Metallurgy

The Birth of Physical Chemistry

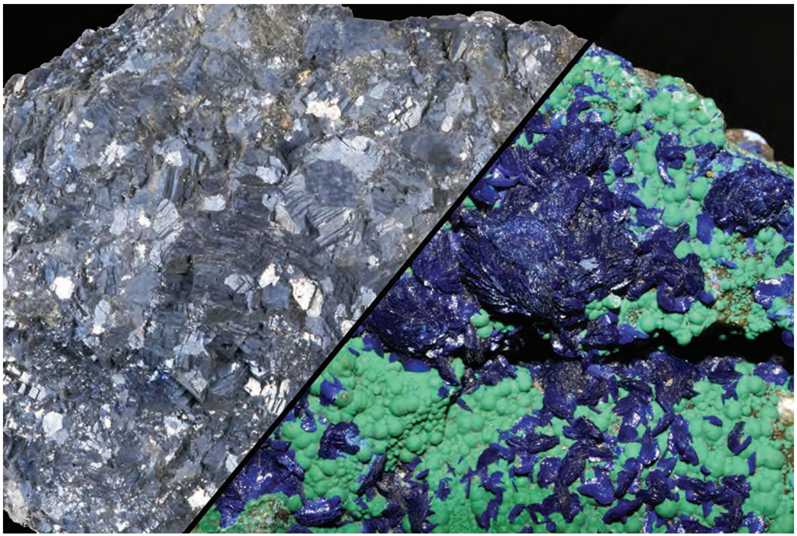
by Jason Ross

Jonathan Zander

A sample of native copper. Some metals, such as copper, gold, and silver, are found natively, in small quantities, in their metallic form on Earth.

Modern civilization makes extensive use of metals for tool-making, structural, and electronic purposes, yet the origins of the bold power of the human mind to create lustrous metal from dull stone are almost completely unknown to most people. We use steel in automobiles and the frames of buildings, nails for carpentry, wires for electricity, pipes for water, metal cans and aluminum foil for food, rivets and zippers in clothing, and jewelry. The casual disposal of aluminum foil after one use would amaze any chemist from the 1800s, when it was one of the most difficult metals to produce.[1]

The development of metallurgy required many individual techniques, from trade in individual metals and ores to water pumps for mines, from prospecting to smithing, but, above all, it required the application of absolutely tremendous amounts of heat. While a wood fire burns hot enough to cook meat (and kill the parasites within it), the temperature is not sufficient to melt copper and produce bronze for casting. For this, the higher energy density of charcoal is required. Every town had its charcoal makers, who would produce the fuel by partially burning wood in an oxygen-poor environment—a pile of smoldering wood covered with turf. The resulting charcoal burned much hotter, and much cleaner than did the original wood. The heats achievable with charcoal fires allowed the working of bronze, and, with the centuries later technique of blast furnaces, which forced more air into the fire, the heats required to melt even iron and steel.


left: Hannes Grobe

Silvery-gray galena (left), has an appearance that is both metallic and crystalline, giving an indication of the metal (lead) it contains. In contrast, the azurite (blue) and malachite (green) give no indication of the copper that can be produced from them.

Modern steel production makes use of precise chemical assays to control the processes of alloying and managing carbon content, allowing for specialty steels with unique properties for different environments, such as stainless steel, steel meant to be used underwater, and ultra high-quality steel for such applications as aerospace.[2] Totally new techniques for metallurgy, such as plasma processing with magnetic separation of metal from oxygen, could dramatically reduce the complexity of the process, making in-situ resource utilization in space a real possibility.

The development of metallurgy, from pre-history to today to the future, provides a thrilling image of man the creator, and one of our greatest uses of "fire." Without the power required for processing buried ores into specialty alloys, we'd literally be back in the stone age!

"Native" Metals

In the so-called Stone Age (human history up to approximately 3200 BC in Europe), fire was used for cooking, baking, wood-working, pottery, hardening of stone tools, land-clearing, heat, and light. The use of fire was extended to working with those metals known to the ancients. Even before the advent of extractive metallurgy around 3200 BC, there were certain kinds of metals which could be found in a pure, "native" state. These included gold, copper, silver, and, in the form of meteorites, even iron.[3] Unlike other materials, gold was lustrous, did not decay or corrode, and could be shaped into any form desired by hammering. Copper tools could be made nearly as sharp as stone tools, but could last longer. Incredibly rare meteoritic iron was used for daggers and ornamentation in ancient Egypt, and although inconceivable today, copper was found in nature, as one might find a quartz rock in our day.

These first metals led to the development of the first

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[1] While today a common metal, aluminum was so difficult to produce without modern methods of electrolysis, that is was the then-exotic and valuable metal used to cap the Washington Monument, and used by Napoleon III for his most honored guests, while others had to eat off of mere gold!

[2] Take, as an example, the hooks on aircraft carrier-launched planes. A pilot landing on an aircraft carrier uses the plane's tailhook to hook onto one of the series of "arresting wires" that are fastened across the deck. These arresting wires are made of high-tensile steel that can stop a 54,000-pound aircraft traveling at 150 miles per hour in only two seconds.

[3] The Egyptians called weapons formed from meteoritic iron "daggers from heaven."

metal-working skills: hammering, curling, and the use of fire to anneal metal which had become hard by hammering.[4] In search of more of these metals, mines were created, in which pure veins of valuable materials such as gold could be gathered.[5]

Yet, most of the metals used today do *not* come from pure veins: they do not come from native metals. Rather, they are created from *ores*. But most ores don't look the least bit metallic. While it may be no surprise that metallic galena (PbS) was a source for lead, who would think of using rocks such as green malachite or blue azurite to produce copper, or hematite for iron? At this point, we can only speculate. Perhaps malachite (which was used by the Egyptians as a cosmetic) was used to paint a piece of pottery, and transformed to copper in the kiln. The creation of metals from ores bearing no resemblance to the metals that could be extracted from them, marked the beginning of extractive metallurgy.

A bronze head produced by the lost-wax process.

Metal from Ores: The Bronze Age (3200BC–1200BC)

As most metal ores are compounds of the desired metal element with either oxygen or sulfur, some technique must be applied to free the metal from these other elements. The primary technique for millenia has been the use of carbon to draw out oxygen by forming carbon dioxide. Although this chemical theory was not known at the time, the processes by which metals could be extracted from their ores, were.

We take, as an example, the stunning transformation of malachite ($Cu_2CO_3(OH)_2$) to copper, which was performed by using charcoal both to provide the necessary heat, and to remove the oxygen. By setting layers of malachite between layers of burning charcoal and allowing the necessary heat to build, the carbon monoxide formed by the partially combusted charcoal will react with malachite, drawing out the oxygen as it forms carbon dioxide. As the process comes to completion, the malachite will have been transformed into copper. Such charcoal-fueled kilns could also reach the temperature required to melt copper (1,083ºC), making it possible to pour the copper out into a mold, producing a *cast* copper form.

Whether it was originally developed from ores that also contained tin, or by means of willful experimentation of combining metals, mixing tin (or tin ore) with copper was discovered to produce a new substance, superior in every respect. This new material, *bronze*, was much stronger than copper, could be worked to a sharper edge, and melted at a lower temperature, making it easy to form cast* bronze objects.[6]

Many of the tools we use today—including the hammer, ax, chisel, and carpenter's rasp, were developed in the Bronze Age, as was the casting art known as the lost-wax process. In this technique, a wax model of the desired form to be cast in bronze is produced, with extra wax channels or guides (called *sprues*) added to it. This wax model is then coated in plaster or silica, which sets, and when it is baked, the wax melts out. This mold can then be filled with molten bronze, allowed to cool, and then the clay can be broken off, leaving the cast bronze object remaining. This technique is still used today for the casting of bronze sculptures.[7]

While copper could be found in the Mediterranean, tin could not, and the production of bronze required importing tin from trade routes stretching to what are today the British Isles, if not further.[8] The breakdown of these trade routes, and the lack of available tin, made the production of bronze impossible around 1200 BC.

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[4] As a metal piece is hammered, it gets stronger and stronger, and reaches a point at which further hammering will cause it to shatter, rather than bend. Heating the work-piece relieves internal stresses, and allows it to be further worked. This process is called "annealing."

[5] Gold was mined in Egypt over 5000 years ago.

[6] *Casting* means to pour liquid metal into a mold, into which shape it hardens. NB: terms marked with an asterisk (*) appear in the Glossary at the end of this section.

[7] With the additional steps of the sculptor's clay work being coated in rubber, which is cut off, reassembled, and then filled with wax, which is then ready for the lost-wax process described here. See the video "Lost Wax Casting Process" by the National Sculpture Society: http://youtu.be/uPgEIM-NbhQ

[8] Some evidence suggests that these trade routes extended to the New World.

Charcoal production: a century ago, and as recreated in modern times. The production of charcoal represented an important transformation. Wood, which contains many different chemical substances, is stacked in a large pile, covered with soil, and burned slowly in an oxygen-poor environment for a few days. The resulting product, charcoal, is almost entirely pure carbon. Charcoal is highly porous, allowing greater airflow in a furnace, and therefore higher temperatures and more rapid heating.

Wolfgang Sauber

Istvan Takacs

Above: Bronze casting. Molten bronze is poured into molds, where it hardens. Bronze melts at a lower temperature than copper and develops less air bubbles, making it easier to work with.

Left: A bronze sword. While copper was more durable than stone tools, it could not be made sharper than flint. Bronze is sharper than stone tools, and significantly stronger and tougher than copper.

Metal from Ores: The Iron Age (1200BC–)

The next great breakthrough in metallurgy was the introduction of a new metal source, known today to be the most plentiful metal in our planet's crust: iron. While iron requires greater temperatures and more extensive working than bronze in order to be as useful, this is more than made up for by its dramatically greater abundance.[9]

Iron was initially produced in a "bloomery furnace," in which iron ore and charcoal were heated together, producing carbon monoxide which removed the oxygen from the iron, as in the copper smelting discussed above. Heat for the chemical process was usually amplified by using a bellows to force more air into the furnace. This process did not reach temperatures great enough to melt iron, however, and the resulting bloom (known as "sponge" iron) had to be worked to remove the impurities, many of which did melt at these temperatures, and could be drawn out of the bloom by repeated hammering. After many cycles of heating and hammering, the bloom was sufficiently worked ("wrought") and relatively pure wrought iron* was the result. This labor-intensive process resulted in a product that could be formed into many shapes and whose ore was more plentiful than copper, yet could not be made as sharp as bronze, and was weaker.

Wrought iron implements were useful, but the production of steel was the advance that made iron a full replacement for bronze.[10] Steel* was made by the careful addition of carbon to wrought iron, by carburizing the surface of an iron implement by hammering it into charcoal, or by doing this repeatedly with iron sheets, until the whole material had become steel.

Modern Breakthroughs: Into The Industrial Era

Blast furnaces, which forced hot air into the furnace column, were introduced in Europe in the twelfth century AD and reached temperatures hot enough to melt iron, producing *pig iron,** which contained a high level of carbon from the charcoal (or, later, coke) that it was surrounded by. This pig iron would then be worked in a finery forge (or later a puddling forge) to introduce oxygen to remove the carbon from the iron (inverting the initial smelting process).

Top: Eurico Zimbres, Bottom: Harvey Henkelmann

Hematite and taconite: two iron-containing mineral ores. Note how little they resemble iron in this form. Iron ores are much more plentiful on earth than are copper ores.

Morgan Riley

An iron "bloom" having the impurities beaten out of it by repeated hammering. This process is known as shingling. *Considering how much work is required, the name wrought iron is not such a mystery.*

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[9] While copper melts at 1,083°C, pure iron melts at 1,535°C, and cast iron objects (poured into molds from molten iron) were not produced in significant degree in Europe until the fifteenth century AD. In China, however, cast iron objects were made two millenia earlier, in the fifth century BC.

[10] Today the use of steel is orders of magnitude greater than that of bronze.

Tamorlan

A "damascus steel" knife blade, produced by repeated carburization and folding of wrought iron. The technique for producing damascus steel has been lost: exact replicas of this type of steel cannot currently be produced.

A major problem in the production of iron and steel was the intense use of charcoal: producing 10,000 tons of steel could require 100,000 acres of trees to be converted to charcoal in the Middle Ages.[11] Recall that wood, which burned at too low a temperature, and had too many impurities, could be converted to charcoal for steel production. Coal had the same problems as wood—too low a temperature and too many impurities. These problems with coal were solved by the brewing industry: it was purified in a way similar to that done with the transformation of wood to charcoal. Coal was burned in a low-oxygen environment to produce *coke*, in the same way that charcoal was produced from wood. This invention made possible the production of much more iron for society, and saved Europe's forests in the process. Even so, not all coal made coke that was acceptable for iron-work. Impurities in coal (particularly phosphorous) were not all removed in the coke-producing process, and only "metallurgical grade" coal was acceptable. In comparison, charcoal is almost completely pure carbon. The benefit of coke was not in its producing more heat, but in its being much easier to produce.[12]

The next major breakthrough was the use of the Bessemer process (invented in the middle of the ninteenth century), in which air was blown into melted carbon-rich

Sander van der Molen

A blast furnace. These huge structures can tower over a hundred feet in the air, and continuously process enormous amounts of coke, iron ore, and flux to produce molten pig iron. In the production process, the iron picks up carbon from the blast furnace, which makes it quite strong, but it cannot be hammered or reshaped. It can be poured into molds as cast iron, but requires carbon removal to make steel.

Dave Pickersgill

A Bessemer converter, which was used to remove the carbon from high-carbon pig iron, by blowing air through the molten metal. The oxygen in the air combines with the carbon to form a gas, which escapes. This made for the beginnings of the modern steel era, by producing low-carbon iron much more cheaply than through the previous processes.

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[11] Iron production moved from county to county, or even nation to nation, based in significant part on the availability for forests to convert to charcoal. This figure comes from *Cathedral, Forge, and Waterwheel: Technology and Invention in the Middle Ages* by Frances and Joseph Gies, Harper-Collins, 1995, New York, N.Y. One cord of wood (transformed into charcoal) was required to process fifteen pounds of iron.

[12] It did have one physical benefit: coke is stronger than charcoal, and does not compress or crumble as easily as charcoal when stacked in a furnace. This is important for allowing air to flow through the fuel and ore.

pig iron. The oxygen in the gas reacts with the carbon (and silicon) in the pig iron, producing more heat and allowing the process to continue without additional fuel. This process brought about a huge (nearly order-of-magnitude) reduction in the cost of steel, and its use expanded dramatically into applications that had called for wrought iron before. With the Bessemer process, steel was no longer produced by adding carbon to wrought iron, but could be produced from decarburized pig iron.[13] Again, the required carbon for steel (around 1%) required *adding* carbon to wrought iron (which had almost no carbon), or *removing* it from pig iron (which was 2–4% carbon).

Later advances in steelmaking built upon Bessemer's technique; easier-to-produce pig iron was to become the primary source of iron for steel, rather than wrought iron. The open-hearth furnace (used in the Siemens-Martin process) was similar to the Bessemer process, but operated more slowly, and used iron ore as an oxygen source, rather than air (which had the trouble of incorporating too much nitrogen into the metal). Because of its slower speed (some eight hours, rather than half an hour per Bessemer batch), open-hearth steelmaking could reduce the carbon content of pig iron to the proper amount for the desired steel, cutting the recarburizing step out of the process. That is, the Bessemer process required three steps: creating pig iron in a blast furnace, removing *all the carbon* by blowing air through molten pig iron, and then adding carbon again to produce steel; whereas the open-hearth process had only two steps: producing pig iron in a blast furnace, and removing the *appropriate amount of carbon* in the open-hearth to produce steel.

With a better control over the basic steelmaking process, and the longer process time of the open-hearth furnace, specific, "tuned" alloys of steel became an increasing portion of output. The most stunning example was the 1910s development of stainless steel, which contains a large amount of chromium (over ten percent) alloyed into the steel. This chromium forms a layer of chromium oxide film, which protects against the corrosion and rust that would otherwise eventually destroy steel. Because the chromium is mixed into the steel, rather than just coating it,[14] scratches and dents are self-healing: the newly exposed steel also contains chromium which quickly oxidizes, forming a new protective layer. Other common alloying metals are nickel, molybdenum, and manganese. Like per capita energy use (by source), which serves as an important physical economic indicator of development, stainless steel consumption per capita reflects high-technology economic activity.


Steve Nuccia

New York City's Chrysler Buildling. Completed in 1930, the top of the building was wrapped in stainless steel. Scratching and abrassion do not damage the corrosion resistance of this steel.


Wikimedia Commons user TMg

The "spangled" appearance of a galvanized steel handrail. The thin zinc coating, less than a millimeter thick, protects the steel from corrosion, but will wear off over time, and can be scratched or abraded off.

Today, the open-hearth furnace has been replaced by basic oxygen steelmaking (BOS, developed in the middle of the twentieth century) which is quite similar to the Bessemer process, but uses pure oxygen (unavailable in the needed quantities in Bessemer's day) rather than air. Using turboexpander-generated liquid oxygen, BOS steelmaking can transform pig iron into steel in a fraction of the time required by the open-hearth furnace, and is the primary method of producing steel today, capable of operating on metal scrap and pig iron. Advances in chemistry and spectroscopic instrumentation make it possible for BOS steelmaking to stop at just the right point, when the desired carbon level is reached, even though the process occurs quickly.

Nearly one third of steel production comes from recycling scrap metal in electric arc furnaces (EAFs), which pass an electric current through the metal, directly heating it in the process.[15] This electricity-intense process consumes around 400kWh of electricity per ton of steel, and can be easily scaled down for small batches of specialty steel. Obviously, a fully nuclear economy and the cheaper electricity (and process heat for pre-heating) would make electric arc furnaces much cheaper (physically) relative to coke-fired blast furnaces.

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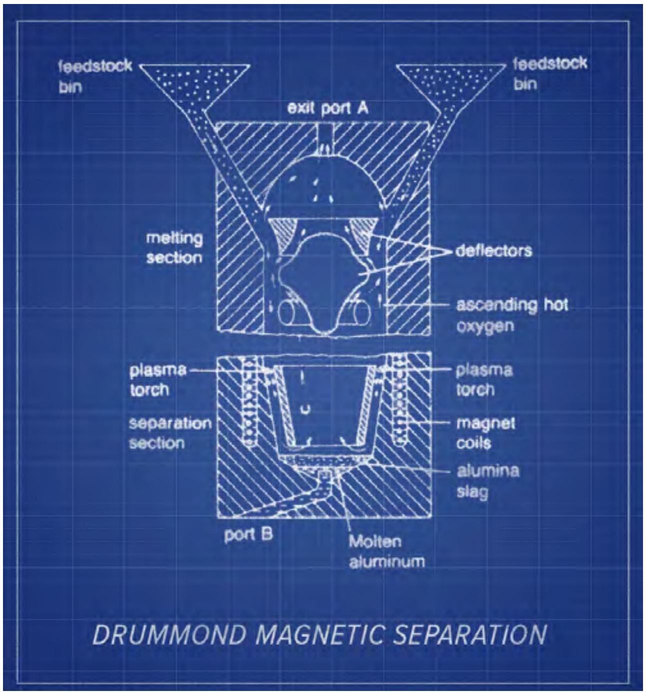
[13] On top of the coke already required to produce iron, the process of adding carbon to wrought iron to produce steel required several additional tons of coke per ton of steel produced.

[14] *Galvanized* steel, which is coated with a thin layer of zinc (producing a characteristic "spangled" appearance) is also protected against corrosion, but scratches that penetrate the thin zinc coating will cause the rusting away of the steel.

[15] EAFs account for 29% of steel production. This stunning process is worth seeing! One example video: http://youtu.be/G6Uxh-xtU-g

Fully replacing blast furnaces and the use of coke requires another breakthrough. Even though EAFs can reach great heats, the other aspect of ore processing is *reducing** it chemically: removing the oxygen to which the iron is bound. This is the *chemical* role of coke in the blast furnace, in addition to its heating role. An EAF cannot perform this chemical reduction, and is therefore only useful, at present, for processing metals, but not ores.

In an economic platform capable of large-scale deployment of *plasma torches*, the reduction of ores could be performed without using coke at all, as the chemical change can be brought about directly, without carbon to bond with the oxygen.[16] The metal would still need to be separated from the oxygen, which currently occurs by a phase change (producing carbon dioxide gas), but which could be performed by ionizing the metal and separating it with a magnet, before it cools out of its plasma state and recombines with the oxygen. With such technologies, multiple processes could be combined into one: the coke ovens required to produce coke, the blast furnaces to produce pig iron, the refining processes to remove carbon, and even the totally different technology used to produce aluminum, could all have their tasks performed by such a "universal machine," operating with plasmas.



J Drummond, D Chang, D Mahaffey, US Patent 3,942,975

A design for a magnetic separation machine for ore processing. This diagram indicates its role for aluminum production, but the same basic design would function for iron processing as well.

Metallurgy in the Modern Era: the Future of Metals and Metallurgy

Until the recent two centuries almost the sole use of metals discussed here had been for structural, rather than specifically chemical use. The characteristics of the metal that were sought out were *physical* properties, such as strength, flexibility, hardness, density, and ductility. Advances in chemical understanding gave new uses to metals and alloys, and with the advent of the electrical era, entirely new characteristics of metals became important. The employment of electric motors, rather than steam engines in factories, required metals that were economical, workable, and conducted electricity well. The excellent electrical conductivity of copper (exceeded only by silver) and its flexibility makes it the primary metal used for building wiring. Where weight and cost are an issue (as in high-voltage transmission lines), aluminum is used.

The recent few decades' change in the applications of electricity has brought to life previously unconsidered properties of metals and similar elements. The invention of the transistor in 1947 marked the beginning of the intense use of semiconductor materials, in which the electrical properties of silicon (a metalloid) are engineered by the incorporation of other elements, in order to bring out very specific electrical properties. Computer-automated control of machining and industrial processes was possible on a large scale with the development of semiconductor integrated circuits. Relatively rare metals, whose structural characteristics in alloys are sometimes impressive, are increasingly being used for their chemical and electrical characteristics, serving specialized roles as chemical catalysts, phosphors, magnets, and motors.

And now, the engineering and science breakthroughs made possible by these increasingly precise components open the way to "universal machines" operating with plasmas and magnetic separation, machines which can fundamentally transform the way metals, both common and rare, are formed into useful products. These changing roles of metals are a specific case of the discovery of new types of physical principles, as brought about by the creation of modern chemistry and electrodynamics.

In the next section of this report, we move from physical properties of materials to the chemical nature of matter, which brought a new understanding of metallurgy, and opened the way to the next dimension of physical actions by man. Modern chemistry brought together many different chemical properties, to develop the unity of matter expressed by Mendeleev in his periodic table of the elements.

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[16] See article on plasma torches in "Nuclear NAWAPA XXI: Gateway to the Fusion Economy," available at http://21stcenturysciencetech.com/Nuclear_NAWAPA.html

Metallurgy Glossary

Ore Reduction

In the chemical sense of *reduction*, this refers to separating the metal element (e.g., copper or iron) from the oxygen to which it is bound. Coke or charcoal act as reducing agents, binding oxygen in the ore to their carbon and producing carbon dioxide in the process, which escapes as a gas.

Casting

When molten metal is poured into a mold and allowed to cool into a desired shape, this process is called *casting*, and the resulting object is *cast*, such as cast bronze, or a cast iron frying pan. Cast iron objects (produced from the material known as pig iron) have high levels fo carbon, which makes them strong but very brittle. Cast iron cannot be worked by a blacksmith, even when heated. Hammering it would break it, rather than bend it.

Wrought Iron

Iron produced in a bloomery furnace (or another process that does not cause it to actually melt) contains many impurities. As the resulting hot iron bloom is hammered, slag is worked out, and when the iron has been sufficiently worked in this manner, it is said to be wrought (an old form of "worked"). Wrought iron can be hammered and worked by a blacksmith into desired shapes, although it is not very strong. Wrought iron is no longer produced on a commercial scale today, and many of its former applications are now met with steel. Wrought iron has a low carbon content.

Pig Iron

Iron ore that has been melted in a furnace, picking up excess carbon along the way, containing 2–4% carbon. The resulting "pig iron" gets its name from the shape molten iron would take when poured out into sand molds: the central runner and side ingots resembled a mother sow feeding her piglets. Molten pig iron can be cast into molds to form cast iron, or further processed to remove carbon for steel production.

Steel

Steel is iron that has a specific carbon content (around 1%), giving it both strength and workability. Wrought iron is workable but weak, and cast iron is strong but cannot be reshaped. Steel combines beneficial characteristics of both materials, and has almost completely replaced wrought iron, although cast iron still finds applications.

German Federal Archives

Working in a steel plant. Protective clothing keeps employees safe as they work with molten metal at temperatures exceeding 1500°C.