ME & MA

A SHORT HISTORY OF METALS

Process Metallurgy is one of the oldest applied sciences. Its history can be traced back to 6000 BC. Admittedly, its form at that time was rudimentary, but, to gain a perspective in Process Metallurgy, it is worthwhile to spend a little time studying the initiation of mankind's association with metals. Currently there are 86 known metals. Before the 19th century only 24 of these metals had been discovered and, of these 24 metals, 12 were discovered in the 18th century. Therefore, from the discovery of the first metals - **gold and copper** until the end of the 17th century, some 7700 years, only 12 metals were known. Four of these metals, **arsenic, antimony, zinc and bismuth** were discovered in the thirteenth and fourteenth centuries, while **platinum** was discovered in the 16th century. The other seven metals, known as the Metals of Antiquity, were the metals upon which civilisation was based. These seven metals were:

(1) Gold (ca) 6000BC

(2) Copper, (ca) 4200BC

(3) Silver, (ca) 4000BC

(4) Lead, (ca) 3500BC

(5) Tin, (ca) 1750BC

(6) Iron, smelted, (ca) 1500BC

(7) Mercury, (ca) 750BC

These metals were known to the Mesopotamians, Egyptians, Greeks and the Romans. Of the seven metals, five can be found in their native states, e.g., gold, silver, copper, iron (from meteors) and mercury. However, the occurrence of these metals was not abundant and the first two metals to be used widely were gold and copper. And, of course, the history of metals is closely linked to that of coins and gemstones.

Gold

Gold articles are found extensively in antiquity mainly as jewelry e.g. Bracelets, rings etc. Early gold artifacts are rarely pure and most contain significant silver contents. This led to the ancients naming another metal - electrum, which was an alloy of gold and silver, pale yellow and similar in color to amber. Therefore, early gold varied from pure through electrum to white gold. The symbol for gold is Au from the latin aurum meaning shining dawn.

Stone age man learned to fashion gold into jewelry and ornaments, learning that it could be formed into sheets and wires easily. However, its malleability, which allows it to be formed into very thin sheet (0.000005 inches), ensures that it has no utilitarian value and early uses were only decorative. As gold is a noble metal, being virtually noncorrosive and tarnish free, it served this purpose admirably.

Gold is widely dispersed through the earth's crust and is found in two types of deposits: lode deposits, which are found in solid rock and are mined using conventional mining techniques, and placer deposits which are gravelly deposits found in stream beds and are the products of eroding lode deposits. Since gold is found uncombined in nature, early goldsmiths would collect small nuggets of gold from stream beds etc., and then weld them together by hammering.

Thus we find the first problem in process metallurgy: The metal deposit must be identified. In the case of the first metals color was the most important factor as it allowed the metal to be recognized in surrounding rock, stones, gravel and dirt (gangue) and separated. Clearly, after recognition, separation is next problem followed by concentration. These three steps are very important and the economics of these steps usually define whether it is viable to produce the metal from a set deposit. In the early days all three steps were carried out simultaneously. Gold is widely dispersed throughout the earths crust (0.005 ppm) at a very small level, therefore, it is very important to find naturally occurring concentrations. The scarcity of gold and its value, due to mankinds fascination with its color, have lead to gold being the one of the more important metals in daily life.

Copper

The use of copper in antiquity is of more significance than gold as the first tools, implements and weapons were made from copper. From 4,000 to 6,000 BC was the Chalcolithic period which was when copper came into common use. The symbol for copper is Cu and comes from the latin cuprum meaning from the island of Cyprus. Initially copper was chipped into small pieces from the main mass. The small pieces were hammered and ground in a manner similar to the techniques used for bones and stones. However, when copper was hammered it became brittle and would easily break. The solution to this problem was to anneal the copper. This discovery was probably made when pieces were dropped in camp fires and then hammered. By 5,000 BC copper sheet was being made.

By 3600 BC the first copper smelted artifacts were found in the Nile valley and copper rings, bracelets, chisels were found. By 3000 BC weapons, tools etc. were widely found. Tools and weapons of utilitarian value were now within society, however, only kings and royalty had such tools; it would take another 500 years before they reached the peasants.

Malachite, a green friable stone, was the source of copper in the early smelters. Originally it was thought that the smelting of copper was by chance dropping of malachite into campfires. However, campfire temperatures are normally in the region of 600-650 C, whereas, 700-800 C is necessary for reduction. It is more probable that early copper smelting was discovered by ancient potters whose clay firing furnaces could reach temperatures of 1100-1200 C. If Malachite was added to these furnaces copper nodules would easily be found. Although the first smelted copper was found in the Nile valley, it is thought that this copper was brought to Egypt by the Gerzeans and copper smelting was produced first in Western Asia between 4000 and 4300 BC.

Although copper can be found free in nature the most important sources are the minerals cuprite, malachite, azurite, chalcopyrite and bornite. Copper is reddish colored, malleable, ductile and a good conductor of heat and electricity. Approximately 90% 0f the worlds primary copper originates in sulfide ores.

Lead

Lead is not found free in nature but Galena (lead sulfide) was used as an eye paint by the ancient Egyptians. Galena has a very metallic looking appearance and was, therefore, likely to attract the attention of early metalworkers. The production of metallic lead from its ore is relatively easy and could have been produced by reduction of Galena in a camp fire. The melting point of lead is 327 C, therefore, it would easily flow to the lowest point in the fireplace and collect. At first lead was not used widely because it was too ductile and the first uses of lead were around 3500 B.C.. Lead's use as a container and conduit was important and lead pipes bearing the insignia of Roman emperors can still be found. Lead is highly malleable, ductile and noncorrosive making it an excellent piping material. Its symbol is Pb from the latin plumbum.

The ability of lead to flow and collect at the bottom of the campfire is an important concept in process metallurgy as reduction reactions to be useful must cause a phase separation between the metal and the gangue. Also, the phase separation should also enable the metal to be cast into a desired shape once concentrated.

Silver

Although silver was found freely in nature, its occurrence was rare. Silver is the most chemically active of the noble metals, is harder than gold but softer than copper. It ranks second in ductility and malleability to gold. It is normally stable in pure air and water but tarnishes when exposed to ozone, hydrogen sulfide or sulfur. Due to its softness, pure silver was used for ornaments, jewelry and as a measure of wealth. In a manner similar to gold, native silver can easily be formed. Silver's symbol is Ag from the latin argentum.

Galena always contains a small amount of silver and it was found that if the lead was oxidized into a powdery ash a droplet of silver was left behind. Another development in this process was the discovery that if bone ash was added to the lead oxide, the lead oxide would be adsorbed and a large amount of material could be processed. By 2500 BC the cupellation process was the normal mode of silver manufacture.

Tin

Smelted copper was rarely pure, in fact, it is clear that by 2500 BC the Sumerians had recognized that if different ores were blended together in the smelting process, a different type of copper, which flowed more easily, was stronger after forming and was easy to cast, could be made. An axe head from 2500 BC revealed that it contained

11% tin and 89% copper. This was of course the discovery of @b(Bronze). However, by 2000 BC copper implements contained very little tin as local reserves of tin had been exhausted. The Sumerians were forced to travel to find the necessary ores. Bronze was a much more useful alloy than copper as farm implements and

weapons could be made from it, however, it needed the discovery of tin to become the alloy of choice.

Native Tin is not found in nature. The first tin artifacts date back to 2000 B.C., however, it was not until 1800 B.C. that tin smelting became common in western Asia. Tin was reduced by charcoal and at first was thought to be a form of lead. The Romans referred to both tin and lead as plumbum where lead was plumbum nigrum and tin was plumbum candidum. Tin was rarely used on its own and was most commonly alloyed to copper to form bronze. The most common form of tin ore is the oxide casserite. By 1400 BC. bronze was the predominant metal alloy. Tin's symbol is Sn from the stannum.

Tin is highly malleable and ductile and has two allotropic forms which lead to tin initially having its own disease (tin pest or blight) which was actually formation of alpha-tin below 13 C. As alpha-tin is a highly friable cubic structure with a greater specific volume than beta-tin, during the phase change, which is kinetically limited, nodules of alpha-tin become visible on the surface of beta-tin giving rise to early belief of sickness and the first true doctors of metallurgy. Tin is highly crystalline and during deformation is subject to mechanical twinning and an audible tin cry. Tin is also quite resistant to corrosion.

Tin is found as vein tin or stream tin. The tin ore is stannic oxide and is generally found with quartz, feldspar or mica. The ore is a hard , heavy and inert substance and is generally found as outcroppings as softer impurities are washed away.

Mercury

Mercury was also known to the ancients and has been found in tombs dating back to 1500 and 1600 BC. Pliny, the Roman chronicler, outlined purification techniques by squeezing it through leather and also noted that it was poisonous. Mercury, also known as quicksilver, is the only metal which is liquid at room temperature. Although it can be found in its native state, it is more commonly found in such ores as calomel, livingstonite, corderite and its sulfide cinnabar. Extraction is most simply carried out by distillation as mercury compounds decompose at moderate temperatures and volatilize.

Mercury was widely used because of its ability to dissolve silver and gold (amalgamation) and was the basis of many plating technologies. There is also indications that it was prized and perhaps worshipped by the Egyptians. In 315 B.C., Dioscorides mentions recovery of quicksilver (which he called hydrargyros, liquid silver) by distillation, stating " *An iron bowl containing cinnabar is put into an earthenware container and sealed with clay. It is then set on a fire and the soot which sticks to the cover is quicksilver*". Methods changed little until the 18th century. Mercury's symbol is Hg from hydragyrum, liquid silver.

Iron

Iron was available to the ancients in small amounts from meteors. This native iron is easily distinguishable because it contains 6-8% nickel. There is some indication that man-made iron was available as early as 2500 B.C., however, iron making did not become an everyday process until 1200 BC. Hematite, an oxide of iron, was widely used by the ancients for beads and ornaments. It is also readily reduced by carbon. However, if reduced at temperatures below 700-800 C it is not suitable for forging and must be produced at temperatures above 1100 C. Wrought iron was the first form of iron known to man. The product of reaction was a spongy mass of iron intermixed with slag. This was then reheated and hammered to expel the slag and then forged into the desired shape. In the early days iron was 5 times more expensive then gold and its first uses were as ornaments.

Iron weapons revolutionized warfare and iron implements did the same for farming. Iron and steel was the building block for civilization. Interestingly, an iron pillar dating to 400 A.D., remains standing today in Delhi, India. Corrosion to the pillar has been minimal a skill lost to current ironworkers. Iron is rarely found in its native state the only known sources being Greenland where the iron occurs as nodules in basalt that erupted through beds of coal and two very rare nickel-iron alloys. Iron's symbol is Fe from the latin ferrum.

These seven metals: gold, silver, copper, lead, tin, mercury and iron, and the alloys bronze and electrum were the starting point of metallurgy and even in this simple, historic account we find some of the basic problems of process metallurgy. The problems are:

The ores must be found, separated and sized before use.

The ores must be reacted under a controlled temperature and gas atmosphere.

The liquid metal must be collected and cast into a desired shape.

The metal must be worked to achieve desired final properties and shape.

After the seven metals of antiquity: **gold, silver, copper, mercury, tin , iron and lead**, the next metal to be discovered was **Arsenic** in the 13th century by Albertus Magnus. Arsenicus (arsenious oxide) when heated with twice its weight of soap became metallic. By 1641 arsenious oxide was being reduced by charcoal. Arsenic is steel gray, very brittle and crystalline; it tarnishes in air and when heated rapidly forms arsenious oxide with the odor of garlic. Arsenic compounds are poisonous. The symbol As is taken from the latin arsenicum. Arsenic was used in bronzing and improving the sphericity of shot. The most common mineral is Mispickel or Arsenopyrite (FeSAs) from which arsenic sublimes upon heating.

The next metal to be isolated was **antimony**. Stibium or antimony sulphide was roasted in an iron pot to form antimony. Agricola reported this technique in 1560. Antimony whose name comes from the Greek "anti plus monos"- a metal not found alone, has as its symbol Sb from the latin stibium. It is an extremely brittle flaky metal. Antimony and its compounds are highly toxic. Initial uses were as an alloy for lead as it increased hardness. Stibnite is the most common ore. It was commonly roasted to form the oxide and reduced by carbon.

By 1595,**bismuth** was produced by reduction of the oxide with carbon , however, it was not until 1753 when bismuth was classified as an element. **Zinc** was known to the Chinese in 1400; however , it was not until 1738 , when William Champion patented the zinc distillation process, that zinc came into common use. Before Champion's process, zinc, which was imported from China, was known as Indian Tin or Pewter. A Chinese text from 1637 stated the method of production was to heat a mixture of calamine (zinc oxide) and charcoal in an earthenware pot . The zinc was recovered as an incrustation on the inside of the pot. In 1781 zinc was added to liquid copper to make brass. This method of brass manufacture soon became dominant.

One other metal was discovered in the 1500's in Mexico by the Spaniards. This metal was **platinum**. Although not 100% pure, it was the first metal to be discovered and sourced from the "New World". The property which brought this metal to the prospectors attention was its lack of reactivity with known reagents. Early use of platinum was banned because it was used as a blank for coins which were subsequently gold coated, proving that the early metallurgists understood not only density but also economics. Although, platinum was known to the western world, it was not until the 1800's that platinum became widely used.

Several other metals were isolated during the 1700's. These were **Cobalt, Nickel, Manganese, Molybdenum, Tungsten, Tellurium, Beryllium , Chromium, Uranium, Zirconium and Yttrium** . Only laboratory specimens were produced and all were reduced by carbon with the exception of tungsten which became the first metal to be reduced by hydrogen.

Therefore, before 1800 there were 12 metals in common use:

Gold	**Mercury**	**Antimony**
Silver	**Iron**	**Bismuth**
Copper	**Tin**	**Zinc**
Lead	**Platinum**	**Arsenic**

Before 1805 all metals were reduced by either carbon or hydrogen, however, the majority of the metals once smelted were not pure. Refining of gold, which is the separation of silver from gold, has a very old history. During the second millennium it is clear that an amalgamation process using molten lead was used to separate the metal from crushed quartz. The lead then being cupelled to separate the gold and the silver. Purification was then carried further (but not until the first millennium) by a cementing process where a mixture of the alloy was closely mixed with common salt. The silver reacted, formed a chloride which was soluble and easily rinsed off. The cementation process was used until about 1100 A.D. when other refining processes became popular. One method used sulphur addition to the molten bullion to form silver sulfide which was removed as "black" during gentle beating. Mineral acids were developed by the alchemists. Nitric acid was used to dissolve silver in the 1200's as a purification technique. By the end of the 15th century, Stibium (antimony sulfide) was also used in the cementation process. Generally, a mixture of salt, stibium and sulphur was heated with the gold foil.

Gold plating of silver was very popular and in 1250 Bartholommeus Anglicus gave the following advice:

"And when a plate of gold shall be melded with a plate of silver, or joined there to, it needeth to beware namely of three things, of powder, of winde and of moisture: for if any hereof come between gold and silver, they may not be joined together,then one with another: and therefore it needeth to meddle these two metals together in a full cleane place and quiet and when they be joined in this manner, the joining is inseparable, so that they may not afterward be departed asunder,"

This advice is good today. Amalgamation processes were also popular. The gold was dissolved in mercury. The amalgam was coated onto the piece and then heated to drive off the mercury leaving a gold coated piece. Gold could also be removed by the reverse process (1567).

Before 1807 all metals which had been separated had been reduced by either carbon or hydrogen. The separation of other metals needed the invention of the galvanic cell. Sir Humphrey Davy used the generating pile developed by Volta and demonstrated that water could be decomposed into hydrogen and oxygen . Next he tried a solution containing potash and again gained hydrogen and oxygen. Then he tried a piece of moistened potash which produced at the negative electrode something that burned brightly. His next experiment was decisive, he placed the potash on an insulated platinum dish which was connected to the negative pole of the battery. He then connected the positive pole to the upper surface of the potash and produced small metallic globules. In this manner he produced **potassium and sodium**.

The Swedish chemist , Berzelius, found that the metals contained in lime and baryta (barium oxide) could also be separated in this way. He used mercury as a cathode which caused the separated metals to dissolve in the mercury. After electrolysis the mercury was distilled away and **Calcium and Barium** were left behind. Later, Davy produced **Strontium** by the same technique. By allowing the manufacture of sodium and potassium Davy and Berzelius had opened the door to the reduction of many refractory materials.

In 1817 **Cadmium** was discovered. Stroymeyer noted that zinc carbonate had a yellowish tinge not attributable to iron. Upon reduction he thought that the alloy contained two metals. The metals were separated by fractional distillation. At 800 C, as cadmium's boiling point is lower than zinc, the cadmium distilled first.

In 1841 Charles Askin developed a method of separating cobalt and nickel when both metals are in solution. Using a quantity of bleaching powder he found that if the quantity of powder was small enough only cobalt oxide was precipitated and separated. The nickel could then be easily precipitated with lime and a source for pure cobalt and nickel was available. Pure cobalt oxide revolutionized the pottery industry as the blues were now available.

Chromium although it had been produced by reduction with carbon was the first metal to be extensively produced using another metal (zinc). Wohler in 1859 melted chromium chloride under a fused salt layer and attracted the chromium with zinc. The resulting zinc chloride dissolved in the fused salt and chromium produced.In 1828, Wohler produced beryllium by reducing beryllium chloride with potassium in a platinum crucible.

Aluminium was first produced by Christian Oersted in 1825. However it was not until 20 years later that significant quantities were produced. Wohler fused anhydrous aluminum chloride with potassium to set free aluminum. Later Ste Claire Deville in 1854 put together a production process using sodium instead of potassium.

The current from Galvanic cells were also used for electroplating. This was first practiced in the 1830's when silver was deposited on baser metals. After silver plating, copper and nickel plating was developed. In the middle of the 18th century it was found that metallic separation could be carried out by the application of galvanic electricity. The current was passed from an anode made of an impure , crude metal into a suitable electrolyte and the pure material plated out onto a resistant cathode. Impurities present in the crude cathode dropped to the bottom of the vessel and formed a sludge.

From this short review of metallurgical developments it can be seen that as the early metallurgists became more sophisticated their ability to discover and separate all the metals grew. However in all of their work it was necessary for all the basic steps to be carried out e.g. the ore had to be identified, separated from gangue, sized, concentrated and reduced in a manner which accomplished a phase separation.

Table 1: METALS DISCOVERED IN 18th CENTURY

1735 Cobalt	1782 Tellurium	1791 Titanium
1751 Nickel	1783 Tungsten	1794 Yttrium
1774 Manganese	1789 Uranium	1797 Berylium
1781 Molybdenum	1789 Zirconium	1797 Chromium

Table 2: METALS DISCOVERED IN 19th CENTURY

1801 Niobium	1823 Silicon	1875 Gallium
1802 Tantalum	1827 Aluminum	1878-1885 Holmium, Thulium, Scandium, Samarium, Gadalinium,Praseodynium, Neodynium, Dysprosium
1803 Iridium, Palladium, Rhodium	1828 Thorium	1886 Germanium
1807 Potassium, Sodium	1830 Vanadium	1898 Polonium, Radium
1808 Boron, Barium, Calcium, Magnesium, Strontium	1839 Lanthanum	1899 Actinium
1814 Cerium	1843 Erbium, Terbium	
1817 Lithium, Cadmium, Selenium	1844 Ruthenium	
	1860 Cesium, Rubidium	
	1861 Thallium	
	1863 Indium	

Table 3: METALS DISCOVERED IN THE 20th CENTURY

1901 Europium	1939 Francium	Curium
1907 Lutetium	1945 Promethium	Americum
1917 Protactinium	1940-61Transuranium elements.	Berkelium
1923 Hafnium	Neptunium	Californium
1924 Rhenium	Plutonium	Einsteinium
1937 Technetium		Fermium

Mendelevium Nobelium Lawrencium

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