

CHAPTER 4

Discovering Metals— A Historical Overview

THE ANCIENT WORLD passed from the Stone Age through the Bronze and Iron Ages to our modern developed society—a society that is dependent on metals and alloys for its very existence. However, an impressive body of metallurgical knowledge developed in the thousands of years since ancient man first found copper and became curious enough to investigate the behavior of this naturally occurring, relatively pure, native metal. Metallurgical knowledge evolved from an art to a science, until the body of scientific knowledge on how each metal and alloy behaves has become quite extensive. A historical summary of developments in metallurgy from the use of native metals to the electrolytic refining of aluminum in 1884 is provided in Table 4.1.

Six metals were used by prehistoric man: gold, silver, copper, tin, lead, and iron. Gold and silver were too soft to be useful for much except decoration. Copper could be hardened by hammering or forging and was therefore useful as a tool but had little value as a weapon. Bronze, developed by alloying copper with tin, had useful strengths, could be hardened by forging, and could be cast to shape. The discovery of bronze significantly altered the development of civilization. Lead was soft, easily worked, and could be made into vessels; later in history it was made into pipes such as those used to transport water in the early Roman Empire. Iron was so important to civilization that its discovery led to the Iron Age and a transition from the Bronze Age.

4.1 Native Metals

Most metals naturally occur as minerals or compounds. The metal atoms have reacted with

other metals or with nonmetallic atoms. One of the primary tasks of the metallurgist is to extract the metal from the compound. The few metals that are found in an unreacted state are termed native metals. Through the use of native metals, the science of metallurgy was born.

The Chalcolithic period is the name that archaeologists give to the time period that immediately preceded the Bronze Age in which metals were first being mastered, and they date this period between approximately 5000 and 3000 B.C. (Table 4.1). Ancient man first used native or naturally occurring and relatively pure metals such as gold, silver, and copper. Nuggets of gold could be found mixed with the quartz sands of river beds in many areas of the world. Such gold nuggets were hammered into decorative shapes, but because of the low strength the metal was useless as a weapon or tool. Gold was shiny, lustrous, and, even as today, useful for jewelry and prized for possession. Silver, which was much less common, also was used in a similar fashion. Even the naturally occurring alloys that were mixtures of silver and gold served no practical purposes. Historians frequently refer to the Copper Age as a precursor to the Bronze Age. The use of copper (or more specifically copper alloys) gave birth to this first practical age of metallurgy.

Copper, like gold and silver, existed in a native or natural state. Ores that were more than 99.9% pure were found in many parts of the world. Some civilizations, such as the mound-building Indians of the Ohio plains, found or traded for native copper. The copper metal was most commonly used for ornamental purposes, hammered into decorative shapes and used as jewelry and to line burial sites of important citizens. There are a few examples of copper spear

Table 4.1 Chronological list of developments in the use of materials

Date	Development	Location
9000 B.C.	Earliest metal objects of wrought native copper	Near East
6500 B.C.	Earliest life-size statues, of plaster	Jordan
5000–3000 B.C.	Chalcolithic period: melting of copper; experimentation with smelting	Near East
3000–1500 B.C.	Bronze Age: arsenical copper and tin bronze alloys	Near East
3000–2500 B.C.	Lost-wax casting of small objects	Near East
2500 B.C.	Granulation of gold and silver and their alloys	Near East
2400–2200 B.C.	Copper statue of Pharaoh Pepi I	Egypt
2000 B.C.	Bronze Age	Far East
1500 B.C.	Iron Age (wrought iron)	Near East
700–600 B.C.	Etruscan dust granulation	Italy
600 B.C.	Cast iron	China
224 B.C.	Colossus of Rhodes destroyed	Greece
200–300 A.D.	Use of mercury in gilding (amalgam gilding)	Roman world
1200–1450 A.D.	Introduction of cast iron (exact date and place unknown)	Europe
Circa 1122 A.D.	Theophilus's <i>On Divers Arts</i> : the first monograph on metalworking written by a craftsman	Germany
1252 A.D.	Diabutsu (Great Buddha) cast at Kamakura	Japan
Circa 1400 A.D.	Great Bell of Beijing cast	China
16th century	Sand introduced as mold material	France
1709	Cast iron produced with coke as fuel, Coalbrookdale	England
1715	Boring mill or cannon developed	Switzerland
1735	Great Bell of the Kremlin cast	Russia
1740	Cast steel developed by Benjamin Huntsman	England
1779	Cast iron used as architectural material, Ironbridge Gorge	England
1826	Zinc statuary	France
1838	Electrodeposition of copper	Russia, England
1884	Electrolytic refining of aluminum	United States, France

Source: Ref 4.1

points found in North America, but most of the copper was used for ornaments.

Other civilizations, such as those in Egypt and the Middle East, noted that copper hardened and strengthened significantly when hammered. Although the term *nanotechnology* was clearly not used, these ancient metallurgists were hammering to control the number and configuration of the nanocrystalline elements of the structure of copper. The hardened copper became useful as a tool, and thus the Copper Age was born. Knives could be fabricated for agricultural uses and for cutting the flesh of fish and game. However, such knives were generally useless for the penetration of hides or the cutting of bones. Thus, although copper knives served a purpose, they lacked the strength to serve as effective weapons. The discovery that copper could be obtained by heating covellite, malachite, and other bright blue stones or minerals was made between 4000 and 3000 B.C. These were primarily copper sulfide ores. An ore is a natural mineral that can be mined and treated for the extraction of any of its components, metallic or otherwise. The metallic component of copper sulfide minerals is copper. Sulfur is one of the nonmetallic elements. Extraction of copper from copper sulfide ores provided ancient man with another source of copper. Once extraction techniques were developed, the use of native metals was not restricted.

The transition from hammering pieces of native copper into a desired shape to extraction of copper from copper sulfide minerals required both high temperatures and significant insight. There is little doubt that the discovery that copper could be extracted from copper sulfide was not made in a deliberate quest for copper. Some think copper resulted when a fire was built beside an ore deposit; others suggest copper was produced by chemical reactions in early pottery kilns. However, in spite of the accidental nature of the discovery, these early “extractive metallurgists” must be given credit for their powers of observation. Metal, specifically copper, could be won from ores by the application of heat, in this case the heat of a wood or charcoal fire. Extracting copper from its ores is not an easy task. First the metallurgist must heat the ore to temperatures over 982 °C (1800 °F)—not an easy task with a wood fire—and second, the metallurgist needed something to contain the molten (liquid) copper. As a thought experiment, how would you accomplish either of these tasks without access to modern technology or materials?

The ancient “metallurgists” were aware of two important metallurgical facts: first, that the strength of a metal (in this case copper) could be increased by hammering, and second, that metals could be extracted from ores. The process of hammering or forging is frequently termed cold working. If the process of shaping was conducted

at elevated temperatures (~300 °C, or ~570 °F) the strength of copper was not significantly increased. Thus, metal fabricated at elevated temperatures had different properties than metal fabricated at low temperatures. This difference in the behavior of a metal processed at elevated temperatures and that of a metal processed at near ambient or room temperature remains an important factor in the shaping of metals and alloys today. The observation that metals could be extracted from ores was vital to the development of metallurgy, because the number and supply of native metals was quite limited. Before metallurgy could emerge as an art or science, the ancient metallurgists had to be aware that the supply of raw materials was not limited to the native metals.

The development of high temperatures to melt copper also expanded the amount of material available. Large pieces of copper could not be cut and therefore were not of significant importance until melting techniques became available.

4.2 The Bronze Age

The Bronze Age began when it was discovered that mixtures of two metals, or alloys, were stronger than either of the metals taken individually. This discovery was probably made about the same time that extractive metallurgy was discovered. The discovery that tin alloy additions strengthen copper was the crux of the Bronze Age. A chemical analysis of a typical bronze alloy from the ancient Middle East shows that the alloy contained approximately 87% copper, 10 to 11% tin, and small amounts (less than 1%) of iron, nickel, lead, arsenic, and antimony.

It is rather startling to realize that approximately 4000 to 5000 years passed between the advent of the Bronze Age and the development of sterling silver, a more modern application of the strengthening effect of alloy additions. Sterling discovered that the strength of silver could be improved greatly by the addition of small amounts of copper. These small additions, approximately 7.5%, did not affect the appearance but significantly improved the serviceability of silver vessels, jewelry, and utensils.

Even more startling may be the persistence of ancient metallurgical practices into relatively modern times. An eleventh century description of bronze states that it is an alloy consisting of one pound of copper and two ounces of tin

(88% Cu and 12% Sn). This alloy is remarkably similar to the 87% Cu found in the ancient bronze. Other publications suggest that a soft bronze or gun metal is formed when 16 parts of copper are mixed with one part of tin, and that a hardened gun metal, such as was used for bronze ordnance, is formed when the proportion of tin is approximately doubled. This hardened gun metal contains 88% Cu.

The historical evolution of metallurgical practice from the production of copper to the production of bronze is difficult to trace. Certainly many of the early attempts to produce copper by heating copper sulfide ores in the presence of red hot charcoal produced arsenic-containing copper alloys. The mineral enargite is frequently found with other copper sulfide ores, and the reduction of this mineral would provide arsenic as well as copper. Such coppers (termed arsenical bronzes) are significantly stronger than arsenic-free copper. These first copper-tin bronzes probably resulted from the accidental inclusion of an alloy element through its presence in an ore body.

From a technological viewpoint, accidental improvement in properties of metals is far different than the intentional mixing of two or more ores or refined metals to obtain an alloy with specific desired properties. However, by 3000 B.C., ancient metallurgists had learned to intentionally mix ores of copper and tin to produce bronze that is very similar in composition to some modern alloys. The alloys that were made from intentionally mixed ores marked the real onset of the Bronze Age. Mankind now had a metallic alloy that could be cast (i.e., poured as a liquid) or forged (hammered) to shape.

Bronze was significantly stronger than relatively pure copper and was useful both as a tool and as a weapon. A photograph of an ancient bronze casting is shown in Fig. 4.1. This casting is an example of the high level of perfection achieved in Chinese foundry “technology” in the 7th century B.C. The bronze in this casting contains less tin than was typical of bronze weapons from the same era.

Low-tin bronze was probably produced because of the difficulty in locating good supplies of tin. Tin-rich ores were not as common as copper-rich ores. Frequently tin had to be transported over large distances. Because of these problems, bronze was an expensive material and unalloyed copper was probably used whenever practical. The metals for use in farming and domestic quarters did not require strength



Fig. 4.1 A bronze Kuei handled vessel on a rectangular plinth (34.30 × 44.50 cm) cast in China in the 7th century B.C. Courtesy of ©The Cleveland Museum of Art, Leonard C. Hanna, Jr. Fund, 1974.73

as high as the metals for use in hunting and fighting. Even during the Bronze Age there were material shortages, and tin was a critical material.

4.3 Making Metals—Extractive Practices

Most metallic elements occur naturally as minerals or ores, which are compounds that result from a reaction between metallic and non-metallic atoms. Common native and mineral occurrences of metals are listed in Table 4.2. Most copper, zinc, and lead ores are sulfides, while iron and aluminum are generally found in oxide ores.

Minerals are frequently brightly colored, iridescent, and attractive. Because of such attractiveness, ancient man (and modern miners as well) collected mineral samples. For example, a typical copper-containing sulfide mineral is bornite, which contains copper (Cu), iron (Fe), and sulfur (S) in the ratio of five copper atoms to one iron atom to four sulfur atoms, designated as Cu_5FeS_4 . This ore is reddish purple when freshly broken and becomes iridescent blue or blue-green when exposed to the atmosphere. This change in color (tarnishing, due to atmospheric exposure) results from the chemical reaction of the ore with oxygen in the atmosphere. Chalcopyrite is a yellow copper sulfide ore that also contains iron, while covellite is a

Table 4.2 Common occurrences of metals

Type of ore	Elements or compounds
Carbonates	CaCO_3 , $\text{CaCO}_3 \cdot \text{MgCO}_3$, MgCO_3 , FeCO_3 , PbCO_3 , BaCO_3 , SrCO_3 , ZnCO_3 , MnCO_3 , $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, K_2CO_3 , $(\text{BiO})_2\text{CO}_3 \cdot \text{H}_2\text{O}$
Fluorides	CaF_2
Halides	NaCl , KCl , AgCl , $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl and MgCl_2 in sea water
Native metals	Cu , Ag , Au , As , Sb , Bi , Pt (Os , Ir , Pd), Mn (modules on ocean floor)
Oxides	Al_2O_3 , Fe_2O_3 , Fe_3O_4 , SnO_2 , MnO_2 , TiO_2 , $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, $\text{FeO} \cdot \text{WO}_3$, Cu_2O , ZnO , ThO_2 , Bi_2O_3 , (Fe , Mn) (Nb , Ta) $_2\text{O}_6$
Phosphates	$\text{LiF} \cdot \text{AlPO}_4$, $\text{Th}_3(\text{PO}_4)_4 \cdot \text{X}$ (Re) (a) PO_4
Silicates	$\text{Be}_2\text{AlSi}_6\text{O}_{18}$, ZrSiO_4 , $\text{Sc}_2\text{Si}_2\text{O}_7$, $\text{NiSiO}_3 \cdot \text{X}$, MgSiO_3 , ThSiO_4 , $\text{LiAlSi}_3\text{O}_8$
Sulfates	BaSO_4 , SrSO_4 , PbSO_4 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$
Sulfides	Ag_2S , Cu_2S , CuS , PbS , ZnS , HgS , $\text{FeS} \cdot \text{CuS}$, FeS_2 , Sb_2S_3 , Bi_2S_3 , MoS_2 , NiS , CdS , $\text{FeAs}_2 \cdot \text{FeS}_2$ (Fe , Ni) $_9$ (S , Te) $_8$, (Ti , Pb) S
Miscellaneous	(Fe , Mn) WO_4 , CaWO_4 , (Co , Ni) As_2 , (Co , Fe) As_2 , NiSb , PtAs_2 , (Cu , Ti , Ag) $_2\text{Se}$

(a) Rare earth metal such as Ce, Nd etc., or La. Source: Ref 4.2

deep blue copper ore that contains only copper and sulfur.

Extraction of metals from their respective ores requires work or energy to separate the metal from the sulfur or oxygen. This energy can be supplied in the form of heat, and the first extractions were probably accidental: A fire got out of hand and mineral samples that had been collected for their beauty were heated, resulting in copper metal; a fire was built near or against a copper sulfide mineral deposit and copper was produced; or it is even possible that during an act of worship an ancient man intentionally cast bright stones into a fire and subsequently found that the “gods” had turned the stones into copper metal.

Pyrometallurgy is the extraction of metal from ores by chemical reaction at high temperatures in fuel-fired furnaces. Pyrometallurgy may involve roasting and/or smelting for the extraction or refinements of metals. *Smelting* refers to melting processes that separate metals in fused form from nonmetallic materials. Other more modern methods of extraction and refinement include hydrometallurgy and electrometallurgy. *Hydrometallurgy* is the leaching or removal of the metal from an ore body by passing a strongly acidic or alkaline solution over the ore. *Electrometallurgy* involves the extraction of metals from their ores by the application of large amounts of electrical energy.

Experimentation with copper smelting began in the Chalcolithic period (Table 4.1) at some

time after the melting of copper was discovered. As the supply of native copper and readily available copper sulfide ores was depleted, the metallurgist was forced to turn to the extraction of metals from other ore deposits to obtain a supply of copper. The extraction of copper from the copper sulfide ores and from other ore deposits required that the early metallurgist reverse a reaction that had occurred between copper and another element found in the earth's crust. Melting of copper also resulted in the discovery of alloying and the Bronze Age.

Although modern extraction processes are complex, the smelting process can be very simple. For example, early North American settlers smelted lead sulfide (galena) to produce lead ball for bullets used by most colonial woodsmen. Galena is the most common lead ore, and the lead was extracted by building a fire inside a hollow tree stump and roasting the galena ore on the fire. This process resulted in the lead sulfide (galena) reacting with oxygen in the air to form molten lead and sulfur dioxide.

Although extraction of lead from galena had been widely practiced for many years, it was not widely recognized until relatively recent times that silver is associated with lead extraction from galena. Lead sulfide ore generally contains appreciable quantities of silver, and be-

cause of the potential for silver recovery, lead smelting is currently practiced under very controlled conditions.

A schematic of a lead blast furnace for smelting the galena ores is illustrated in Fig. 4.2. Basically, such processes are the key to any pyrometallurgical extraction process. An ore is heated in the presence of a selected and (in most cases) controlled environment. This environment reacts with the ore to produce both the desired metal and the other (frequently less desirable) products of the smelting reaction. To illustrate the undesirable nature of some smelting reaction products, note that the hydrogen sulfide gas produced by lead smelting is poisonous. Lead smelting was successful because at temperatures commonly reached in a wood fire, oxygen in the air reacted with the lead sulfide to free the lead and produce both sulfur dioxide and hydrogen sulfide gas.

4.4 Iron

The early name for iron means “stone from heaven” in several languages. This name probably resulted because the first iron used by ancient man was literally “from heaven.” Meteorites weighing from a few ounces to tens of tons

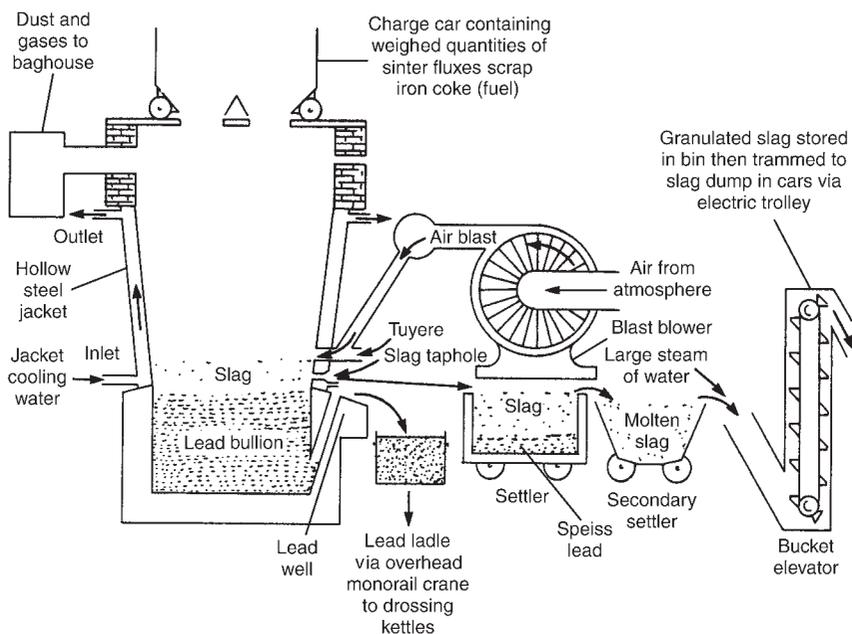


Fig. 4.2 Lead blast furnace, open-top type. This furnace is termed a blast furnace because of the air blast used to smelt the ore/coke mixture. Source: United States Smelting, Mixing, and Refining Co.

have been falling on the earth since its beginning. The meteorites frequently contained large quantities of metallic iron, and the first iron used by ancient man was from these “stones from heaven.”

The first iron extracted from the naturally occurring iron oxide deposits could have resulted from primitive man building a wood (or charcoal) fire at the base of some windswept cliff. If the cliff outcropping happened to be rich in iron oxide, after days—or even months—of use, the fire cooled and the ashes contained a small amount of iron sponge. This sponge was the iron that remained after the oxygen had been removed. The iron had not been melted during its production. Like the iron in the stones from heaven, the sponge could be hammered into shapes and was relatively strong. Spears, arrow tips, daggers, and other tools and weapons could be fabricated.

The first iron to be developed was wrought iron. Wrought iron can readily be forged to shape. In fact, the term *wrought* means “to shape by hammering or beating.” Wrought iron is very ductile for forging because it contains very little carbon (less than 0.05%). Carbon is an interstitial impurity that strengthens the iron lattice. In fact, iron alloys that contain between approximately 0.1 and 2.0 wt% C have a special name: steels.

Iron Smelting. As with the reduction of copper sulfide ores, the first reduction of iron oxide was probably accidental. It was the powers of observation that led these ancient metallurgists (who also served as the miners, chemists, and technologists of their day) to realize that iron could be produced in simple furnaces by direct carbon reduction of the oxide ore. The exact date of this first intentional reduction of iron cannot be established, but it is certain that the making and shaping of iron was widespread in Egypt by 1500 B.C. For the next 3000 years, techniques for the production of iron did not significantly change. Iron sponge was produced by carbon reduction of the oxides; iron products were made by pounding the sponge.

Iron oxide ores are present in many areas of the earth. Thus, roughly at the same time ancient man was reducing iron ores in Egypt, it also was being done in other areas. China, India, Africa, and Malaya served as sites for this initial development of ironmaking practices. It is perhaps significant that the furnaces developed in these countries were all quite similar. There were differences in shape and size, but the fur-

naces were functionally identical. The chemical reduction to iron occurred without melting, and the resulting metal was relatively pure and soft. It could be hammered into useful shapes and was termed wrought iron.

Unlike the reduction of copper sulfide ores, field smelting of iron is not practical because higher temperatures and a more carefully controlled environment are needed. Smelting of iron oxides requires some carbon or carbon monoxide to react with the iron oxide to produce iron and carbon dioxide. Iron smelting, therefore, must use carbon in the form of charcoal or coke, for two purposes. The carbon must react with oxygen or burn to supply the heat necessary for the smelting operation. In this case, the carbon is serving as a fuel. However, the carbon also serves as a reducing or reacting agent to free the iron from the iron oxide. The carbon reacts with the iron ore, forming carbon dioxide and iron. Early iron smelting operations were conducted in chimney furnaces, such as the one illustrated in Fig. 4.3. These furnaces could easily have been developed after the first accidental reduction of iron oxide.

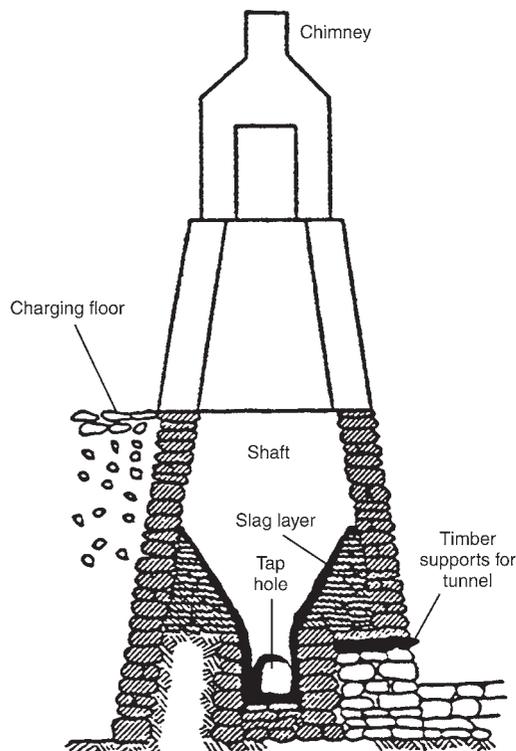


Fig. 4.3 Early American chimney or blast furnace

Improved blast furnace designs enabled higher temperatures to be reached until the temperature exceeded the melting point of the iron. The molten iron dissolved carbon and other impurities, which was not the case in the production of sponge and wrought iron. The product from the furnaces that melted the iron was called pig iron. Typical pig iron compositions are given in Table 4.3. The raw material used in the production of pig iron also differed from the raw materials used for wrought iron. Instead of iron ore and wood, iron ore, coke (made from coal), and a flux (usually limestone) were used. The limestone aided in the formation of slag that floated on top of the iron and removed impurities from the molten iron. Because of the blast of air that was forced through the furnace, the furnaces became known as blast furnaces.

The use of blast furnaces greatly increased the rate at which iron could be produced. A schematic of a blast furnace is shown in Fig. 4.4. In such a furnace approximately two units of iron ore, one unit of coke, one-half unit of limestone, and four units of air (the blast) are required for each unit of pig iron produced. The smelting process in a blast furnace begins when the charge of ore, coke, and limestone is loaded into the top.

The temperatures in a blast furnace are approximately 150 to 200 °C (300 to 400 °F) because of a rising stream of hot carbon monoxide that results from combustion (burning) of the coke. At this temperature, the carbon monoxide begins to react with the iron ore to free some of the iron. At the same time, some of the carbon monoxide is cooled by the charge and forms carbon dioxide and free carbon. This free carbon is the soot that darkened the skies over iron-producing cities from the 16th through the mid-20th century. Removal of this soot from the rising blast is difficult and represents an ever-present problem common to the production of metals from their ores.

The control of production practices to produce high-quality products without the contamination of the environment is a relatively modern

innovation. Environmental contamination was not considered a problem until recently. However, the production of soot was well known, as illustrated in Fig. 4.5, which is a drawing of an early version of the blast furnace. This drawing appeared in Georgius Agricola's book *De Re Metallica*, which was prepared in 1556 and translated from Latin into English by Herbert Hoover and his wife Lou Henry Hoover.

The pig iron produced in blast furnaces has the advantage of being rapidly produced, but pig iron is very hard and brittle due to high levels of carbon (Table 4.3). Wrought iron is ductile and tough but has little strength, while pig iron is strong but brittle and lacks the toughness to withstand sudden blows without breaking. In fact, the cast bar of a pig iron sword would shatter if it was hit against a tree. The reason for this difference in behavior is mainly due to the potent strengthening effects of carbon in iron.

Wrought iron is highly refined metallic iron that contains minute, relatively uniformly dis-

Table 4.3 Chemical composition of typical pig iron

Carbon, %	3.50–4.25
Silicon, %	1.25–2.0
Manganese, %	0.90–2.50
Sulfur, %	0.04
Iron, % (by difference)	94.25–88.96

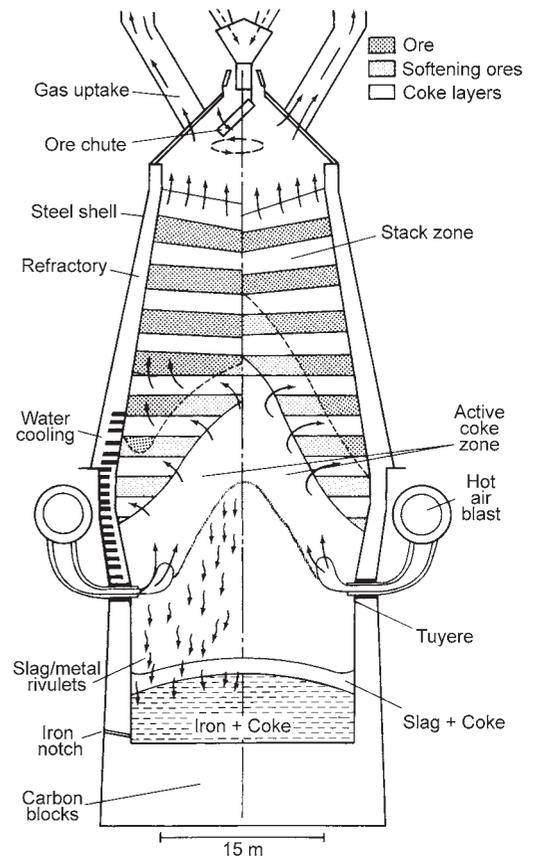


Fig. 4.4 Schematic of a blast furnace

tributed insoluble nonmetallic particles. Typical distribution of these particles in a section of wrought iron is shown in Fig. 4.6. The individual particles are termed inclusions. When inclu-

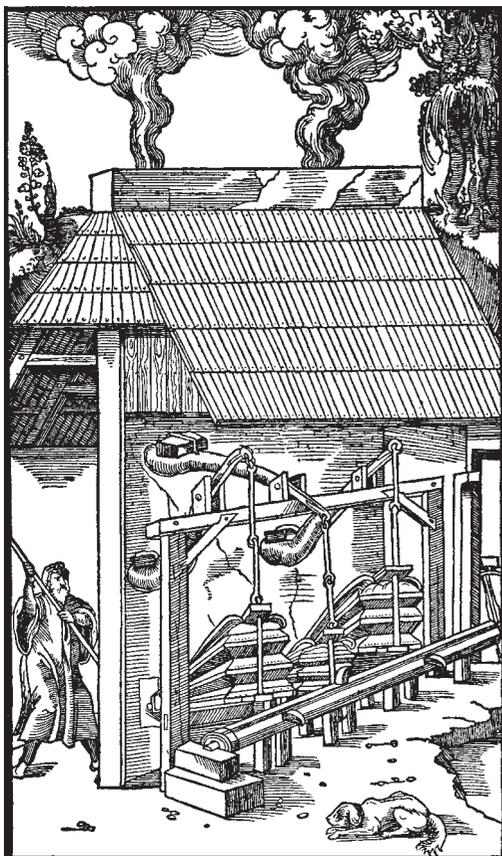


Fig. 4.5 Sketch from *De Re Metallica* showing soot emissions from a medieval blast furnace

sions are aligned in the direction of metal flow during hammering as shown in Fig. 4.6, the groupings of inclusions are designated as stringers. Although approximately 1 to 4% of the volume of any wrought iron sample is inclusions, a typical chemical analysis of wrought iron shows the presence of very little carbon, silicon, and other elements found in pig iron (Table 4.3).

Unlike wrought irons, the lack of purity (i.e., high carbon content) in pig iron makes it hard and brittle. This brittleness makes pig iron difficult to shape by hammering or forging techniques. However, pig iron can be cast. In fact, carbon levels of pig iron (Table 4.3) approach the eutectic point of 4.30 wt% C in the iron-carbon system (see the iron-carbon phase diagram in Chapter 9, “Heat Treatment of Steel,” in this book). In the iron-carbon system, the eutectic composition (4.30 wt% C) results in a melting point of 1140 °C. This is much lower than the melting point of pure iron. As described in Chapter 2, “Structure of Metals and Alloys,” in this book, eutectic compositions offer the advantage of complete melting at lower temperatures and rapid solidification (without a mushy zone).

Steels, which are irons containing between approximately 0.1 and 2% C, combine the toughness of wrought iron with the strength of pig iron. Steels can be made from wrought iron by heating the iron for a long period of time in a red hot charcoal fire. The hot iron absorbs carbon from the charcoal, so that carbon atoms diffuse into the iron lattice. The result is an iron-carbon solid-solution alloy that we know as steel. The increase in carbon also provides other advantages in the strengthening of steel when it

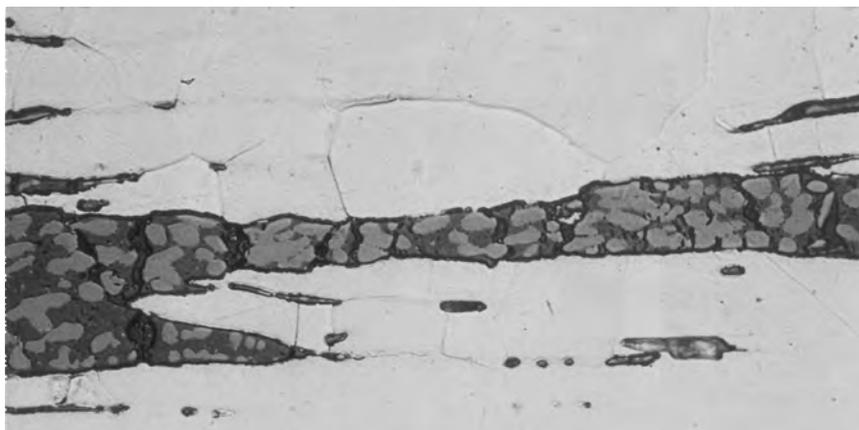


Fig. 4.6 Micrograph showing typical slag inclusions in wrought iron. Original magnification: 500×

is quenched from elevated temperatures. The Hittites played a major role in the early development of steel, and by the time of the writing of *The Odyssey*, heat treatment of steel was well known to the Greeks. The blinding of Polyphemus by Odysseus was described, “As when the smith plunges the hissing blade deep in cold water [whence the strength of steel], so hissed his eye around the olive wood.”

The development of steel into a material of common use was critical to history. For example, the Celtic invasion of Italy in 223 B.C. was unsuccessful partially because of the poor quality of Celtic weapons. The Romans had steel; the Celts had iron. The iron swords and daggers easily bent, and although one man might be killed or injured if the first blow was successful, it was difficult to fight with swords that had to be straightened between blows. The nation without steel was therefore not equipped to fight a nation with steel. Therefore, the possession of steel shaped the development of nations.

4.5 Discovery of Modern Metals

The use of the Latin “-um” suffix in naming of metals (such as beryllium) is typical of the suffix on all metals discovered or isolated after 1800. Many of these “-um” metals have tremendous commercial importance, primarily because of their use as alloying elements. Alloying elements are generally added to improve the mechanical, electrical, or chemical properties of other metals in a fashion similar to the addition of tin to copper to improve strength. Some of the commercial uses of several of the “-um” metals are described subsequently.

Beryllium (Be) is added to copper to improve its strength. The mechanism or process by which beryllium increases the strength of copper is very different than the strengthening that results by tin or zinc additions to copper. (Zinc additions to copper produce brasses). The copper-beryllium alloys contain only a small amount of beryllium (approximately 2%), but can be processed or heat treated to be much stronger than any low tin-brass or copper-zinc alloy. These very high-strength copper alloys are used for the production of springs in the electrical industry and to make nonsparking tools for use in potentially explosive atmospheres.

Cadmium was discovered in 1817 and is primarily found in zinc ores. Cadmium coatings or platings were used to protect nuts, bolts, and

other components made of high-strength steels or other relatively corrosion-prone metals. The cadmium plating acts much like some paints and limits the access of the environment to the protected component. Many of the components in commercial aircraft are “cad” plated. Cadmium is also an addition for some dental alloys because it increases the strength of the filling. The increase in strength improves the wear resistance of the filling and prolongs its life expectancy. However, cadmium has adverse environmental consequences, and efforts to replace cadmium with an equally effective coating are ongoing.

Chromium was discovered in 1798 and is used mainly as an alloy addition in steel production. Chromium improves the resistance of steels to oxidation and corrosion and is an essential ingredient in stainless steels. Corrosion would severely limit the utility of the steels if chromium was not added. Stainless steels contain up to 30% Cr, and although the primary function of chromium additions is to improve the corrosion or chemical behavior, chromium in small quantities improves the strength of alloy steels.

Molybdenum was discovered in 1781 and is primarily used as an alloy addition to steels. However, molybdenum melts at 2620 °C (4750 °F), compared to 1535 °C (2795 °F) for iron. This difference in melting temperature complicates combining the two metals into an alloy. Because of this high melting point, molybdenum, along with tungsten and rhenium, is called a refractory metal. The term *refractory* generally applies to a wide range of ceramic materials made of SiO₂, Al₂O₃, and other high-melting-point compounds. The refractory metals are not compounds, but have relatively high melting points. Because of its high melting temperature, molybdenum is used in the manufacture of high-temperature heating elements and furnace trays. Work to develop molybdenum alloys for gas turbine applications is one of many studies designed to obtain metals and alloys for very high-temperature applications.

Tungsten was first refined from ore in 1783 and was originally called wolframium. Tungsten was first used as the filament for the incandescent light bulb, and this use accounts for 15 to 20% of all tungsten use. The major use of tungsten today is in the form of tungsten carbide, which is a very hard, wear-resistant material. Carbide-tipped drills and machine tool inserts account for 65 to 70% of all tungsten use and are found throughout the home and indus-

try. It is interesting to note that tungsten, which is a very brittle, high-strength material at room temperature, can be fabricated into the fine wires required for light bulbs.

Vanadium is among the hardest of all relatively pure metals. It was discovered in 1830 and is actually more abundant than copper, nickel, or zinc but is very difficult to purify. Vanadium is primarily used as an alloy addition to steels for the manufacture of woodworking and metalworking tools.

Magnesium is the lightest of the widely used structural metals. Magnesium is more than one-third lighter than aluminum, having a density of 1.7 g/cm^3 compared to the 2.7 g/cm^3 density of aluminum. Because of its low density, magnesium has been used in aircraft frames. It is also an important alloying element in aluminum. Magnesium, however, can ignite very readily when finely divided and is actually used in flares and other pyrotechnic devices. Like many other metals, magnesium is rarely used for structures in its pure form but becomes a useful structural material when alloyed with aluminum, manganese, or zinc.

Titanium was discovered about 1790, but because of the difficulty of freeing titanium from oxygen and nitrogen, it was not readily available as a structural material until the 1940s. Titanium is difficult to process and to shape, but has both a high strength and a low density. This gives titanium the desirable property of having a high strength-to-weight ratio. It is the strength-to-weight ratio that makes titanium alloys desirable for aircraft and spacecraft applications. Because of its natural corrosion resistance, titanium is also used in the chemical process industry and for orthopedic implants.

Iridium, rhodium, palladium, and platinum are, along with gold, termed the precious metals. They are all very dense and very corrosion resistant. However, the term *precious metals* comes from the fact that all these metals are expensive. Because of this expense, the precious metals are used as catalysts and for applications that typically call for small quantities of material. Pen points, electrical connectors, dentistry, and pivot points in fine balances are examples of uses of precious metals. Platinum-iridium alloys are very resistant to food acids and are useful in dental restorations.

Aluminum, the third most abundant element on the face of the earth, is a member of the family of metals that includes gallium, indium, and thallium. Aluminum was not discovered until

1825, and when very pure, aluminum—like copper, gold, and silver—is too soft to be of much value as a structural material. However, commercially pure aluminum and aluminum alloyed with copper, silicon, magnesium, zinc, and other metals, have many industrial applications and are second to steel in volume of material produced commercially.

Most aluminum is extracted from its ores by electrometallurgy. Because electrical energy is required for this type of extraction, it is common for aluminum production plants to be located in areas where electricity is inexpensive. Hence, many aluminum production plants in North America are located in the regions having less expensive hydroelectric power (e.g., the Tennessee Valley Authority region, Pacific Northwest, and Quebec), even though high-quality aluminum ores are not common in that area. It is less expensive to transport the ore to the source of the energy than to transport the electricity to the source of the ore.

4.6 Refining of Metals

Refining of metals refers to processes that purify extracted metal. Refining of metals, like the extraction of metals from ores, includes many ancient practices and more modern advances. For example, gold always occurs in the metallic state, and it can be “extracted” from minerals by relatively simple means. That is, panning and sluicing for gold effectively separates the gold from minerals (such as sand or gravel) because the density of gold (19.3 g/cm^3) is much higher than that of minerals. For example, the quartz in sand has a density of approximately 3.2 g/cm^3 . Panning and sluicing with water washes away light sediments from gold nuggets or flakes.

However, the remaining gold flakes or nuggets are not necessarily pure. Further purification steps may be needed. Gold refining is the relatively simple process of heating the gold to a very elevated temperature. At these high temperatures, most of the impurities in the gold react with oxygen in the air to form metal oxides. Some of the oxides formed by such reactions are gaseous and, therefore, carried away by the surrounding air. Other oxides are not gaseous, but the reactions to form these oxides produces relatively low-density compounds that float on molten gold as a slag or dross. The slag floats on gold in much the same manner as wood floats on water. Therefore, gold can be

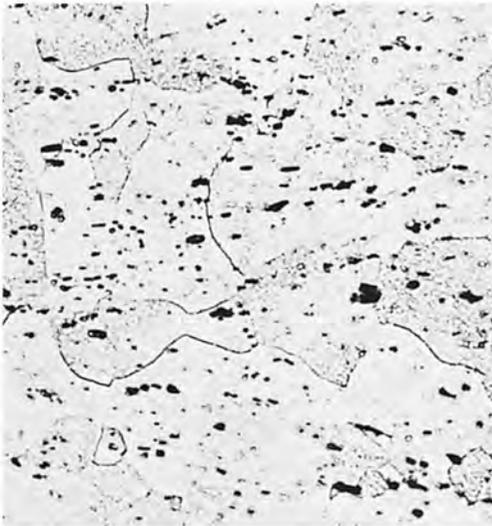
refined by simply scraping the floating debris from the pool of molten metal. This technique for refining gold was known by the period 2000 to 1000 B.C.

Refining techniques for most metals are much more complicated but involve similar phenomena. Many techniques now used were not developed until quite recent times. Today, refining can be used to produce very pure metals. Copper, gold, silver, aluminum, iron, and many other metals can be purchased at purity levels of

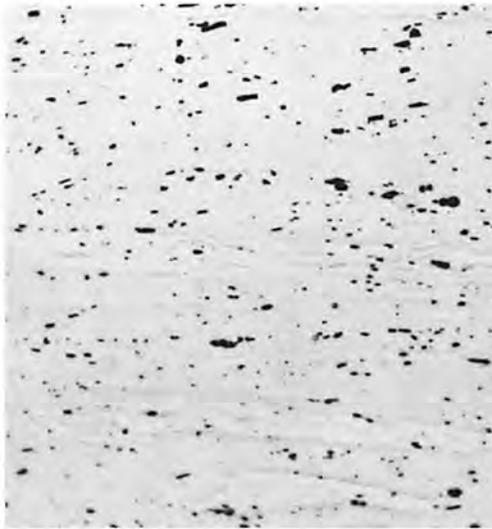
99.999+%—which is equivalent to 1 part impurity in a million.

Clearly, modern refining practices are excellent, and metals and alloys that are virtually free of unwanted elements can now be obtained. Unfortunately, such purification is typically expensive, and most engineering alloys contain significant quantities of impurity atoms. This can be readily seen in a micrograph of commercially pure aluminum (99+% pure) at 500 \times magnification (Fig. 4.7). The dark particles in the micrograph are concentrations of impurity compounds, in this case Al_2O_3 . These impurity concentrations or particles are similar to the inclusions or stringers in wrought iron.

Although very high-purity metals are typically too soft for structural applications, the small amount of impurities in some commercially pure metals imparts adequate strength for some structural applications. For example, commercial heat exchangers for certain applications are made of commercially pure titanium (Fig. 4.8). Although titanium is characterized by a somewhat low thermal conductivity (compared to that of other metals such as copper-base alloys), the major design factor in heat transfer relates to material thickness, corrosion resistance, and surface films—not just to the thermal conductivity of the metal. For these reasons, commercially pure titanium can have advantages over other metals in the design of heat exchangers. It offers good strength, resistance to erosion and erosion-corrosion, a very thin, conductive oxide surface film, and a hard, smooth surface that limits adhesion of foreign materials and promotes drop-wise condensation.



(a)



(b)

Fig. 4.7 Micrograph of nonmetallic inclusions in typical, commercially pure aluminum. Original magnification: 500 \times . (a) Annealed structure. (b) Cold worked structure

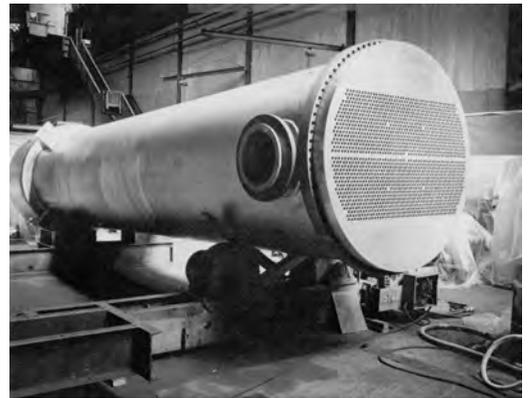


Fig. 4.8 Titanium heat exchanger using several grades of commercially pure titanium (ASTM grades 2, 7, and 12). Courtesy of Joseph Oat Corporation

Very high-purity metals (99.999+% pure) are often too soft for any type of structural application. For example, gold that is 99.999+% pure is not practical—even for use as chains or pins in jewelry. However, some modern materials specifications require exceptional refining techniques. Silicon (as well as germanium and other metals) used in the semiconductor industry must be produced at controlled purity levels equal to and exceeding less than one impurity atom for every million atoms of pure element. Such high purity is needed when strength is less important than other properties such as electrical conductivity. In the transistor industry it is now common to be concerned about both alloy additions (elements added on purpose) and impurity levels (elements whose removal is desirable) at concentration levels of one part per billion. That concentration level is 0.0000001%.

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