Class Notes on Early Metallurgy

"The appearance of metals in everyday life coincided with the change from nomadic existence of hunting and food gathering to settlements in communities, the development of agriculture, domestication of animals, and craftwork."

What led early man to begin using metals in the first place? This was not to make better tools or weapons ("A man in search of food or a weapon is in no mood of discovery - he only exploits what is already known to exist"). He would have just improved the techniques of working with flint and obsidian.

From about 8000 to 5000 BC the development of the crafts of spinning, weaving, and working with pottery came about. These crafts gave mankind time to think. "Liberation of the human imagination provided the springboard for almost all progress towards civilization as we know it today."

Innovation and discovery arise out of curiosity. How did man first become aware of metals? It would have been a gradual process as they saw that this metal was pot like other rock, it seemed heavier, and did not crack when hammered. The first use for metals would have been for **decoration or ornaments**, rather than knives.

These would have been **native metals**. These are metals not combined with other elements in mineral ores but existing in a pure state. They would have been lying on the ground or exposed to the surface. Examples are gold, copper, and iron.

Gold had been known to the ancients for several reasons. It was soft, the same color as the sun, and it didn't tarnish or react with anything.

The first sign of copper being used is about 6000 BC. It exist both as native and in a combined state (as malachite). Copper appears to have been much more common that gold or iron. **All earliest known metal artifacts are of native copper**.

The earliest dated usage of iron appears around 4000 BC. This would have been **meteoric iron**. This special type of iron contains a high percentage of nickel which helps the iron to resist oxidation. Meteoric iron is clearly different from iron found on earth and all early iron products would have been from meteoric iron.

To get larger amounts of the metals the process of smelting the metals from ores containing the metals were developed. "The discovery of Neolithic man of how to smelt metals from ores (where they are chemically bonded to elements like sulfur, oxygen, and carbon) must stand as one of the greatest achievements in human history."

Neolithic = near end of the Stone Age

COPPER: Copper ore is called malachite. It is green with dark black bands and is made of copper, oxygen, and carbon. To smelt copper from malachite there must be two conditions met.

1) must apply heat to 1084° C (melting point of pure copper)
2) must do this in a **reducing atmosphere** (this atmosphere is rich in carbon but starved of oxygen - the process draws oxygen from the hot ore and 'reduces' the ore to molten metal)

These steps to smelting are difficult to perform. A camp fire built on outcrops of malachite or using malachite fire stones is usually not hot enough and the carbon monoxide in the air (providing the reducing atmosphere) is intermittent. However, **pottery making and smelting had similar conditions.**

Pottery: Clay is soft and easily shaped when wet but dries in the sun. If clay is fired (heated in **kiln** by stacking pots on top of fuel and covering entire arrangement) to about 450° C it undergoes a chemical change and becomes hard and waterproof. If it is heated above 1400° C. it undergoes a second change and takes on a glass like structure. The partial melting produces some glassy (vitreous) phase which bonds the still crystalline mineral particles together. This process is similar for porcelain.

Chemistry of Firing Ceramics:

$3Al_2Si_2O_5(OH)_4\ (s) \rightarrow Al_6Si_2O_{13}\ (s) + 4SiO_2\ (s) + 6H_2O\ (g)$

Kaolinite fired clay silica water vapor

During the firing water is driven off while the quartz melts. The clay crystals are fused together by the glassy silica. The coloring due glazes is due oxides absorbing some wavelengths of natural light making it appear colored.

Glass:
Glass cracks because it is a poor conductor of heat. When one side is heated the other side remains cool. As the heated side tries to expand, the glass cracks. When silica is heated above 1600° C the natural bonds of the silica break down and crystals change to a noncrystalline, amorphous, glass material called fused silica. If metal compounds are added it creates the transparent material called glass. Glass contains a flux (Na_2CO_3 sodium carbonate) that makes the glass melt more easily. It also needs a stablilizer ($CaCO_3$ which is limestone or calcium carbonate). This makes soda-lime glass (about 90% of all glass). If boron oxide is added the glass does not expand or contract significantly with changes in temperature (i.e., It will not crack when heated or cooled suddenly and thus is used in cooking applications and labware. Borosilicate glass has a high melting point but also resist changes in size both on heating and cooling, thus preventing cracking.)

The kiln could repetitively maintain a temperature in excess of 1000° C and the enclosed space creates a reducing atmosphere. Copper had been used as decoration

on pottery. By this combination of events and circumstances we believe that copper was first smelted in conjunction with pottery making.

To really improve the process of smelting copper:
1) use a more enclosed space with more concentrated reducing gases
2) bring ore closer to source of heat by mixing it with burning charcoal
(charcoal = charred wood from fire in reducing atmosphere)
3) blow air into heart of furnace to raise temperature
4) other substances (like iron ore) are added as flux which assist the reduction process and improves separation of molten copper from the melted ore called slag

Problems with copper:
1) copper was attractive and easy to work with, it was good for ornament and small tools, but **it was too soft to hold an edge**
2) by repeated hammering and reheating (annealing) it could be hardened

BRONZE: From the beginning smelted copper was *known to* contain some traces of other metals (Ag, Pb, As, Sb, Fe, Sn). The next major step was to find a way to remove the undesirable elements and increase the proportion of those that made the copper more useful.

The first metal added was arsenic - when copper with a bit of arsenic was worked by hammering it was much harder than pure copper. The bad side effects would seem to have prevented it's use but it was added to copper for many years.

The best metal to add was TIN - why: the way atoms interlock together in metallic matrix

1) the addition of tin lowered the temperature to melt copper (to 950° C)
2) the molten mixture flowed freely into mold
3) during the cooling process bubbles did not for
4) the new mixture of metals was much harder than pure copper

This new metal was called **Bronze.** By about 3000 BC fearful weapons made of this new bronze helped create the Bronze Age.

Bronze is an **alloy**. This is a mixture of 2 or more metals melted together resulting in a new metal with new and different properties. It can usually be separated can be separated back into its component metals by heating.

Later turmoil in the civilized Western world destroyed cultural and commercial centers. Trade routes were overrun and cut. This caused a collapse of the Bronze Age due to a breakdown in the availability of supplies of tin.

IRON: "Iron has changed life away from agriculture toward industry due to plentiful tools and weapons." The main reason iron did not show up in use earlier

in the Western world than about 1500 BC was that it could not be melted or cast due to its very high melting point of 1537° C.

Western approach to iron - the WROUGHT IRON METHOD: At the temperature of bellows' fires iron could be reduced to a spongy mass mixed with slag called bloom. With repeated hammering the blacksmith could drive out the slag to get a bar of almost pure iron. However, this iron had several bad properties:
1) it was softer than bronze
2) did not hold a good edge
3) it rusted

There were two ways to improve the iron:
1) **steeling**: when working with bloom the charcoal and carbon monoxide produced by the fire will diffuse into the surface; it the content of the carbon goes to 0.3% it is better than bronze, and it is excellent iron if the carbon content goes to 1.2%.

2) **tempering**: this involved two steps; a) **quenching** which is the sudden cooling of hot metal by plunging it into water which makes it harder but somewhat brittle,
b) after quenching re-heat it to about 700° C and then cool it to remove some of the brittleness and hardness.

"Because they could not heat the iron to its melting point and cast it this was to tie them to their anvils and frustrate mass production of iron goods for a thousand years."

Eastern approach to iron; The Chinese used cast iron for 2000 years before it was used in the West. They could melt iron with better furnaces due to:
1) achieved higher furnace temperatures due to
   a) **horizontal bellows** and
   b) **double acting box bellows**.
2) the burning of large amounts of **high carbon fuel** in relation to the amount of iron ore being smelted caused carbon monoxide to enter the iron and lower the melting point to about 1150° C.

These processes allowed the Chinese to **CAST** iron. In this process melted iron is poured into molds. Cast iron is more brittle and must be made malleable. To do this heat the cast iron object between 800 and 900° C in the presence of air. The oxygen removes some carbon from the surface which reduces some of the brittleness and forms a tough skin on the casting. Casting was found to be much easier to form original shapes.

Gold and lead also had great influences on early metallurgy.

Notes taken from "Out of the Fiery Furnace - The Impact of Metals on the History of Mankind" by Robert Raymond. The Pennsylvania State University Press - 1984

Review Guide for Metallurgy

The format for this assignment: typed or handwritten is fine, answer each question in complete sentences, skip a minimum of 2 lines (double double space) between each answer, and only use the front of paper (nothing on the back of paper).

Question #1 sample answer:

The four major changes in society as man left the Neolithic age were settlement in communities, domestication of animals, development of agriculture, and craftwork.

1. What four major changes occurred in society as Neolithic man left the Stone Age?

2. What steps must be taken to make a cast metallic object useful (i.e., what must be done immediately after removing the object from the mold?)

3. What modifications did the Chinese make in metal working to allow them to cast metals?

4. Before any metal can be smelted from its ore two conditions must be established. Discuss the equipment and conditions necessary for smelting to occur.

5. Compare pottery making with the production of glass.

6. To improve the process of copper smelting 4 ideas were presented. List several of those.

7. The wrought iron process of metal working involved both steeling and tempering. Discuss each process in terms of how it makes iron becomes a more useful product.

8. Alloys are mixtures of metals melted together. Describe why the addition of tin to copper is so beneficial.

9. Describe why the Bronze Age came to such an early end.

10. Tell why the theory of camp fires first smelting copper is not valid?

11. Explain what our society might have been like had we not so fully developed the use metals or had our planet not been so rich in easily obtainable metals.

12. The growth of our civilization has coincided with our ability to create hotter and hotter fires. Explain how this is so. This question will require research.