material travels downward, the counter-current gases both preheat the feed charge and decompose the limestone to calcium oxide and carbon dioxide:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

As the iron(II) oxide moves down to the area with higher temperatures, ranging up to 1200 °C degrees, it is reduced further to iron metal:

$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$

The carbon dioxide formed in this process is re-reduced to carbon monoxide by the coke:

$C(s) \rightarrow CO_2(g) \rightarrow 2\ CO(g)$

The main reaction controlling the gas atmosphere in the furnace is called the Boudouard reaction:

$C + O_2 \rightarrow CO_2$

$CO_2 + C \rightarrow 2CO$

The decomposition of limestone in the middle zones of the furnace proceeds according to the following reaction:

$CaCO_3 \rightarrow CaO + CO_2$

The calcium oxide formed by decomposition reacts with various acidic impurities in the iron (notably silica), to form a fayalitic slag which is essentially calcium silicate, $CaSiO_3$:

$SiO_2 + CaO \rightarrow CaSiO_3$

The "pig iron" produced by the blast furnace has a relatively high carbon content of around 4–5%, making it very brittle, and of limited immediate commercial use. Some pig iron is used to make cast iron. The majority of pig iron produced by blast furnaces undergoes further processing to reduce the carbon content and produce various grades of steel used for tools and construction materials.

Although the efficiency of blast furnaces is constantly evolving, the chemical process inside the blast furnace remains the same. According to the American Iron and Steel Institute: "Blast furnaces will survive into the next millennium because the larger, efficient furnaces can produce hot metal at costs competitive with other iron making technologies." One of the biggest drawbacks of the blast furnaces is the inevitable carbon dioxide production as iron is reduced from iron oxides by carbon and there is no economical substitute – steelmaking is one of the unavoidable industrial contributors of the $CO_2$ emissions in the world.

The challenge set by the greenhouse gas emissions of the blast furnace is being addressed in an on-going European Program called ULCOS (Ultra Low $CO_2$ Steelmaking). Several new process routes have been proposed and investigated in depth to cut specific emissions ($CO_2$ per ton of steel) by at least 50%. Some rely on the capture and further storage (CCS) of $CO_2$, while others choose decarbonizing iron and steel production, by turning to hydrogen, electricity and biomass. In the nearer term, a technology that incorporates CCS into the blast furnace process itself and is called the Top-Gas Recycling Blast Furnace is under development, with a scale-up to a commercial size blast furnace under way. The technology should be fully demonstrated by the end of the 2010s, in line with the timeline set, for example, by the EU to cut emissions significantly. Broad deployment could take place from 2020 on.

## *Manufacture of stone wool*

Stone wool or Rock wool is a spun mineral fibre used as an insulation product and in hydroponics. It is manufactured in a blast furnace fed with diabase rock which contains very low levels of metal oxides. The resultant slag is drawn off and spun to form the rock wool product. Very small amounts of metals are also produced which are an unwanted by-product and run to waste.

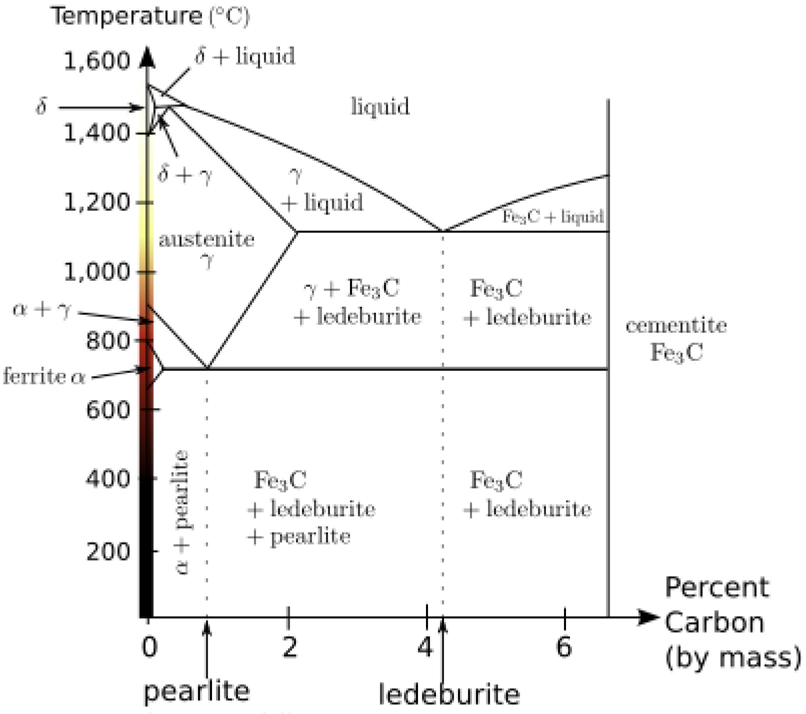
## *Decommissioned blast furnaces as museum sites*

For a long time, it was normal procedure for a decommissioned blast furnace to be demolished and either be replaced with a newer, improved one, or to have the entire site demolished to make room for follow-up use of the area. In recent decades, several countries have realized the value of blast furnaces as a part of their industrial history. Rather than being demolished, abandoned steel mills were turned into museums or integrated into multi-purpose parks. The largest number of preserved historic blast furnaces exists in Germany; other such sites exist in Spain, France, the Czech Republic, Japan, Luxembourg, Poland, Romania, Mexico, Russia and the United States.

## Chapter 8

# Austenite & Amorphous Metal

## Austenite



Iron-carbon phase diagram, showing the conditions under which **austenite** (γ) is stable in carbon steel.

**Austenite**, also known as **gamma phase iron**, is a metallic non-magnetic allotrope of iron or a solid solution of iron, with an alloying element. In plain-carbon steel, austenite exists above the critical eutectoid temperature of 1,000 K (1,340 °F); other alloys of steel have different eutectoid temperatures. It is named after Sir William Chandler Roberts-Austen (1843–1902).

## *Allotrope of iron*

From 912 to 1,394 °C (1,674 to 2,541 °F) alpha iron undergoes a phase transition from body-centred cubic (BCC) to the face-centred cubic (FCC) configuration of gamma iron, also called austenite. This is similarly soft and ductile but can dissolve considerably more carbon (as much as 2.04% by mass at 1,146 °C (2,095 °F)). This gamma form of iron is exhibited by the most commonly used type of stainless steel for making hospital and food-service equipment.

## *Austenitization*

**Austenitization** means to heat the iron, iron-based metal, or steel to a temperature at which it changes crystal structure from ferrite to austenite. An incomplete initial austenitization can leave undissolved carbides in the matrix.

For some irons, iron-based metals, and steels, the presence of carbides may occur or be present during the austenitization step. The term commonly used for this is **two-phase austenitization**.

## *Austempering*

**Austempering** is a hardening process that is used on iron-based metals to promote better mechanical properties. The metal is heated into the austenite region of the iron-cementite phase diagram and then quenched in a salt bath or other heat extraction medium that is between temperatures of 300–375 °C (572–707 °F). The metal is annealed in this temperature range until the austenite turns to bainite or ausferrite (bainitic ferrite + high-carbon austenite).

By changing the temperature for austenitization, the austempering process can yield different and desired microstructures. A higher austenitization temperature can produce a higher carbon content in austenite, whereas a lower temperature produces a more uniform distribution of austempered structure. The carbon content in austenite as a function of austempering time has been established.

## *Behavior in plain-carbon steel*

As austenite cools, it often transforms into a mixture of ferrite and cementite as the carbon diffuses. Depending on alloy composition and rate of cooling, pearlite may form. If the rate of cooling is very fast, the alloy may experience a large lattice distortion known as martensitic transformation in which it transforms into a BCT-structure instead of into ferrite and cementite. In industry, this is a very important case, as the carbon is not allowed to diffuse due to the cooling speed, which results in the formation of hard martensite. The rate of cooling determines the relative proportions of martensite, ferrite, and cementite, and therefore determines the mechanical properties of the resulting steel, such as hardness and tensile strength. Quenching (to induce martensitic transformation), followed by tempering will transform some of the brittle martensite into tempered martensite. If a low-hardenability steel is quenched, a significant amount of austenite will be retained in the microstructure.

## Behavior in cast iron

Heating white hypereutectic cast iron above 727 °C (1,341 °F) causes the formation of austenite in crystals of primary cementite. This austenization of white iron occurs in primary cementite at the interphase boundary with ferrite. When the grains of austenite form in cementite, they occur as lamellar clusters oriented along the cementite crystal layer surface. Austenite is formed by withdrawal of carbon atoms from cementite into ferrite.

## Stabilization

The addition of certain alloying elements, such as manganese and nickel, can stabilize the austenitic structure, facilitating heat-treatment of low-alloy steels. In the extreme case of austenitic stainless steel, much higher alloy content makes this structure stable even at room temperature. On the other hand, such elements as silicon, molybdenum, and chromium tend to de-stabilize austenite, raising the eutectoid temperature.

Austenite is only stable above 910 °C (1,670 °F) in bulk metal form. However, the use of a face-centered cubic (fcc) or diamond cubic substrate allows the epitaxial growth of fcc transition metals. The epitaxial growth of austenite on the diamond (100) face is feasible because of the close lattice match and the symmetry of the diamond (100) face is fcc. More than a monolayer of γ-iron can be grown because the critical thickness for the strained multilayer is greater than a monolayer. The determined critical thickness is in close agreement with theoretical prediction.

## Austenite transformation and Curie point

In many magnetic alloys, the Curie point, the temperature at which magnetic materials cease to behave magnetically, occurs at nearly the same temperature as the austenite transformation. This behavior is attributed to the paramagnetic nature of austenite, while both martensite and ferrite are strongly ferromagnetic.

## Thermo-optical emission

A blacksmith causes phase changes in the iron-carbon system in order to control the material's mechanical properties, often using the annealing, quenching, and tempering processes. In this context, the color of light emitted by the workpiece is an approximate gauge of temperature, with the transition from red to orange corresponding to the formation of austenite in medium- and high-carbon steel.

Maximum carbon solubility in austenite is 2.03% C at 1,420 K (1,150 °C).

# Amorphous Metal

Samples of amorphous metal, with centimeter scale

An **amorphous metal** is a metallic material with a disordered atomic-scale structure. In contrast to most metals, which are crystalline and therefore have a highly ordered arrangement of atoms, amorphous alloys are non-crystalline. Materials in which such a disordered structure is produced directly from the liquid state during cooling are called "glasses", and so amorphous metals are commonly referred to as "**metallic glasses**" or "**glassy metals**". However, there are several ways besides extremely rapid cooling in which amorphous metals can be produced, including physical vapor deposition, solid-state reaction, ion irradiation, melt spinning, and mechanical alloying. Some scientists do not consider amorphous metals produced by these techniques to be glasses. However, materials scientists commonly consider amorphous alloys to be a single class of materials, regardless of how they are prepared.

In the past, small batches of amorphous metals have been produced through a variety of quick-cooling methods. For instance, amorphous metal wires have been produced by sputtering molten metal onto a spinning metal disk. The rapid cooling, on the order of millions of degrees a second, is too fast for crystals to form and the material is "locked in" a glassy state. More recently a number of alloys with critical cooling rates low enough to allow formation of amorphous structure in thick layers (over 1 millimeter) had been produced; these are known as **bulk metallic glasses** (**BMG**). Liquidmetal sells a number of titanium-based BMGs, developed in studies originally carried out at Caltech. More recently, batches of amorphous steel have been produced that demonstrate strengths much greater than conventional steel alloys.

## *History*

The first reported metallic glass was an alloy ($Au_{75}Si_{25}$) produced at Caltech by W. Klement (Jr.), Willens and Duwez in 1960. This and other early glass-forming alloys had to be cooled extremely rapidly (on the order of one megakelvin per second, $10^6$ K/s) to avoid crystallization. An important consequence of this was that metallic glasses could only be produced in a limited number of forms (typically ribbons, foils, or wires) in which one dimension was small so that heat could be extracted quickly enough to achieve the necessary cooling rate. As a result, metallic glass specimens (with a few exceptions) were limited to thicknesses of less than one hundred micrometers.

In 1969, an alloy of 77.5% palladium, 6% copper, and 16.5% silicon was found to have critical cooling rate between 100 to 1000 K/s.

In 1976, H. Liebermann and C. Graham developed a new method of manufacturing thin ribbons of amorphous metal on a supercooled fast-spinning wheel. This was an alloy of iron, nickel, phosphorus and boron. The material, known as **Metglas**, was commercialized in early 1980s and used for low-loss power distribution transformers (Amorphous metal transformer). Metglas-2605 is composed of 80% iron and 20% boron, has Curie temperature of 373 °C and a room temperature saturation magnetization of 1.56 teslas.

In the early 1980s, glassy ingots with 5 mm diameter were produced from the alloy of 55% palladium, 22.5% lead, and 22.5% antimony, by surface etching followed with heating-cooling cycles. Using boron oxide flux, the achievable thickness was increased to a centimeter.

The research in Tohoku University and Caltech yielded multicomponent alloys based on lanthanum, magnesium, zirconium, palladium, iron, copper, and titanium, with critical cooling rate between 1 K/s to 100 K/s, comparable to oxide glasses.

In 1988, alloys of lanthanum, aluminium, and copper ore were found to be highly glass-forming.

In the 1990s, however, new alloys were developed that form glasses at cooling rates as low as one kelvin per second. These cooling rates can be achieved by simple casting into metallic molds. These "bulk" amorphous alloys can be cast into parts of up to several centimeters in thickness (the maximum thickness depending on the alloy) while retaining an amorphous structure. The best glass-forming alloys are based on zirconium and palladium, but alloys based on iron, titanium, copper, magnesium, and other metals are also known. Many amorphous alloys are formed by exploiting a phenomenon called the "confusion" effect. Such alloys contain so many different elements (often a dozen or more) that upon cooling at sufficiently fast rates, the constituent atoms simply cannot coordinate themselves into the equilibrium crystalline state before their mobility is stopped. In this way, the random disordered state of the atoms is "locked in".

In 1992, the first commercial amorphous alloy, Vitreloy 1 (41.2% Zr, 13.8% Ti, 12.5% Cu, 10% Ni, and 22.5% Be), was developed at Caltech, as a part of Department of Energy and NASA research of new aerospace materials. More variants followed.

In 2004, two groups succeeded in producing bulk amorphous steel, one at Oak Ridge National Laboratory, the other at University of Virginia. The Oak Ridge group refers to their product as "glassy steel". The product is non-magnetic at room temperature and significantly stronger than conventional steel, though a long research and development process remains before the introduction of the material into public or military use.

## *Properties*

Amorphous metal is usually an alloy rather than a pure metal. The alloys contain atoms of significantly different sizes, leading to low free volume (and therefore up to orders of magnitude higher viscosity than other metals and alloys) in molten state. The viscosity prevents the atoms moving enough to form an ordered lattice. The material structure also results in low shrinkage during cooling, and resistance to plastic deformation. The absence of grain boundaries, the weak spots of crystalline materials, leads to better resistance to wear and corrosion. Amorphous metals, while technically glasses, are also much tougher and less brittle than oxide glasses and ceramics.

Thermal conductivity of amorphous materials is lower than of crystals. As formation of amorphous structure relies on fast cooling, this limits the maximum achievable thickness of amorphous structures.

To achieve formation of amorphous structure even during slower cooling, the alloy has to be made of three or more components, leading to complex crystal units with higher potential energy and lower chance of formation. The atomic radius of the components has to be significantly different (over 12%), to achieve high packing density and low free volume. The combination of components should have negative heat of mixing, inhibiting crystal nucleation and prolongs the time the molten metal stays in supercooled state.

The alloys of boron, silicon, phosphorus, and other glass formers with magnetic metals (iron, cobalt, nickel) are magnetic, with low coercivity and high electrical resistance. The high resistance leads to low losses by eddy currents when subjected to alternating magnetic fields, a property useful for e.g. transformer magnetic cores.

Amorphous alloys have a variety of potentially useful properties. In particular, they tend to be stronger than crystalline alloys of similar chemical composition, and they can sustain larger reversible ("elastic") deformations than crystalline alloys. Amorphous metals derive their strength directly from their non-crystalline structure, which does not have any of the defects (such as dislocations) that limit the strength of crystalline alloys.

One modern amorphous metal, known as Vitreloy, has a tensile strength that is almost twice that of high-grade titanium. However, metallic glasses at room temperature are not ductile and tend to fail suddenly when loaded in tension, which limits the material applicability in reliability-critical applications, as the impending failure is not evident. Therefore, there is considerable interest in producing metal matrix composite materials consisting of a metallic glass matrix containing dendritic particles or fibers of a ductile crystalline metal.

Perhaps the most useful property of bulk amorphous alloys is that they are true glasses, which means that they soften and flow upon heating. This allows for easy processing, such as by injection molding, in much the same way as polymers. As a result, amorphous alloys have been commercialized for use in sports equipment, medical devices, and as cases for electronic equipment.

Thin films of amorphous metals can be deposited via high velocity oxygen fuel technique as protective coatings.

## *Applications*

Amorphous metals (metallic glasses) exhibit unique softening behavior above their glass transition and this softening has been increasingly explored for thermoplastic forming of metallic glasses.

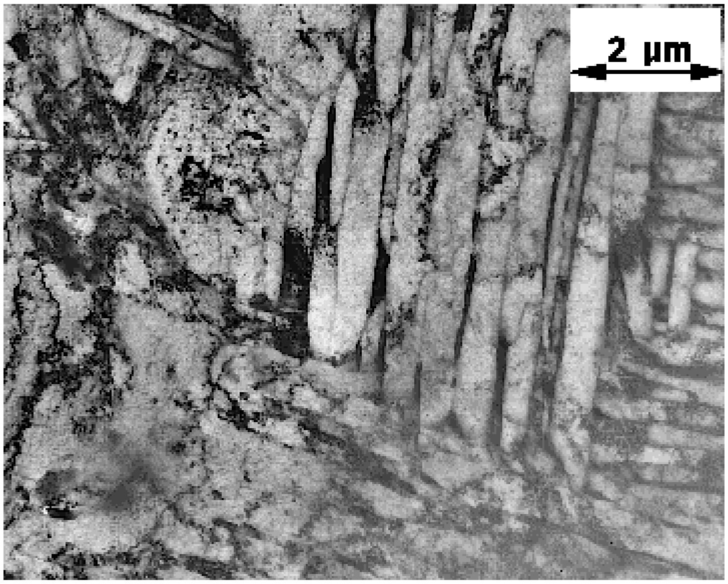
It has been shown that metallic glasses can be patterned on extremely small length scales ranging from 10 nm to several millimeters. It has been suggested that this may solve the problems of nanoimprint lithography where expensive nano-molds made of silicon break easily. Nano-molds made from metallic glasses are easy to fabricate and more durable than silicon molds.

$Ti_{40}Cu_{36}Pd_{14}Zr_{10}$ is believed to be noncarcinogenic, is about 3 times stronger than titanium, and its elastic modulus nearly matches bones. It has a high wear resistance and does not produce abrasion powder. The alloy does not undergo shrinkage on solidification. A surface structure can be generated that is biologically attachable by surface modification using laser pulses, allowing better joining with bone.

$Mg_{60}Zn_{35}Ca_5$, rapidly cooled to achieve amorphous structure, is being investigated as a biomaterial for implantation into bones as screws, pins, or plates, to fix fractures. Unlike traditional steel or titanium, this material dissolves in organisms at a rate of roughly 1 millimeter per month and is replaced with bone tissue. This speed can be adjusted by varying the content of zinc.

## Chapter 9

# Bainite



Bainite in draw quality semi-killed steel

**Bainite** is an acicular microstructure (not a phase) that forms in steels at temperatures from approximately 250-550°C (depending on alloy content). First described by E. S. Davenport and Edgar Bain, it is one of the decomposition products that may form when austenite (the face centered cubic crystal structure of iron) is cooled past a critical temperature of 727 °C (about 1340 °F). Davenport and Bain originally described the microstructure as being similar in appearance to tempered martensite.

A fine non-lamellar structure, bainite commonly consists of cementite and dislocation-rich ferrite. The high concentration of dislocations in the ferrite present in bainite makes this ferrite harder than it normally would be.

The temperature range for transformation to bainite (250-550°C) is between those for pearlite and martensite. When formed during continuous cooling, the cooling rate to form bainite is more rapid than that required to form pearlite, but less rapid than is required to form martensite (in steels of the same composition). Most alloying elements will lower the temperature required for the maximum rate of formation of bainite, though carbon is the most effective in doing so.

The microstructures of martensite and bainite at first seem quite similar; this is a consequence of the two microstructures sharing many aspects of their transformation mechanisms. However, morphological differences do exist that require a TEM to see. Under a simple light microscope, the microstructure of bainite appears darker than martensite due to its low reflectivity.

Bainite is an intermediate of pearlite and martensite in terms of hardness. For this reason, the bainitic microstructure becomes useful in that no additional heat treatments are required after initial cooling to achieve a hardness value between that of pearlitic and martensitic steels.

## *History*

In the 1920s Davenport and Bain discovered a new steel microstructure which they provisionally called martensite-troostite, due to it being intermediate between the already known low-temperature martensite phase and what was then known as troostite (now fine-pearlite). This phase was subsequently named bainite by Bain's colleagues at the United States Steel Corporation  although it took some time for the name to be taken up by the scientific community with books as late as 1947 failing to mention bainite by name. Bain and Davenport also noted the existence of two distinct forms: 'upper-range' bainite which formed at higher temperatures and 'lower-range' bainite which formed near the martensite start temperature (these forms are now known as upper- and lower-bainite respectively). The early terminology was further confused by the overlap, in some alloys, of the lower-range of the pearlite reaction and the upper-range of the bainite with the additional possibility of proeutectoid ferrite.

### *Formation*

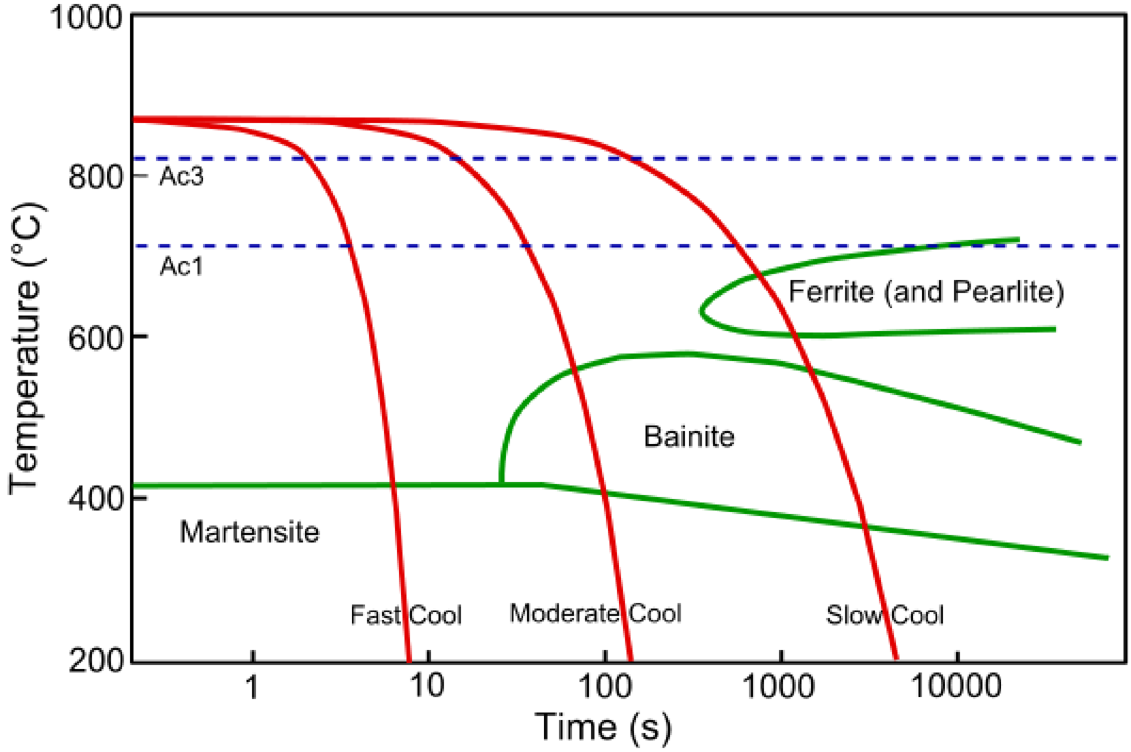


Illustration of a continuous cooling transformation (cct) diagram for steel

At 900 °C a typical low-carbon steel is composed entirely of austenite, the high temperature phase of iron. Below around 700 °C (723 °C in pure iron) the austenite is thermodynamically unstable and, under equilibrium conditions, it will undergo a eutectoid reaction and form pearlite - an interleaved mixture of ferrite and cementite ($Fe_3C$). In addition to the thermodynamic considerations indicated by the phase diagram, the phase transformations in steel are heavily influenced by the kinetics. This leads to the complexity of steel microstructures which are a strongly influenced by the cooling rate. This can be illustrated by a continuous cooling transformation (CCT) diagram which plots the time required to form a phase when a sample is cooled at a specific rate thus showing regions in time-temperature space from which the expected phase fractions can be deduced for a given thermal cycle.

If the steel is cooled slowly the transformation will agree with the equilibrium predictions and pearlite will dominate the microstructure with some fraction of proeutectoid ferrite or cementite depending on the chemical composition. However, the transformation from austenite to pearlite is a time-dependent reconstructive reaction which requires the large scale movement of the iron and carbon atoms. While the interstitial carbon diffuses readily even at moderate temperatures the self-diffusion of iron becomes extremely slow at temperatures below 600 °C until, for all practical purposes, it stops. As a consequence a rapidly cooled steel may reach a temperature where pearlite can no longer form despite the reaction being incomplete and the remaining austenite being thermodynamically unstable.

Austenite that is cooled very rapidly can form martensite, without any diffusion of either iron or carbon, by the shear of the austenite's face-centered crystal structure into a distorted body-centered tetragonal structure. This non-equilibrium phase can only form at low temperatures, where the driving force for the reaction is sufficient to overcome the considerable lattice strain imposed by the transformation. The transformation is essentially time-independent with the phase fraction depending only the degree of cooling below the critical martensite start temperature. Further, it occurs without the diffusion of either substitutional or interstitial atoms and so martensite inherits the composition of the parent austenite.

Bainite occupies a region between these two process in a temperature range where iron self-diffusion is limited but there is insufficient driving force to form martensite. In contrast to pearlite, where the ferrite and cementite grow cooperatively, bainite forms by the transformation of carbon-supersaturated ferrite with the subsequent diffusion of carbon and the precipitation of carbides. A further distinction is often made between so-called lower-bainite, which forms at temperatures closer to the martensite start temperature, and upper-bainite which forms at higher temperatures. This distinction arises from the diffusion rates of carbon at the temperature at which the bainite is forming. If the temperature is high then the carbon will diffuse rapidly away from the newly formed ferrite and form carbides in the carbon-enriched residual austenite between the ferritic plates leaving them carbide-free. At low temperatures the carbon will diffuse more sluggishly and may precipitate before it can leave the bainitic ferrite. There is some controversy over the specifics of bainite's transformation mechanism; both theories are represented below. Note that the author of this portion maintains neutrality and is simply presenting the two competing theories.

### Displacive Theory

One of the theories on the specific formation mechanism for bainite is that it occurs by a shear transformation, as in martensite. The transformation is said to cause a stress-relieving effect, which is confirmed by the orientation relationships present in bainitic microstructures. There are, however, similar stress-relief effects seen in transformations that are not considered to be martensitic in nature, but the term 'similar' does not imply identical. The relief associated with bainite is an invariant—plane strain with a large shear component. The only diffusion that occurs by this theory is during the formation of the carbide phase (usually cementite) between the ferrite plates.

### Diffusive Theory

The diffusive theory of bainite's transformation process is based on short range diffusion at the transformation front. Here, random and uncoordinated thermally activated atomic jumps control formation and the interface is then rebuilt by reconstructive diffusion. The mechanism is not able to explain the shape nor surface relief caused by the bainite transformation.

## Morphology

Typically bainite manifiests as aggregates, termed *sheaves*, of ferrite plates (*sub-units*) separated by retained austenite, martensite or cementite. While the sub-units appear separate when viewed on a 2-dimensional section they are in fact interconnected in 3-dimensions and usually take on a lenticular plate or lath morphology. The sheaves themselves are wedge-shaped with the thicker end associated with the nucleation site.

The thickness of the ferritic plates is found to increase with the transformation temperature. Neural network models have indicated that this is not a direct effect of the temperature per se but rather a result of the temperature dependence of the driving force for the reaction and the strength of the austenite surrounding the plates. At higher temperatures, and hence lower undercooling, the reduced thermodynamic driving force causes a decrease in the nucleation rate which allows individual plates to grow larger before they physically impinge on each other. Further, the growth of the plates must be accommodated by plastic flow in the surrounding austenite which is difficult if the austenite is strong and resists the plate's growth.

### Upper Bainite

So-called "upper bainite" forms around 400-550°C in sheaves. These sheaves contain several laths of ferrite that are approximately parallel to each other and which exhibit a Kurdjumov-Sachs relationship with the surrounding austenite, though this relationship degrades as the transformation temperature is lowered. The ferrite in these sheaves has a carbon concentration below 0.03%, resulting in carbon-rich austenite around the laths.

The amount of ferrite that forms between the laths is based on the carbon content of the steel. For a low carbon steel, typically discontinuous "stringers" or small particles of cementite will be present between laths. For a higher carbon steel, the stringers become continuous along the length of the adjacent laths.

### Lower Bainite

Lower bainite forms between 250-400°C and takes a more acicular form than upper bainite. There are not nearly as many low angle boundaries between laths in lower bainite. In lower bainite, the habit plane in ferrite will also shift from <111> towards <110> as transformation temperature decreases. In lower bainite, cementite nucleates on the interface between ferrite and austenite.

## Incomplete bainite transformation

Early research on bainite found that at a given temperature only a certain volume fraction of the austenite would transform to bainite with the remainder decomposing to pearlite after an extended delay. This was the case despite the fact that a complete austenite to pearlite transformation could be achieved at higher temperatures where the austenite was *more* stable. The fraction of bainite that could form increased as the temperature decreased. This was ultimately explained by accounting for the fact that when the bainitic ferrite formed the supersaturated carbon would be expelled to the surrounding austenite thus thermodynamically stabilising it against further transformation. In order to transform more of the austenite to bainite it is necessary to reduce the temperature and so increase the driving force for the reaction.