History of Metallurgy

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1 Ancient Civilizations

Native gold was the first metal used by man. It was washed from ores and melted. As civilization progressed, metallic copper was produced by the reduction of its oxide ores in primitive furnaces. This is believed to be the first metal produced chemically by man, around 4000 BC. This was, however, slowly superseded by bronze which is a copper alloy containing about 10% tin that is easy to melt and to cast. Bronze was either produced by mixing tin, derived from its oxide by reduction, with metallic copper or by reducing a mixture of copper ore with a tin ore. This period of civilization, from approximately 2400 BC, became known as the Bronze Age. Iron became known much later than copper although iron ores are more abundant than copper ores and almost as easy to smelt. This may be due to the fact that copper can be shaped by cold-hammering, whereas iron must be hammered hot. The Iron Age began around 2000 BC.

Over time two more metals, lead and mercury, became known. These, along with gold, silver, copper, tin, and iron, were the only metals known to the ancient peoples, and are known as the seven metals of antiquity (Fig. 1). There are reasons for the early availability of these metals:

1. some of these metals occur in the native state, for example, gold, silver, copper, iron (meteoric), and mercury;
2. the oxides of copper, iron, tin, and lead are readily reduced below 800°C. Such a temperature can be achieved easily by burning carbonaceous material; and
3. some of the metals have low melting points, for example, lead and tin, while mercury is already liquid at room temperature, and are thus easy to recover. Impurities in a metal lower the melting point considerably; for example, iron containing 4% carbon melts at 1100°C while the pure metal melts at 1540°C. Metals used by the ancient peoples were seldom pure.

Primitive furnaces were used in which alternate layers of charcoal and ore were added and a fire made and kept burning for 3–4 days. The fire was then raked off, and the lump of metal, probably 1–2 kg, was collected. Charcoal, made by anaerobic burning of

![Fig. 1 Ancient metals.](image-url)
harvested forest wood, was used as a reducing agent. Ancient Egyptian wall paintings show blow-pipes being used with small furnaces, and later they depict the use of bellows to achieve high temperatures by blowing air into the furnace.

During the Roman Empire, the seven metals were used extensively as well as brass – an alloy of copper with zinc prepared by smelting a copper ore and another ore known as calamine. Pliny the Elder, the Roman philosopher who lived between AD 23 and 79, was the author of *Natural History* in 37 volumes in which he discussed the mining and metallurgy of his time. When, however, the Empire collapsed in the 5th century, mining activities deteriorated because of the lack of a central organizing power.

## 2 The Middle Ages

The alchemists of the 8th and 9th centuries thought they could change a base metal like iron into a precious metal like gold, a process which became known as the transmutation of metals. Nothing worthwhile in the field of metallurgy took place during the Dark Ages of magic, superstition, and alchemy except that many acids and salts were prepared, described, and used for a variety of purposes.

The production of metallic zinc was described in a Hindu book written around AD 1200. The new “tin-like” metal was made by indirectly heating calamine with organic matter in a covered crucible fitted with a condenser. Zinc vapor was evolved and air-cooled in the condenser located below the refractory crucible. By 1374, the Hindus had recognized that zinc was a new metal, the eighth known to man at that time, and a limited amount of commercial zinc production developed.

In the 13th and 14th centuries three new metals, arsenic, antimony, and bismuth, became known in Europe in the elemental state. It was only with the translation of Arabic texts into Latin, and henceforth the flow of chemical knowledge to Europe, coupled with the Renaissance in Italy, that the art of metal extraction started to take shape. From India, zinc manufacture moved to China sometime around AD 1600, where it developed as an industry to supply the needs of brass manufacture. Zinc production became known in Europe from China about a century and half later. The Chinese also prepared another alloy which looked like silver but rather contained copper, not silver. They called it pai-thung, white copper. It was imported to Europe in small quantities in the early 1700s. Much later, it was discovered that this alloy contained a new metal that was called nickel.

In the 16th century, two important books on metallurgy appeared. The first, *De La Pirotechnia*, appeared in 1540. Its author Vannoccio Biringuccio (1480–1538) was working in the Armory of Siena in Italy, and had traveled widely through Germany and Italy. The book, written in Italian, was concerned with ores, assaying, smelting, separating gold from silver, the making of alloys, melting, casting, and fireworks. The second book, *De Re Metallica*, appeared in 1556, a year after the death of its author, Georgius Agricola, a medical doctor from Saxony who traveled widely in the mining districts of that area, and wrote many books in Latin, the language of scholars at that time. The title means “of things metallic” and it was the reference book on mining and metallurgy for at least two centuries. It was translated into many languages and an English translation was made in 1912 by Herbert Hoover and his wife. Hoover was a mining engineer from Stanford who was President of the United States between 1929 and 1933.

For centuries the American Indians in Ecuador collected silver-like metallic particles found near the river bed and mixed them with gold to make jewelry. They were unable to melt these particles. After the Spanish Conquest, the Spaniards, also unable to melt them, called them platina. The metal platinum was later found to be the main component.

In the early smelting processes, charcoal made from forest wood was used. Later mined coal was introduced, but it was soon realized that it softened in the furnace and spoiled the metallurgical processes. This factor, together with the mining difficulties such as coal-gas explosions in mines, ventilation and drainage, as well as the laws prohibiting destruction of the forest, contributed to the increased price of timber. This problem was solved in 1607 when coal was first converted into coke. This simple step revolutionized the iron industry. Being hard and porous, coke is able to withstand a far greater burden without crushing, thereby making possible the construction of much larger furnaces with a resultant increase in output.

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*Fig. 2* Metals of the Middle Ages.
3 The 18th Century

In the 18th century, mineralogists, travelers, and analysts played an important role in the discovery of new metals. Mineral specimens from different localities were continually supplied to laboratories where they were analyzed. As a result, 13 new metals were discovered. These are, in order of their discovery: cobalt, platinum, nickel, manganese, molybdenum, tellurium, tungsten, uranium, zirconium, titanium, yttrium, beryllium, and chromium (Fig. 4). A need for training students in the fields of geology, mining, metal extraction, and metallurgy was met by establishing schools in many European cities as well as in the New World where important mining activities were taking place in the Spanish colonies.
Other important activities led to the understanding of the nature of fire and the smelting process. It was once believed that when coal was burnt, phlogiston, which in Greek means flame, was released and a calx, that is, ash, remained. If an ore or an oxide was heated with coal it took up the escaping phlogiston in the fire to form the metal:

\[
\text{Ore (oxide)} + \text{Phlogiston (from coal)} \rightarrow \text{Metal}
\]

It was the French chemist Antoine Laurent Lavoisier (1743–94) who in 1772 finally delivered the fatal blow to the theory. Oxygen had been discovered a few years earlier, and he interpreted the phenomenon of combustion as an oxidation process.

Another revolutionary step in the technique of smelting took place when hydrogen was used for the first time to prepare metallic tungsten by the gaseous reduction of its oxide around 1783. It should be pointed out, however, that although hydrogen is a more powerful reducing agent than hot carbon, it failed to liberate the alkali metals, the alkaline earth metals, or aluminum from their oxides.

4 The 19th Century

In the 19th century more metals were discovered (Fig. 5). The sequence of their discovery was a result of a preceding discovery.

4.1 The Beginning of the Century

At the very beginning of the century the Italian scientist Alessandro Volta (1745–1827) discovered electric current and this proved to be a very important tool for metallurgists. The newly invented Volta cell was used for the first time by the British chemist Humphry Davy (1778–1829) to discover new metals. He joined a large number of these cells in series, and thus was able to generate a large current. He tried to decompose aqueous potash, but produced nothing but hydrogen and oxygen. Later, he tried solid potash, just moistened to conduct current; in this way he noticed that something burned brightly at the cathode. That was potassium metal, which being strongly reactive, burned in air. In the same way, he electrolyzed soda ash and demonstrated that sodium metal could be liberated.

The work of Davy and others opened an entirely new area in metallurgy, though the fact was not recognized at that time. The intense difficulties to be overcome when removing the oxygen from such oxides as those of potassium, sodium, barium, calcium, and magnesium clearly suggested that the alkaline metals themselves might be used to extract the oxygen from other oxides that prove difficult to split. Aluminum oxide was so resistant to all methods of decomposition that it was considered at one time to be an element. It was the Danish scientist Christian Oersted (1777–1851) who in 1825 reacted aluminum chloride with potassium amalgam from which minute particles of aluminum were recovered by distilling off the mercury. The method was later applied to other compounds such as chlorides and fluorides, and in this way zirconium, titanium, cerium, thorium, beryllium, boron, silicon, tantalum, and yttrium were isolated. Once aluminum became available, it was used for liberating other metals from their oxides.
4.2 The Second Half of the Century

The spectroscope was invented by the German chemists Bunsen and Kirchhoff in 1859. This led to the discovery of four new metals in the period 1860–63, namely cesium, rubidium, thallium, and indium. In 1869 the Russian chemist Dimitry Ivanovitch Mendeleev (1834–1907) discovered the Periodic Law leaving gaps in this Table for elements not yet discovered, and was able to predict their properties. This prediction helped the chemists of the time to search for these elements. Within two decades the three metals gallium, scandium, and germanium had been discovered. The great similarity between the chemical properties of the rare earths made their isolation a difficult task and the success in separating them contributed to the knowledge of a dozen new metals during this period.

In the 1850s Henry Bessemer (1813–98) invented the pneumatic process for steel-making in England. This made a great advance in metallurgy because it reduced the time of transforming iron into steel from a few days to a few minutes, saving large amounts of fuel which decreased its cost greatly and rendered it available as a material of construction for bridges, ships, and buildings.

Another great technological advance was the invention of the dynamo in the 1870s that made available electricity in bulk. This encouraged the expansion of electrolytic copper refining to supply the pure copper needed for the electrical industry. Another important application was in the electrolytic production of aluminum. Once aluminum was available inexpensively, it was used for reducing other oxides to metals. Thus, chromium and manganese were prepared a few years later by this technique.

At end of the 19th century a new phenomenon in science was discovered. In 1897 radioactivity was discovered by the French physicist Henri Becquerel. This led Marie Curie (1867–1934) to the discovery of polonium and radium in 1898. A year later André Debriére, a coworker with Curie, discovered actinium.

5 The 20th Century

At the beginning of the 20th century, europium and lutetium, and later promethium, the last members of the rare earths, were discovered. Also, two new radioactive metals, protactinium and francium, were discovered. Just as the invention of the spectroscope led to the discovery of four metals in the 19th century, so the invention of X-ray spectrum analysis by Henry Moseley (1887–1915) in 1914 led to the discovery of two more metals in the 20th century: hafnium and rhenium. Similarly, the invention of the cyclotron was responsible for the discovery of the new metal technetium and the transuranium elements (Fig. 6).

Shortly after the discovery of uranium fission in 1939, the possibility of harnessing atomic energy was realized. To achieve this goal, metallic uranium would be required on a large scale. Since no rich deposits of the metal were known at that time, poor-grade ores had to be processed. This introduced the large-scale application of ion exchange and solvent extraction in metallurgy. Also, the need for metals having special properties for their use in nuclear reactors resulted in the sudden interest in previously rarely used metals such as beryllium, zirconium, cadmium, sodium, potassium, thorium, and the rare earths. Thus, novel methods of extraction were devised and applied on a large scale, for example, chlorination, fluorination, and fused-salt electrolysis.

The improvement in the design of the jet engine, and the suitability of titanium and its alloys to meet the strains imposed by ultrahigh speed flight, in addition to their exceptional high strength-to-weight ratio, resulted in the rapid development of the commercial production of titanium. The discovery of the semiconductive properties of germanium led not only to commercial production of this metal but also to the preparation of related metals such as silicon, selenium, and tellurium on a commercial scale. Further, the use of such metals for the electronics industry called for very high purity, not known before. This resulted in the invention of new methods for metal refining such as zone refining. If high purity had to be achieved, laboratory methods for the determination of impurities at such previously undetected low levels had to be devised. Polarography, activation analysis, atomic absorption spectroscopy, etc. were therefore either invented or improved to meet the new challenges.

![Metals of the 20th century.](Fig. 6)
The competition to send men to the moon was a strong reason to develop new alloys, new rocket fuels, and new materials for construction. The presentation of new ideas in chemical thermodynamics and kinetics by Nernst, Van’t Hoff, Haber, Ostwald, Le Chatelier, Arrhenius, and others laid the foundation for a theoretical approach with which to tackle and solve problems related to metal recovery. The improvement in chemical engineering practice resulted in the cheap and large-scale production of important gases such as oxygen, chlorine, and hydrogen. Thus, the oxygen lance technique for steel-making became a reality, and the oxygen pressure leaching of ores became feasible. The use of chlorine in extracting metals from ores was greatly advanced and the hydrogen reduction of iron ores, or the production of metals by hydrogen reduction from aqueous solution, became commercial processes. The role played by refractories, and especially the basic refractories, was also a milestone in the development of pyrometallurgical practice. Closely related to these achievements was the introduction of new unit operations such as flotation and fluidization.

**Further Reading**