# REMOVAL OF IMPURITIES FROM COPPER AND ITS ALLOYS USING ANCIENT REFINING TECHNIQUES

by

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# ABSTRACT

There were two major objectives of this study both related to purification of impure copper metal using primitive refining techniques believed to have been used in antiquity.

First part of the study was to remove iron impurity from bronze that is introduced when iron containing tin (hard-head) is used as source of tin. In the second part, simple refining methods are applied to highly impure copper metal obtained by smelting polymetallic copper ores.

“Hard-head” which is a mixture of iron-tin compounds are biproduct of tin smelting process where cassiterite is contaminated with iron ores. It was not possible to remove all of the tin held in hard-head and some tin is inevitably lost.

Hard-head prills were prepared composed of 20 per cent iron and 80 per cent tin under controlled conditions, in clay crucibles. The hard-head prills were then added onto the molten copper metal in the muffle furnace at 1200 °C. Since all compositions of Sn-Fe

compounds decompose at 1200 °C and Cu and Fe does not make an alloy, tin is expected to be extracted by copper while rejecting the iron from the medium. The iron was then oxidized selectively either by the addition of natural fluxes (powdered marble and sand) or by fire-refining method.

Experiments were carried out and it showed that, under addition of suitable fluxes, it was possible to remove over 85 per cent iron present in hard-head, leaving the concentration of iron in bronze under 0.5 per cent. The loss of tin, however was less than 20 per cent. It is concluded that unrefinable hard-head can be economically used in the production of bronze.

Most primary copper ores are polymetallic in character and contains iron, lead, arsenic, nickel, antimony and zinc in varying amounts. There is ample evidence that such ores were smelted together in antiquity yielding highly impure copper metal containing Pb, Zn, Sb, Ni, and Fe. To use such copper, it must be excessively refined.

Fire refining methods were applied on the purification of impure copper that contains 20 per cent Pb, 5 per cent Zn, 5 per cent Sb, 2 per cent Ni, and 3 per cent Fe. Without any flux and using only air blast on the molten alloy, it was possible to remove about all of iron and zinc, and up to 50 per cent of the Pb, Sb, and Ni.

# ÖZET

Bu çalışmanın amacı saf olmayan bakır metalin tarih öncesi dönemlerde kullanılan ilkel yöntemlerle saflaştırılmasıdır.

Çalışmanın ilk bölümü demir içeren kalay kullanılarak hazırlanan bronzdan demiri uzaklaştırılması ile ilgilidir. İkinci bölümde ise, polimetalik bakır filizlerinin izabesi sonucu oluşan ve kurşun, demir, çinko ve antimon gibi elementler içeren bakırın basit yöntemler ile saflaştırılmasına çalışılmıştır.

Demir filizleri içeren kasiteritin izabesi sırasında kalayın yanı sıra kalay-demir bileşikleri de (hard-head) oluşur. Kalay-demir bileşiklerinden kalayın ayrıştırılması imkansızdır ve bir miktar kalay böylece kaybolur.

Yüzde 80 kalay yüzde 20 demir içeren kalay-demir boncukları 1200 °C lik fırınlarda hazırlandı. Elde edilen kalay-demir boncukları daha sonra kül fırınında 1200 °C de eritilmiş bakıra ilave edildi. 1200 °C sıcaklığın üzerinde bütün Sn-Fe bileşikleri elementlerine ayrışır. Soğutma sırasında kalay bakıra karışarak bronz oluştururken bakırda çözünmeyen demir dışlanır. Daha sonra

dışlanan demir ortama katılan maddeler ile veya hava üfleme yolu ile oksitlendirilerek cüruflaştırılır. Uygun maddeler kullanılarak yapılan deneyler sonucunda kalay-demir boncuklarından yüzde 85 oranında demirin uzaklaştırılabildiği ve bronzdaki demir miktarının yüzde 0.5 düzeyine indiği gözlenmiştir. Kalay kaybı ise sadece yüzde 20 mertebesindedir. Sonuç olarak saflaştırılamayan kalay-demir alaşımının bronz üretiminde ekonomik olarak kullanılabileceği anlaşılmıştır.

Sülfitli bakır filizleri genelde değişik oranda Fe, Pb, As, Ni, Sb ve Zn gibi metalleri içerir. Antik çağlarda bu tür polimetalik bakır filizlerinin izabe edildiğini gösteren birçok kanıt vardır. İzabe sonucunda Pb, Zn, Sb, Ni ve Fe içeren kalay elde edilir.

İçerisinde bu tür elementler bulunan bakır kullanılmadan önce iyice saflaştırılması gerekir. Bu amaçla içinde yüzde 20 Pb, yüzde 5 Zn, yüzde 5 Sb, yüzde 2 Ni ve yüzde 3 Fe içeren bakır külçeler hazırlanmıştır. Daha sonra grafit potalar içinde eritilen alaşım üzerine hava üfleme metoduyla saflaştırılmalarına çalışılmıştır. Deneyler sonucunda sadece hava üfleyerek külçelerdeki tüm Fe ve Zn yok edilirken, Pb, Sb ve Ni metallerinde de yüzde elli oranında azalma görülmüştür.

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| | |
|---|---|
| AAS | Atomic Absorption Spectroscopy |
| BC | Before Christ |
| $^{o}C$ | Celcius Degree |
| cm | Centimeter |
| $\Delta G$ | Change in Gibbs Free Energy |
| $\Delta S$ | Change in Entropy |
| $e^-$ | electron |
| g | gram |
| l | liter |
| $\mu$ | Micro |

# I. INTRODUCTION

Chemical analysis of ancient copper and bronze objects has been one of the most active field of research during the past 100 years. The purpose of chemical analysis was to determine the type and the amount of various alloying elements such as arsenic, tin and zinc, as well as several minor occurences of elements such as antimony, nickel, silver, gold, bismuth, cobalt, iron and sulphur. Distribution of alloying and trace elements in copper and bronze artifacts are used to interpret the historical development of copper technology such as exploitation and processing of copper ores, smelting and purifications methods, provenance studies and trade.

Even though it is not definitely possible to identify copper objects made from native copper, earliest examples of copper artifacts were asssumed to be made from native copper. Such artifacts were generally quite pure. Native copper supplies, however, could not sustain the increase in demand for copper. As the native copper sources were used up, the metalsmiths started to look for other ways of copper making. It is reasonable to assume that the earliest smelting was done using oxide ores. The colorful oxide ores were easy to recognize and they were conveniently located to the upper zones of ore deposits which made their exploitation quite easy. During the alteration process by physical and chemical processes from primary to secondary ore deposits, many of the metallic impurities in the primary ores are also eliminated. Therefore, metal objects obtained by smelting of relatively pure secondary oxide ores yielded copper of high purity.

After the exhaustion of oxide ores, the primary sulphide ores of copper were started to be exploited. Sulphide ores are polymetallic in nature and are difficult to remove the impurities by primitive ore processing techniques. Thus copper obtained from the smelting of sulphide ores by the use of matte process generally yielded copper metal with considerable impurities. Since the smelting of sulphidic copper ores required iron oxide as fluxing agent, this was also another source for impurities. Evidences from the archaeometallurgical remains such as slags and prills from the Bakırçay region of Merzifon showed that polymetallic ores were smelted prior to any ore processing. Metallic prills from the region contained as much as 20 per cent lead, 5 per cent iron, 7 per cent antimony, 5 per cent arsenic and 0.7 per cent zinc. Smelting of polymetallic copper ores was believed to be the possible starting point of unintentional copper based alloying. Copper metal with blister copper quality from the smelting of sulphidic ores generally also requires elaborate refining procedures before useful artifacts can be manufactured.

When intentional alloy formation technology was developed, the nature of the alloying element such as tin could also be another source of impurities in copper. Tin mineral cassiterite is often found in nature related with iron mineral hematite. During the simultaneous smelting of these minerals under high reducing conditions may yield pure tin metal together with various tin-iron alloys known as “hard-head”. Even though most of the tin can be sweated out from hard-head by sweating process, the refining methods of iron from tin, technically was very complicated for the Bronze Age smelters. Considerable amonts of very valuable tin may be lost this way. Smelting experiments using the cassiterite obtained from Kestel tin mine in the Niğde region yielded considerable quantities of hard head. Kestel cassiterite is associated with hematite and simple gravimetric ore dressing methods cannot remove most of the iron ore. Thus the use of iron containg tin in the production of bronze will be another source of iron contamination for the bronze obtained.

Since most of the copper and bronze artifacts from antiquity which are known to be made from primary polymetallic copper ores are very pure, the ancient metalsmiths should have applied some very effective refining techniques on them.

The aim of this study is to understand some of the refining and alloying techniques which could have been applied in the ancient times, to remove the unwanted metallic impurities selectively from copper and bronze.

# II. THEORY

## 2.1. The Origins of Copper Metallurgy

The beginning of metallurgy can be seen as the first use of the term "pyrotechnology." The ancient metalsmiths first discovered the pyrotechnological methods applied to metalliferous rocks. Then, the development of metallurgy must have come about without any clear notion of elements and compounds.

For metallurgy to develop, man had to be in a situation which would allow him the opportunity to experiment with native copper. This situation did not come about until the Neolithic. The melting, hammering, and annealing of cooper may be considered as the first examples of metallurgical study (1).

The native copper attracted man's attention, as its special properties were quite unlike traditional materials such as bone, wood and clay. It could be bent, flattened and sharpened. It was discovered that if one hammered copper excessively, it would become harder. It was also observed that it could be made pliable again by heating it in a fire; hence, the discovery of annealing. Until the discovery of the fusibility of copper at a high temperature (1083 °C), metal work was limited to the size of the piece of native copper found. But by melting small bits of native copper together, a whole range of large objects became possible.

As the demand for copper became greater, native copper sources were no longer sufficient, and the metallurgist was faced with the problem of finding new sources.

## 2.2. Minerals and Ores

Minerals are natural inorganic substances, which has a definite chemical composition and distinctive physical properties or molecular structure. With few exceptions, minerals are crystalline solids (2).

Mineral deposits include both ores and non-metallic minerals. Technically, an ore is a metal-bearing mineral, or aggregate of such minerals, mixed with nonmetallic siliceous constituents. Ore deposits are portion of earth's crust which is very rich in metals when compared with the rest (3).

Ore minerals are classified as primary and secondary. The primary ores are those originally deposited when the ore body was forming; the secondary ores are produced by the alteration of primary minerals with weathering and the action of rain and ground waters. Except aluminum, iron, manganese, chromium, platinum and tin, all primary ore minerals are sulphides, arsenides, sulpharsenides, sulphantimonides, or similar compounds. Sulphides are of chief importance. Though secondary minerals are largely oxidized compounds, they also comprise a few very important sulphides. Secondary minerals are native metals, sulphates, carbonates and chlorides. The primary and secondary copper minerals are listed in Table 2.2.1.

Table 2.2.1 Primary and secondary occurences of copper minerals (3)

| **Mineral** | **Chemical Formula** |
|---|---|
| Chalcocite | $Cu_2S$ |
| Covellite | $CuS$ |
| Bornite | $Cu_5Fe_2S_4$ |
| Enargite | $Cu_3AsS_4$ |
| Tetrahedrite | $Cu_3SbS_3 + x(Fe,Zn)_6Sb_2S_9$ |
| Azurite | $Cu_3(CO_3)_2(OH)_2$ |
| Malachite | $CuCO_3Cu(OH)_2$ |
| Cuprite | $CuO_2$ |
| Olivenite | $Cu_2(AsO_4)OH$ |
| Chrysocolla | $CuSiO_3$ |
| Native Copper | $Cu$ |

Most of the copper ores have started as sulphides. In a typical sulphide deposit, such as that at Ergani Maden in Turkey, the surface minerals consist of gossan which is the oxidized ferrous component of the sulphide deposit. In these surface layers, some precious metals, native copper and some copper minerals may be found, but most of the copper and other metals will be solubilized by rain waters and washed down to the secondary enrichment zone below which is shown in Figure 2.2.1. Although this zone provides copper in the highest concentrations, it also contains considerable amounts of other metals such as Fe, As, Sb, Pb, Zn

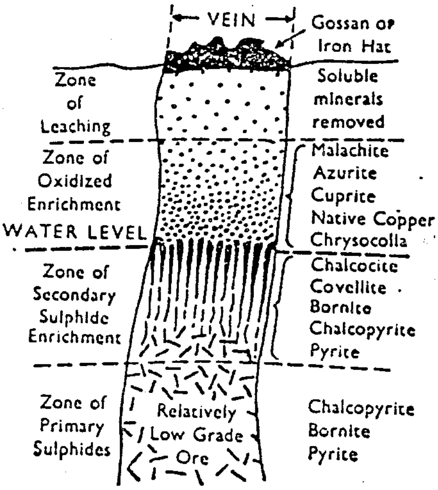


Figure 2.2.1 Cross Section of a copper lode (4)

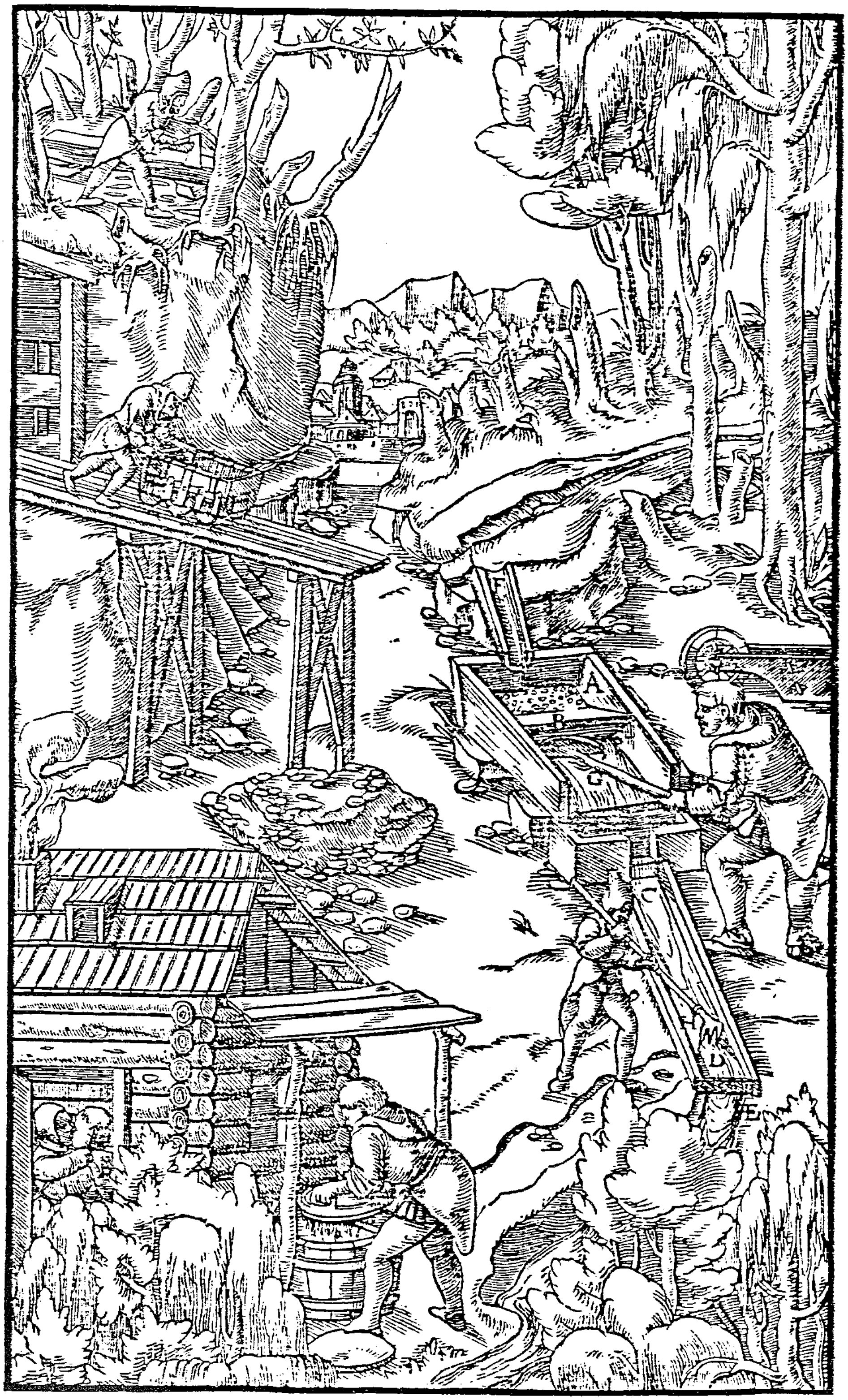
Gangue minerals are the associated undesired materials of an ore deposit. They are mostly non-metallic minerals of rock such as quartz, calcite, and feldspar and are usually discarded during the treatment of the ore. Some of the gangue minerals may be collected as by-products and can be utilized (5).

Ores may yield after smelting a single metal (simple ores) or a mixture of metals (complex or polymetallic ores). Those commonly worked for only a single metal are iron, aluminum, tin, chromium, mercury, manganese, tungsten and some ores of copper. Gold ores may yield only gold, but silver is a common associate. Ores that commonly yield two, three or more metals are gold, silver, copper, lead, zinc, nickel, cobalt and antimony. Most silver is a by-product. Many of the minor metals are obtained only as by-products (5).

## 2.3. Ancient Ore Dressing Methods

Ore dressing is the treatment of ores and mineral products by mechanical, physical or chemical means to separate the valuable minerals from the worthless constituents to increase its concentration (6). (Fig. 2.3.1)

Initially, very pure secondary oxide and carbonate minerals of copper were used, since they are closer to the surface of the earth. Therefore, simple separation techniques were used to remove the siliceous constituents. These methods consist of hand-picking or grinding the ore well and washing the unwanted material.



A—Box. B—Perforated plate. C—Trough. D—Cross-boards. E—Pool.
F—Launder. G—Shovel. H—Rake.

Figure 2.3.1 An illustration of an ore dressing technique (6)

Whereas, for the primary sulphide minerals of copper, more complex processing methods had to be used. The ore should be roasted to remove some of the sulphur in the form of sulphur dioxide.

Recently, the flotation method is used in the modern plants. The ore is crushed and grounded to a fine powder. The copper minerals are removed from the ore by froth flotation. For this procedure, a flotation agent is added to the water suspension of the grounded ore. Then, the sulphide minerals float to the surface and can be skimmed off. The copper minerals are removed by filtration and drying (7).

### 2.3.1. Processing of Copper Oxides

Surface deposits of copper ores tend to be oxides. These have been formed largely by the action of ground water, containing carbon dioxide, oxygen and sulphuric acid, on primary sulphide minerals. The oxide ores, being purer, are much easier to reduce to the metallic state than the sulphide ores.

Depending on the gangue material, different ore processing methods are used. In the case of light gangue, the ore can be washed to remove the unwanted material and thereby make up a concentrate of the ore. This is the case with copper oxides.

Manuel experience is necessary in this step, whether using a washing method or sieve. It was probably quickly understood by the ancient smelters that the wash water still contained some of the derived ore, and it was allowed to settle, permitting a residue to accumulate. The residue was then concentrated further for smelting. This was a common practise in the Middle Ages, but probably hand-cobbing and dry crushing with mortar and pestle were the most common methods of copper ore preparation in antiquity. Hand-cobbing is the process where the ore lumps (i.e. malachite disseminated through limestone) were crushed with stone hammers to break away the limestone gangue. The wet methods using running water are normally associated with the heavy ores such as cassiterite and gold (1).

### 2.3.2. Processing of Sulphide Ores of Copper

The ores of copper which are of greater importance are complex mixtures of copper and iron sulphides, associated with compounds of Sb, As, Bi, Au, Fe, Zn, and Ag in varying amounts (8).

The principal difference between sulphide ore preparation and that of copper oxide is that there is a roasting process involved before the concentrate passes on to the smelting stage. After the preliminary sorting, crushing and concentrating of the ore, it is roasted. This has the effect of driving off most of the sulphur in the ore, the end result being a black copper oxide.

The chemical process of oxidizing copper sulphide may be expressed as follows:

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2 \qquad (2.1)$$

Once roasting has driven off most of the sulphur, the ore is ready for smelting (1).

The most important benefit of the roasting process is the removal of sulphur that is bound to copper. Also, in the absence of sulphur, iron can be oxidized easily and goes into slag phase. The weight percentage of the copper increases in the ore which results in higher yields of metal during smelting (9).

The sulphide associated elements other than Cu such as Fe, Co, Zn, S, As, Se, Ag, In, Au, and Pb are also enriched in the concentrate after the processing, if present in the polymetallic ore (7). Some of these elements are partially volatilized , e.g. As, Pb, Se, Zn, and S, under strong oxidizing conditions and at high temperatures. Some of the minerals present in the copper sulphides, oxidizes during the roasting process. For example, Pb and Sb have a similar affinity to oxygen as sulphur has. .Thus, they are oxidized during roasting, and oxide inclusions in the roasted and smelted samples contains Pb and Sb as well as copper (10).

## 2.4. Smelting Techniques

Ores are converted to metal by smelting. This is the reduction of a metal ore with carbon monoxide in a furnace in the presence of charcoal as fuel.

$$MO + CO \longrightarrow M + CO_2 \qquad (2.2)$$

The reaction of conversion of carbon dioxide back to carbon monoxide is:

$$CO_2 + C \rightleftharpoons 2CO \qquad (2.3)$$

For this procedure, fluxes are added to reduce the melting point of the melt and to remove the unwanted constituents of the ore. These infusible siliceous materials form a fusible fluid mass called slag.

Basic oxides of Ca, Mn, Mg, Fe, Zn, Pb, Na and K are added as flux and provide oxygen ions when dissolved in a slag.

$$MO \longrightarrow M^{+2} + O^{-2} \qquad (2.4)$$

Acidic oxide $SiO_2$, absorbs oxygen ions provided by basic oxides.

$$SiO_2 + 2O^{-2} \longrightarrow SiO_4^{-4} \qquad (2.5)$$

Some ores are self-fluxing, so that they contain appropriate amounts of iron oxides and silicate and produce a fluid slag known as fayalite ($Fe_2SiO_4$) such as the one observed in copper smelting.

The extraction of metals from their oxides can be explained in terms of thermodynamic principles. If chemical reactions are considered as systems, they are usually in thermal contact with their surroundings. The equilibrium conditions of the system give rise to a function of state at constant pressure and temperature:

$$\Delta G = \Delta H - T\Delta S \qquad (2.6)$$

G is called the Gibbs free energy, where H is enthalpy, T is temperature and S is entropy of the system.

Metals can be obtained from their oxides by reduction with carbon and carbon monoxide as reducing agents. The equilibrium below can explain this situation and can be discussed in terms of the thermodynamic functions of the following reactions (2.8), (2.9), and (2.10).

$$MO(s) + C(s) \rightleftharpoons M(s) + CO(g) \tag{2.7}$$

$$M(s) + 1/2O_2(g) \longrightarrow MO(s) \tag{2.8}$$
$$C(s) + 1/2O_2(g) \longrightarrow CO(g) \tag{2.9}$$
$$CO(g) + 1/2O_2(g) \longrightarrow CO_2(g) \tag{2.10}$$

If the free energy of a reaction is to change strongly with temperature, gas must be either produced or consumed in the reaction. In reaction (2.9), there is a net increase in the amount of gas, the standard reaction entropy is positive and $\Delta G^o$ decreases with increasing temperature. In reaction (2.10) there is a net decrease in the amount of gas and $\Delta G^o$ increases with increasing temperature.

Reduction of the oxide depends on the competition of carbon for the oxygen bound to the metal. The standard Gibbs functions of the reduction reactions can be expressed in terms of the reactions (2.8), (2.9), and (2.10) above:

$$MO(s) + C(s) \longrightarrow M(s) + CO(g)$$

$$\Delta G^o = \Delta G^o(2.9) - \Delta G^o(2.8) \qquad (2.11)$$

$$MO(s) + CO(g) \longrightarrow M(s) + CO_2(g)$$

$$\Delta G^o = \Delta G^o(2.10) - \Delta G^o(2.8) \qquad (2.12)$$

Several reactions occur simultaneously in which both C(s) and CO(g) act as reducing agents. The equilibrium which has a negative $\Delta G^o$ value lies to the right, meaning that the reduction is spontaneously occured. (11) (12)

The most convenient form of presenting the free energy data is by means of Ellingham diagram shown in the Figure 2.4.1. It gives the increase in free energy $\Delta G^o$ when a fixed amount (1 mole) of oxidizing agent ($O_2$) at 1 atmospheric pressure combines with a pure element to form oxide.

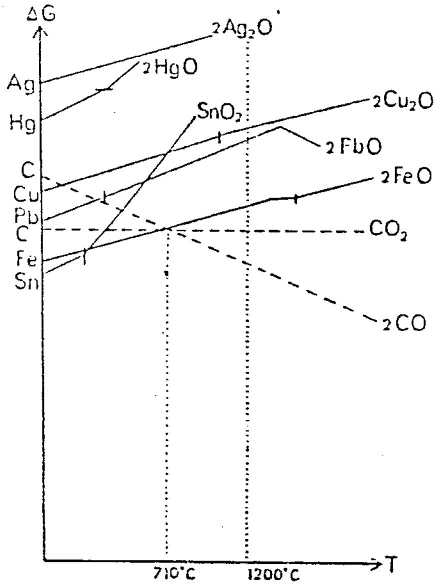


Figure 2.4.1 Ellingham diagram of oxide formation (12)

It can be seen from the Ellingham diagram that metals mostly release free energy during oxidation. They mostly occur in nature in the oxidized state. The easily reducible metals occur at the top of the diagram because of their affinity for oxygen and the highly reactive metals towards the bottom. This is in accordance with the order of historical occurances of metals. (11) (12)

### 2.4.1. Smelting of Copper

After the ore minerals were processed carefully in order to pick out the highest possible concentrate of the ore, it would be smelted in a small clay furnace as can be seen in Figure 2.4.2. The fuel would be charcoal with air supplied from bellows. After about an hour of operation sizeable discrete prills of copper, would form in the bottom of the furnace, covered with a mass of ash and possibly some fused slag (14). After the furnace is cooled, the copper was recovered by smashing the cake of slag.

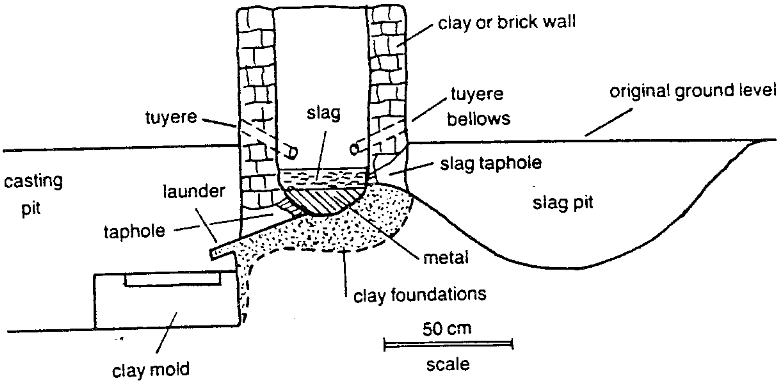


Figure 2.4.2 A representation of ancient smelting furnaces (12)

Selected reactions in combustion, copper smelting and slag formation:

$$C + O_2 \longrightarrow CO_2 \qquad (2.13)$$

$$CO_2 + C \longrightarrow 2CO \qquad (2.14)$$

$$CuCO_3.Cu(OH)_2 \longrightarrow 2CuO + CO_2 + H_2O \qquad (2.15)$$

$$2CuO \longrightarrow Cu_2O + 1/2O_2 \qquad (2.16)$$

$$Cu_2O + CO \longrightarrow 2Cu + CO_2 \qquad (2.17)$$

$$Fe_2O_3(\text{flux}) + CO \longrightarrow 2FeO + CO_2 \qquad (2.18)$$

$$SiO_2(\text{gangue}) + 2FeO \longrightarrow 2FeO.SiO_2 \ (\text{fayalite slag}) \qquad (2.19)$$

$$FeO + CO \longrightarrow Fe + CO_2 \qquad (2.20)$$

The smelting operation of sulphide ores of copper will be described in more details. After removing of some of the sulphur as sulphur dioxide in the roasting step, the concentrate is added to the furnace with some silica. The oxidizing conditions in the furnace cause some of the iron and sulphur to be converted into oxides. Whereas, the copper and some iron sulphides remain as sulphides. Liquid cuprous and ferrous sulphides are soluble in each other, forms a matte which may contain 15-60 per cent copper, and may range in specific gravity from 3.9 to 5.2. The high density sulphide portion, (matte), will not dissolve in the slag and will sink to the bottom. Whereas, the iron oxide and flux in the slag will remain on the top. The matte will dissolve all the precious metals as well as some of the other impurities such as antimony, arsenic, iron and bismuth. (7) (8)

For the copper to be obtained from the matte, two steps of conversion procedure follows the smelting. First, since sulphur has a higher affinity to copper than to iron, the iron sulphides are converted into iron oxides. This can be seen in the sulphide Ellingham diagram (Fig. 2.4.3). The formation of copper sulphide has a more negative ΔG° value as compared to that of iron sulphide, at high temperatures, indicating to a more spontaneous formation. Next, the copper sulphides are converted to molten copper metal which is blister copper. (10)

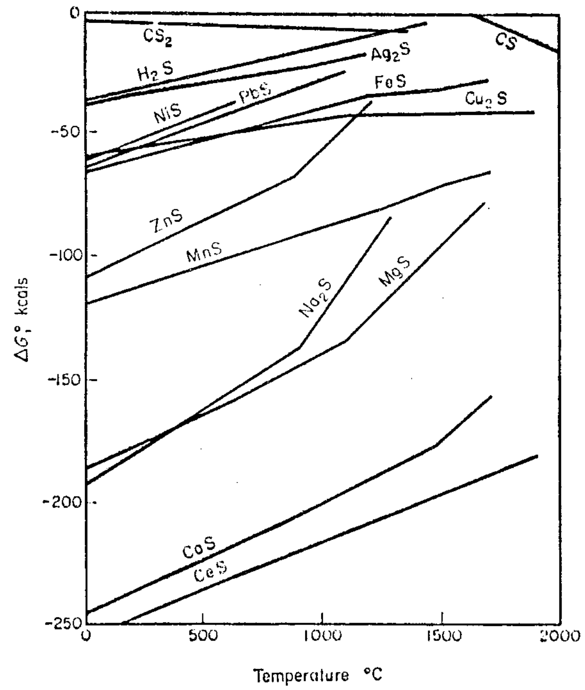


Figure 2.4.3 The Ellingham diagram of the metal sulphides (12)

In the very beginnings of copper smelting, the oxide or carbonate minerals of copper were used which were purer with respect to the sulphide minerals of copper. Also, the reducing conditions were probably not too severe and the process was of relatively short duration. Thus, probably not much metallic iron and other trace elements in the metallic form were formed and the molten copper would not have been in contact with it for a long time. By the main Bronze Age in the Middle East much more efficient smelting processes had evolved. As the use of the minerals of the secondary enrichment zone became more extensive and as the copper production became more specialized, it was realized that the efficiency of the yield of the smelting process was improved. But it also meant that the molten copper was exposed to any metallic impurity in the slag for a much longer time, and quite considerable quantities of iron and other unwanted impurities could therefore dissolve in the copper (15).

## 2.5. Metals and Alloys

### 2.5.1. The Structure of Metals

Many properties of metals can be explained by the knowledge of the structural arrangements of their atoms. When atoms are grouped together as in the crystalline state, nuclear charges of an atom attract the electrons of the adjacent atoms and the electrons repel each other. These interatomic forces are the basis of the strength and rigidity of solids.

As the temperature of a liquid metal comes down to its freezing point, force of attraction between atoms holds them in a definite crystalline structure.The geometrical pattern in which the constituent atoms of any crystal are arranged is called the space lattice.

The principal cubic space lattices are the body-centered cubic (B.C.C.), the face-centered cubic (F.C.C.) (Fig.2.5.1) and the close packed hexagonal (C.P.H.) lattices. Among the metals we consider, iron crystallize in the B.C.C. lattice and copper, nickel, and lead crystallize in the F.C.C. structure. The multiplication of these unit cells in three dimensions and at right angles to each other form the space lattice.

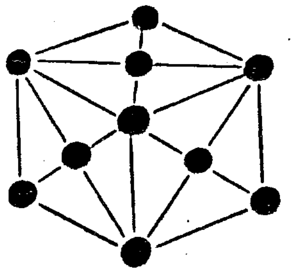


Figure 2.5.1 A unit cell of the face centered cubic lattice (16)

As the liquid starts to solidify, group of atoms form crystal nuclei at many starting points in the liquid simultaneously. The crystals grow radially outwards by attracting other atoms to their space lattices and throw their arms to surrounding liquid. This method of tree-like growth results in the formation of crystal skeletons called as "dendrites" which are shown in Figure 2.5.1.

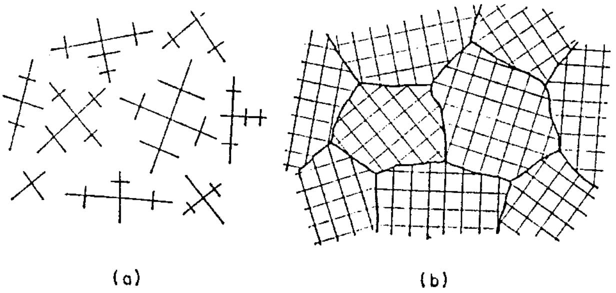


Figure 2.5.2 Formation of dendrites (a) leading to a polycrystalline structure (b) (16)

Grain of a metal is a small volume of lattice and the interface between grains is called the grain boundary. Grains and boundaries can be observed in a cross-section of a pure metal.

If the casting of a molten metal is cooled slowly, the grains are large in size. Rapid cooling rate, on the other hand, causes the grains to be small. This property gives a very important clue of whether an ancient artifact was cast into a metal mould or a clay or sand one. Since the metal gives heat away quickly, the grain size of the cast should be small.

Under the effect of an applied force, the metal layers slip over each other. The slip in one crystal is transmitted to the next crystal by the help of slip planes at the grain boundaries. If the applied force is so great to overcome the slip effect, the size of the grains become smaller. The metal becomes harder and this process is called "work-hardening."

If the hardened metal is heated, the crystals relieve their strain and oscillate. When the temperature is sufficiently high, new crystals form with larger grain boundaries. The metal becomes softer and it is said to be annealed (16).

## 2.5.2. On the History of Alloys

The earliest ancient copper objects contain considerable quantities of arsenic and lead, sometimes nickel or antimony, and occasionally silver, bismuth or tin. Analyses of ancient metal artefacts, from many regions of Europe, the Mediterranean, Near East and India, revealed that the first alloys used were arsenic bronzes containing more than 1 per cent arsenic. The improved mechanical properties of these unintentional Cu alloys must have been recognized by ancient metalsmith. By 3rd millenium B.C. in the Middle East intentional production of Cu-As and Cu-Sn alloys became widespread marking the beginnings of Bronze Age. In many areas tin bronze was not common until the Middle Bronze Age. Besides arsenic and tin, lead, nickel, antimony and silver were found in copper alloys greater than 1 per cent (17).

### 2.5.3. The Structure of Alloys

An alloy is a metallic solid or liquid formed by the combination of two or more metals. One method of alloying by forming a liquid solution as the first step is composed of melting the components separately and then mixing them. Another way of alloying is composed of adding one component as solid into the molten one. If there are two components, the alloy is known as a binary alloy.

There are three basic types of solid phases in binary alloys:
**(A)** First phase is the primary or terminal solid solution. When a pure metal acts as a solvent to form a solid solution with another metal, the solute atoms either replaces the atoms of the lattice of the solvent metal or stays in between these atoms. The former solid solution is called substitutional type, the latter one is called interstitial.

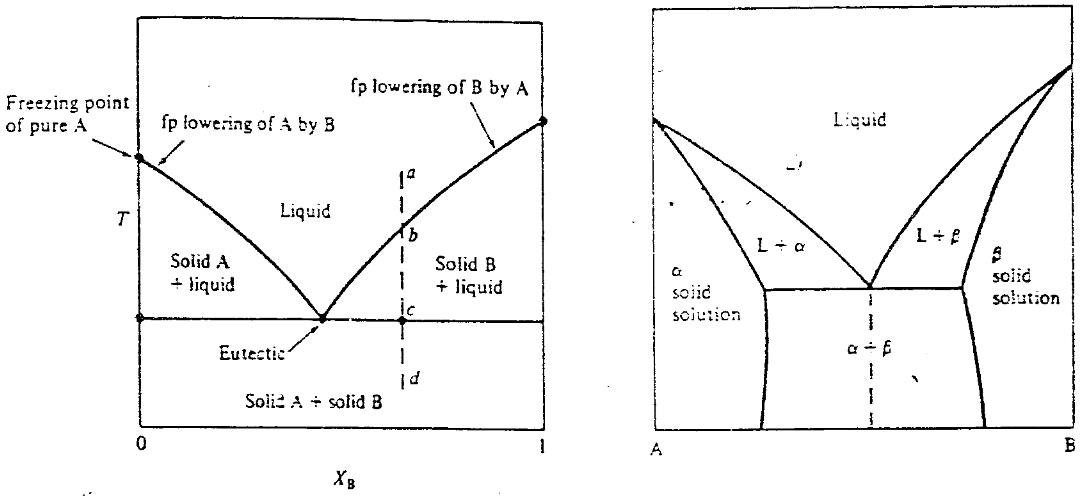
Because the space lattice of the primary solid solution is the same as that of pure metal and and spacings between atoms are occupied by the atoms of the metal, the addition of elements results in an increase in strength and hardness.

Copper forms many primary solid solutions dissolving 5 per cent or more of the metals such as As, Au, Ni, Sn, Zn,and Sb.

(B) Another solid phase is called intermetallic phase which is commonly used as intermetallic compound. They have definite composition and properties, melting or decomposition temperatures. They melt either congruently to a single phase, or incongruently to a mixture of two phases. Intermetallic compounds have characteristic and usually complex space lattices. Thus, they are ordered solid solutions in contrast to the disordered arangement of primary solid solutions. Because of their complex structure and the forces between the unlike atoms, they are very hard and brittle and melt at high temperatures. An intermetallic compound can be represented by a vertical line in a phase diagram.

(C) The last type of phase is the secondary or intermediate solid solutions. These solid solutions are formed by replacing one type of atom in the space lattice of an intermetallic compound with that of the other component. This compound will be stable over a range of compositions. They are, also, quite hard and brittle. In a constitutional diagram, secondary solid solutions can be represented by an area as a stable phase.

Phase diagrams show the results of the specially designed experiments to discover what phase is present under given conditions of pressure and temperature at equilibrium. A phase has a definite chemical composition and physical state, but it does not have to be a single continuous entity. For binary alloys, these diagrams are two dimensional plots of temperature versus composition.



(a) (b)

Figure 2.5.3 The representations of constitutional diagrams

The Figure 2.5.3 (a) and (b) represent simple eutectic systems. The representative constitutional diagram Figure 2.3.5 (a) shows two metals soluble in the liquid state but insoluble in the solid state. The two phase area under the eutectic line in the Figure 2.5.3 (a) is a mechanical mixture of a two pure metals. Figure 2.5.3 (b) is an example of binary alloys in which complete liquid and partial solid solubility (regions α and β) occur.

### 2.5.4. Cu-As Alloys

Either of these two possibilities can be thought to explain the great number of arsenic containing artifacts;

(a) the selection of arsenical copper minerals,
(b) the addition of minerals of high arsenic content to molten copper under reducing conditions.

The reason why the arsenical coppers were so desirable can be explained by the more rapid work hardening of Cu-As alloys. Most pure and arsenical ancient copper artefacts show that they were worked considerably. This can be seen in the elongation of the slag and oxide particles present in the metal, upon hammering. The rapid work hardening effect is also shown by the tin-bronzes. The use of arsenical coppers persisted until the development of tin-bronzes.

As the surface deposit which are native copper and easily smelted oxide ores were used up, the next zone was preferred because it had a higher concentration of copper and was found to give harder copper, because of unintended alloying. Since this secondary enrichment zone contains metals which were leached away from the upper levels by the rain and ground waters and the arsenical and the antimonial minerals are relatively soluble, it contains these also in a high concentration. This zone will often contain "fahlerz" type minerals which is copper-arsenic-antimony sulphides such as $(CuFe)_{12}(AsSb)_4S_{13}$, or solid solutions of tetrahedrite, $(CuFe)_{12}Sb_4S_{13}$, and tennantite, $(CuFe)_{12}As_4S_{13}$. (See Table 2.2.1)

Therefore, it would seem that the main reason for the metallic sequence Cu, Cu-As, Cu-As-Sn lay in the nature of deposit. Once the primary sulphide deposit below the sulphidic secondary enrichment zone was reached, the metal produced would be weaker than the arsenical copper. Then alloying with tin would be essential for the tools and the weapons of the period (18).

## 2.5.5. Cu-Sn Alloys

There are two ways of tin additions in bronze production,

(a) addition of metallic tin as an ingot material,

(b) addition and simultaneous reduction of cassiterite (stannic oxide $SnO_2$) or stannite (tin pyrites $Cu_2FeSnS_4$) to the surface of molten copper covered with charcoal (19).

The endothermic reaction of cassiterite is:

$$SnO_2 + C \longrightarrow Sn + CO_2 \qquad (2.21)$$

The activity of the products can be lowered by dissolving the tin formed in molten copper and the reaction favors the product side (19).

Employing cassiterite directly in the production of bronze prevents the loss of tin in a two stage process; first as being reduction of cassiterite and second as being formation of Cu-Sn alloy.

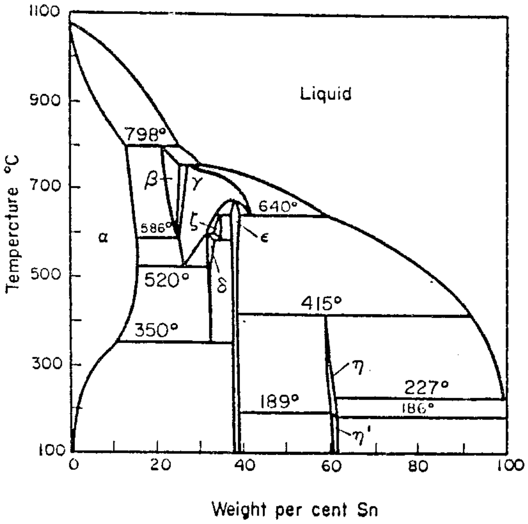


Figure 2.5.4 The copper-tin phase diagram (12)

Most useful alloys of Cu and Sn is composed of 10 per cent Sn and 90 per cent Cu. This ratio gives the limit of commercially important alloys. All bronzes containing less than 13.5 weight per cent Sn freeze in equilibrium as homogeneous copper-rich primary solid solutions (α).

## 2.6. Impurities in Copper

During smelting, the copper may pick up some impurities. The sources of these metallic impurities can be:

(a) ores,
(b) fluxes added during the smelting,
(c) fuels used,
(d) alloying element, in the case of alloy formation.

Among these impurities, most of the Fe is extracted to the slag after the refining as an oxide. Ni, Co, Pb, Ag, and Au remain in the metal. Zn, As, and Sb can be in either phase depending on the smelting conditions.

### 2.6.1. Impurities Originated From the Ores

As mentioned previously in Table 2.2.1, copper ores are either oxidic or sulphidic in nature. If the ore was an oxide or carbonate, it was usually free of iron, but contained large amounts of silica. Whereas copper sulphide ores usually are polymetallic in nature and contains considerable amounts of iron minerals, as well as the metals As, Sb, Ag, Pb, Zn, Ni, and Bi, which had been leached away from the level of secondary oxides. Both the silica and the metallic impurities had to be removed during the smelting and the refining processes.

### 2.6.2. Impurities Originated From the Fluxes

For the removal of iron minerals and the silica, iron oxide was added to the oxide ores and the silica was added to the sulphide ores as the flux. By doing so, a molten slag was formed which to be tapped out of the furnace. Therefore, in the smelting of both oxide and sulphide ores, considerable amounts of iron were already present. If the reducing conditions of the furnace were too severe, some of the iron minerals would also reduce to metallic iron. Although most of iron would stay in the slag, some would dissolve in the molten copper, especially, if the process is of long duration.

### 2.6.3. Impurities Originated From the Alloying Element Sn

The bronze alloy are made by

(a) mixing of metallic copper and tin in proper amounts to make an alloy,

(b) cementation process which is the reduction of the cassiterite concentrate with charcoal over molten copper.

In the case of alloy formation, metallic impurities, either present in the cassiterite ore body or come from the fluxes during the smelting of tin are carried into copper matrix. If the tin metal or the cassiterite concentrate is not pure, then impurities may also end up in the final product. The main impurity that may come from tin is also iron. Therefore, it will be useful to have a detailed look at the processing and the smelting operations of tin ore cassiterite.

### 2.6.3.1. Processing of Tin Ore Cassiterite.

Historically tin has always been a comparatively expensive and limited metal when compared to copper, lead and iron. This is due to the fact that it occurs relatively sparsely in nature and it is not very easy, to recover in mineral form.

Although it occurs in nature mostly as its oxide, $SnO_2$, cassiterite, this mineral is found in two distinct forms of occurances. Firstly, cassiterite is found as distinct particles in the rocks of magmatic origin associated with hematite, pyrite, arsenopyrite and in some places chalcopyrite. These ores are usually mined from considerable depths and are brought to the surface often containing on the average only 0.5-1.0 per cent Sn (20).

The richest tin sources have always been from alluvial deposits, such as stream tin, where wheathering processes have destroyed the host rock and have deposited the chemically and physically stable, dense (specific gravity 6.5-7) and hard (Mohs hardness 6-7) cassiterite mineral in a natural physical concentrating process. Since, the specific gravity of the cassiterite ore is much higher than that of the granite and other siliceous minerals with which it is normally associated and it is insoluble and inert to most chemical attack, concentration techniques mainly centered around gravity methods.(19)

### 2.6.3.2. Smelting of Tin Ore Cassiterite.

If $SnO_2$ is pure, it is easily reduced at a low red heat by carbon or reducing gases such as carbon monoxide (20). If not, the ore concentrates are smelted with a limited amount of reducing agent to give a crude tin, containing as little iron as possible, and a rich slag containing the bulk of iron, since the cassiterite mineral is found in the rocks of magmatic origin. Such tin rich slag is then resmelted at a higher temperature and under stronger reducing conditions to give a reject slag and tin-iron compound "hard-head" which contains about 80 per cent tin and 20 per cent iron. The hard-head is then returned to the first stage of smelting (21).

The early form of tin smelting furnace was either a hole in the ground in which charcoal was burned using hand bellows or a crude low blast furnace made of clay.

These blast furnaces offer a relatively high smelting rate, but it is difficult to avoid reducing a lot of iron into tin metal in the first stage, since the carbon in the shaft is required both for heat generation and for chemical reduction, and these functions can not be separated (21). The chemistry of tin smelting can be summarized by the classical reaction:(20)

$$SnO_2 + C \longrightarrow Sn + CO_2 \qquad (2.22)$$

The true reaction takes place in a number of stages. At the beginning of the process when the charge is heating up, carbon from the reducing agent will react with carbon dioxide of the furnace atmosphere to give carbon monoxide.

$$C + CO_2 \rightleftharpoons 2CO \qquad (2.23)$$

This carbon monoxide reacts at the surface of the solid cassiterite particles to produce tin and carbon dioxide.

$$2CO + SnO_2 \rightleftharpoons Sn + CO_2 \qquad (2.24)$$

Once sufficient liquid tin has been produced for the droplets to coalesce, they drain away by gravity, driving this reaction to the right.

The presence of sulphur causes a volatilization loss to occur. In the reducing atmosphere, cassiterite will react with sulphur to form stannous sulphide which is volatile and which in contact with air, will burn to stannic oxide in the form of dust, which can be collected and re-smelted.

Tin also escapes from molten slag as volatile stannous oxide, SnO, as being another volatilization loss.

Iron has a solubility of only 0.001 per cent in tin at the melting point of tin (232 °C) If iron is present in tin in an amount greater than 0.001 per cent then hard-head is formed. If iron makes up less than 20 per cent of the furnace metal the hard-head phase occurs as crystals of $FeSn_2$. Larger amounts of iron in the furnace metal lead to the formation of FeSn. (Figure 2.6.1) It is these two forms of hard-head that make iron undesirable in tin (22).

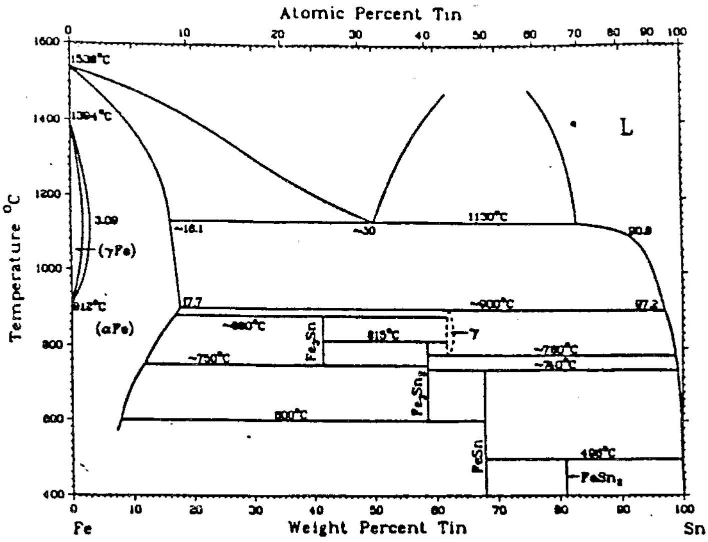


Figure 2.6.1 The tin-iron phase diagram (23)

## 2.6.4. Effect of Common Impurities of Copper on Its Mechanical Properties

### 2.6.4.1. Iron in Copper.

The amount of iron in the unrefined copper depends on:

(a) the abundance of iron minerals in the charge,

(b) the redox conditions within the furnace,

(c) the duration of contact between the molten copper and any metallic iron present.

Iron is the most important impurity in copper and bronze, because it forms seggregates in the artifacts which corrodes away easily, since it has higher affinity for oxygen than copper. If it present in Cu greater than 1 per cent, the Cu ingot responds to magnet (24). Iron has considerable solubility in molten copper at high temperature (about 6 per cent at 1200 °C) The copper containing such high levels of iron is almost impossible to cast or hammer to shape and has to be refined.

The alloys prepared in this study contains about 2 per cent iron. Above 1100 °C, the copper bears that amount of iron in solution. At about 1090 °C, ε solid solution forms. With continued cooling to 950 °C, γ-iron starts to precipitate. As the temperature falls, the precipitated γ-iron goes through magnetic transformations and below 910 °C, it becomes ferromagnetic α-iron. (Fig.2.6.2.)

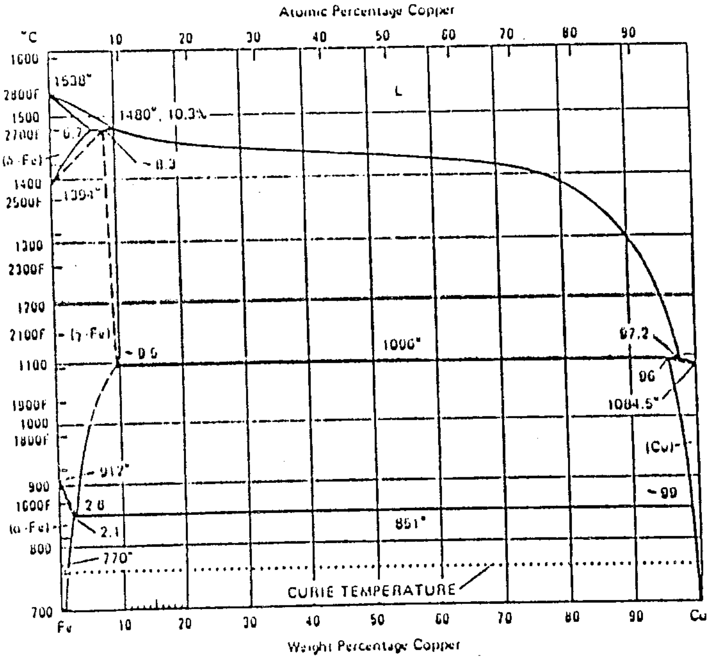


Figure 2.6.2 The copper-iron phase diagram (25)

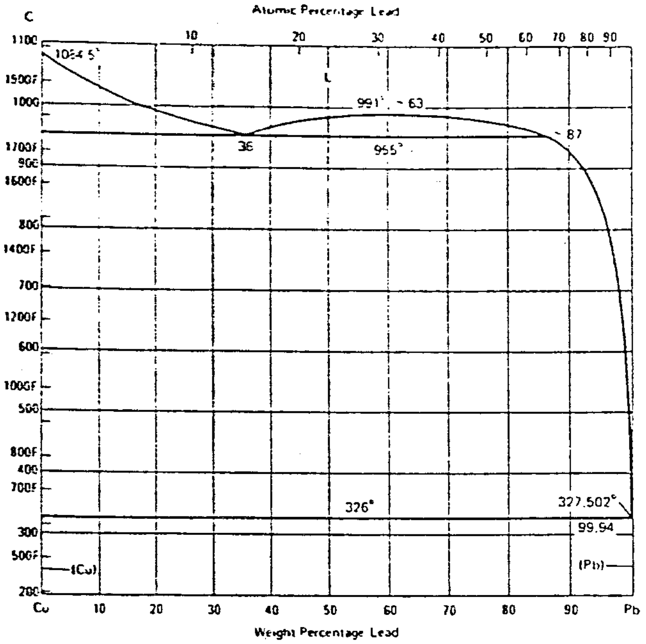


Figure 2.6.3 The copper-lead phase diagram (25)

## 2.6.4.2. Lead in Copper.

It can be seen from the phase diagram in Figure 2.6.3 that lead and copper are immiscible in any composition and they do not form a solid solution. Thus, lead is insoluble in copper. Since lead, up to 2 per cent, increases the fluidity of the molten copper, it would be useful for casting purposes. If it is present in greater amounts, it remains as minute globules in copper and causes weaknesses upon hammering.

### 2.6.4.3. Zinc in Copper.

Prior to 14th century, the introduction of zinc into copper was almost always achieved by cementation process. Appearance of first zinc containing copper objects was dated to 2nd millenium B.C. Zinc oxide can not be reduced by charcoal at temperatures below 1000 °C, whereas zinc boils at 923 °C and the metal is reduced as a vapour. It easily evaporizes depending on the temperature of the smelting furnace. Zinc, up to 30 per cent makes a good alloy with copper which is known as brass. (Fig. 2.6.4) Presence of zinc in copper as a trace element does not make any harm on copper (26).

### 2.6.4.4 Nickel in Copper.

The presence of Ni in Cu can be used for diagnostic purposes for the origin of early Cu artifacts. Nickel forms a perfect solid solution with copper in all compositions. (Fig.2.6.5) After the smelting of Ni containing polymetallic copper ores, Ni is distributed between Cu and slag almost equally. The presence of a few percentages of Ni makes no harm on the properties of Cu. (24) (27)

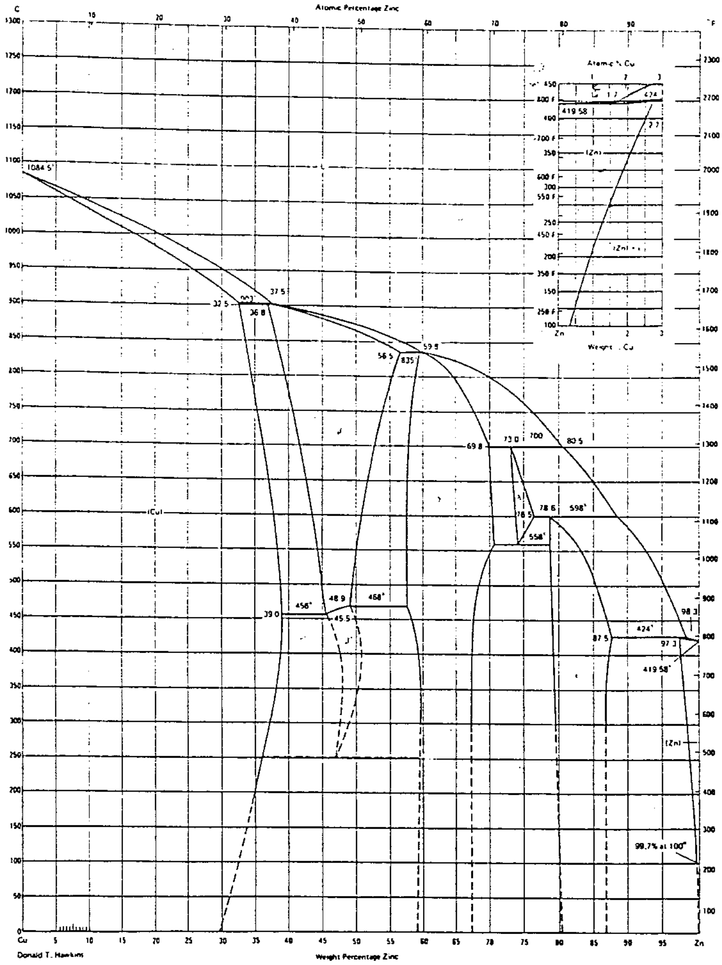


Figure 2.6.4 The copper-zinc phase diagram (25)

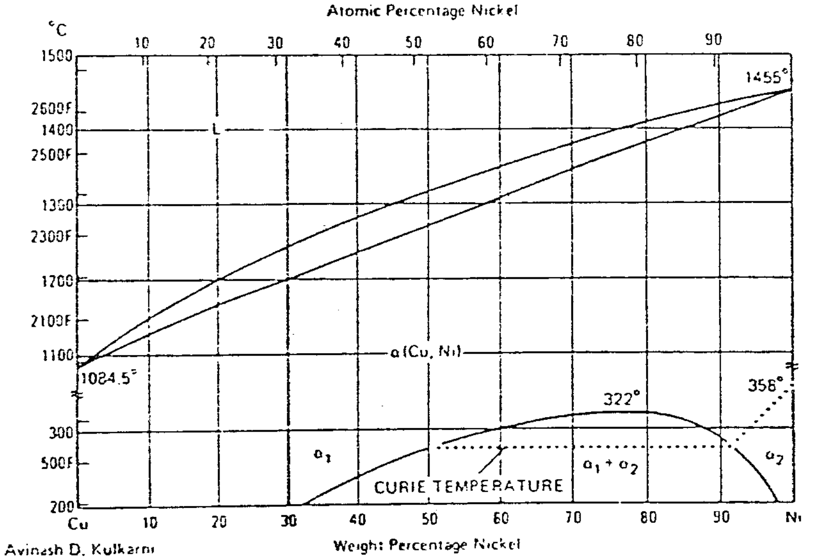


Figure 2.6.5 The copper-nickel phase diagram

### 2.6.4.5. Antimony in Copper.

Antimony is usually incorporated into copper as a result of smelting of antimony containing copper ores. Since Sb is a volatile element its retention in Cu depends on the smelting temperature and on the reducing conditions of the furnace. Presence of it as an impurity makes copper very hard and brittle (18) (27). (Fig. 2.6.6)

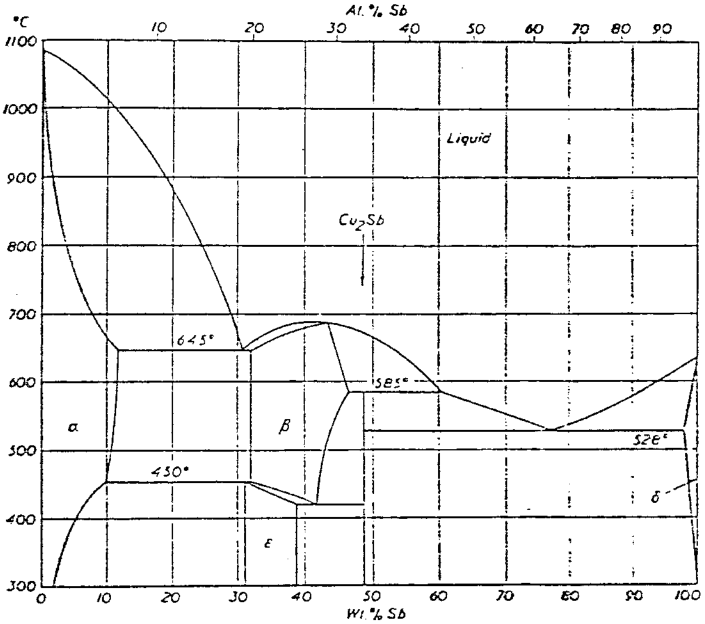


Figure 2.6.6. The copper-antimony phase diagram

## 2.7. Refining of Metals

Copper metal obtained from initial smelting operations of primary ores, such as blister copper may contain some or all of the impurities discussed in section 2.6.4. Before impure copper is converted into a useful object or tool, it has to be refined. There are several reasons of refining copper:

(a) to produce the metal as pure as possible,
(b) to obtain a product with controlled amounts of desired impurities,
(c) to recover impurities which in themselves are valuable (like extraction of silver and gold from lead)

### 2.7.1. Fire-refining of Impure Copper

In ancient smelting of polymetallic copper ores, the process yielded copper with various impurities,which is called black or blister copper, containing 95-98 per cent of copper. Another source of impure copper is from the liquation process. This also makes possible the recovery of valuable minor constituents. Liquation of silver from copper is an example of these processes as described by Agricola in 1556 (6), by Biringuccio in 1540 (28) and by Ercker in 1580 (29). In this process, valuable metals such as gold and silver which may be present in copper are extracted.

The process was carried out in four stages. In the first step, silver and gold containing copper was melted with three or four times its weight of lead in a blast furnace making a molten alloy and casting this into moulds. The second step was the liquation process. The cakes recovered from moulds were heated at a temperature lower than the melting point of copper, but higher than the melting point of lead. The lead was allowed to drain off through an inclination to a channel containing the silver in the copper. Then, the cakes were re-liquated in order to get rid of remaining lead. In the last step. the copper cakes were refined in the furnace using air-bellows. The silver and gold in lead, was then recovered by the method “cupellation.”

Refining of copper also was described by Agricola. The pyrometallurgical principles behind fire-refining of black copper from smelting or liquation are based upon selective oxidation of metallic impurity elements. The selectivity of the removal of impurities depends on electrode oxidation/reduction potentials of metals. The metals with more positive oxidation potentials are more readily oxidized. The tabulated in are the oxidation potentials of metals.

Table 2.7.1 Oxidation potential of metals

| **Reaction** | **E(v)** |
|---|---|
| $Au \longrightarrow Au^{+} + e^{-}$ | -1.691 |
| $Ag \longrightarrow Ag^{+} + e^{-}$ | -0.799 |
| $Cu \longrightarrow Cu^{+2} + 2e^{-}$ | -0.337 |
| $Pb \longrightarrow Pb^{+2} + 2e^{-}$ | 0.126 |
| $Sn \longrightarrow Sn^{+2} + 2e^{-}$ | 0.136 |
| $Ni \longrightarrow Ni^{+2} + 2e^{-}$ | 0.250 |
| $Co \longrightarrow Co^{+2} + 2e^{-}$ | 0.280 |
| $Cd \longrightarrow Cd^{+2} + 2e^{-}$ | 0.403 |
| $Fe \longrightarrow Fe^{+2} + 2e^{-}$ | 0.440 |
| $Zn \longrightarrow Zn^{+2} + 2e^{-}$ | 0.763 |

For the refining process, the copper is heated in an open furnace with charcoal. Then, this molten mass of impure copper is subjected to a strong air-blast. Oxidized impurities go into the slag. During this operation some copper is also oxidized. However, cuprous oxide melts and diffuses through the molten copper carrying its oxygen to the impurities and enhancing their oxidation. The cuprous oxide forms a lower melting point eutectic with copper at the grain boundaries of the solidifying metal. This eutectic makes the copper less ductile and has adverse effects on the cold-workability of copper. Another reason of why cuprous oxide have to be removed from copper is that open-fire heating of cuprous oxide containing copper would result in blistering and cracking (2).

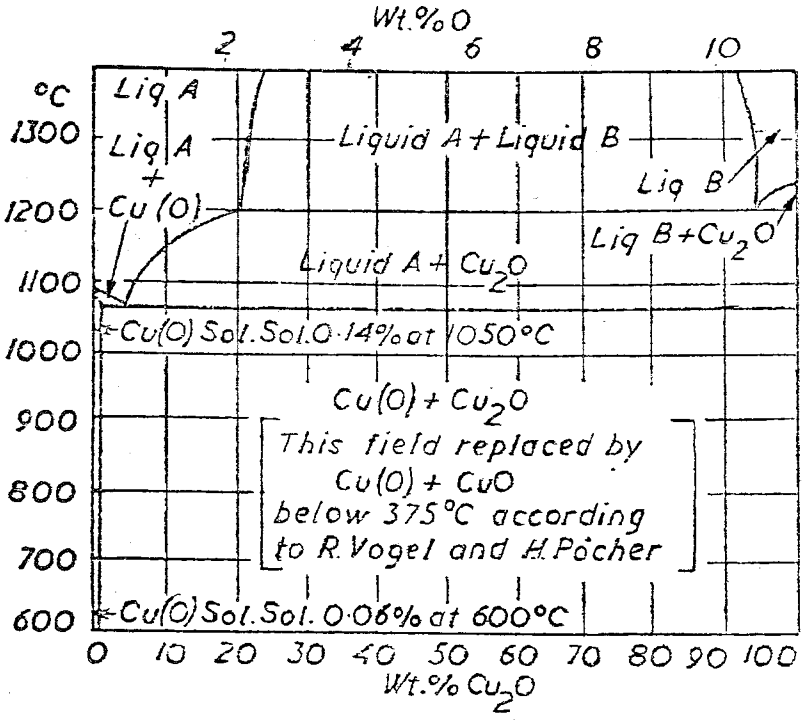


Figure 2.7.1. The copper-copper oxide phase diagram (30)

After the oxidation step, molten copper is stirred with a piece of green wood and the gases generated from the wood help to reduce the cuprous oxide diffused in copper (6). This process is called poling and still is in use in modern plants.

Reactions related with the fire-refining and poling:

$2Fe + O_2 \longrightarrow 2FeO$ (2.25)

$2FeO + SiO_2 \longrightarrow 2FeO.SiO_2$ (fayalite crucible slag) (2.26)

$CuO + CO \longrightarrow Cu + CO_2$ (2.27)

To test whether the refining was done properly, an iron rod is dipped into the molten metal. If the copper on the point of the rod is purified enough, it adheres to the rod easily, has a red colour and is flexible. The copper of this state is called as “rosetta copper.” If it is over-refined, it is thick and brittle.

Iron does not alloy with copper, thus any iron oxide which is reduced to iron in the furnace should be removed. To remove iron, the raw copper is melted in an open crucible and the iron is allowed to oxidize and then form a slag by sprinkling clean sand or crushed quartz on to the surf□□ace. This crucible slag is then skimmed off and discarded. To reduce the iron content to about 0.5 per cent is possible by this method but further refining is progressively more difficult. By subjecting the molten metal in the crucible to an air blast, the iron content can be reduced to 0.014 per cent.

Thus, the iron content in copper based artifacts is a useful indication of the degree of sophistication of the smelting and refining processes. If large groups of samples are considered, a trend in the amount of iron content can be seen. The iron content of the simple process copper lies between 0.005 and 0.05 per cent, whereas copper made by the more sophisticated process contains between 0.05 and 0.5 per cent after refining (14) (31).

Table 2.7.2 The iron content of copper based artifacts (15)

| Technology | Sample size | Average Fe % |
|---|---|---|
| British and Spanish Bronze Age metal | 936 | 0.05 |
| Greek, Etruscan and Roman metal | 3062 | 0.23 |
| Late Bronze Age Spain | 49 | 0.04 |
| Phoenician-Iberian Settlement, Spain | 20 | 0.36 |
| Predynastic and 1st Dynastic Egypt | 12 | 0.033 |
| 2nd Dynasty, New Kingdom Egypt | 250 | 0.33 |

### 2.7.2. Refining of Tin

Refining iron impurity from tin is a difficult process and technically, it was not available for the Early Bronze Age metallurgists

Whatever the source of iron, the formation of iron-tin compounds (hard-head) reduces the yield of pure tin metal and has an adverse effect upon its ductility. Hard-head could be removed by one or two simple refining processes. The simplest is to raise the temperature of the ingot just above the melting point of pure tin (232 °C) The liquid tin can then be drained from the solid hard-head. The process is called liquation.

The second and the more sophisticated technique is drossing which is to oxidize the iron selectively by blowing air through molten tin. The iron oxidizes to form a surface layer (dross) that can be skimmed off (2).

Copper and tin smelting are different in the way that iron is treated in the process. Iron can be drossed out of molten copper without the loss of too much copper. Iron in tin, however, forms hard-head which when drossed out of the furnace metal takes significant amounts tin with it.

As discussed previously iron has a very low solubility in tin at the melting point of the tin (232 °C) and presence of considerable amounts of iron in tin charge, lead to the formation of hard-head. The situation is especially important in the case of cassiterite mineral in which hematite is associated. Simultaneous smelting of these minerals reduces both Sn and Fe together and hard-head is formed.

Hard-head containing Sn could not be used for further alloying without refining. Since, the removal of Fe from Sn is a very technical process which was not possible for the Bronze Age smelters, it was believed that cassiterite mines which contains hematite also was not used to make tin. Kestel mine near Göltepe is an example of such mines.

If hard-head containing Sn is refined by drossing, there is also another problem such that a lot of Sn is lost when hard-head is drossed. $FeSn_2$ is 80 per cent Sn by mass. If, for example, the furnace charge contains 5 per cent Fe, 25 per cent of the mass is hard-head. Removal of it by drossing causes Sn to be lost. (31)

However, if hard-head is used to make bronze containing 10 per cent Sn, the resulting alloy would contain 2.5 per cent of iron.

$FeSn_2$ and FeSn are stable as intermetalic compounds at low temperatures. As the temperature is gradually increased, they lose their crystalline form and become a one phase liquid after 1130 °C. (See Figure 2.6.1)

In this study, this property of hard-head was used to make bronze. When Cu and hard-head were melted together, Cu acted like a solvent and extracted the Sn from the hard-head. The phenomenon is very similar to the extraction process of the organic chemistry, with Cu being the organic solvent, Sn being the organic solute and hard-head being the water phase containing the solute.

The development of this procedure proved that hard-head can be used to make bronze without refining and Kestel mine is obviously considered as a tin mine.

# III. MATERIALS, EQUIPMENT AND EXPERIMENTAL METHODS

## 3.1. Chemical Compounds and Reagents Used

(a) 65 per cent $HNO_3$ (Merck, reagent grade)
(b) 37 per cent HCl (Merck, reagent grade)
(c) 38-40 per cent HF (Merck, reagent grade)
(d) 70-72 per cent $HClO_4$ (Merck, reagent grade)
(e) $Na_2CO_3$ (Merck, Reagent grade)
(f) Charcoal, marble and sand, ground to 200 mesh (75 μm)

## 3.2. Equipment and Instruments

(a) Carbolite CWF 1200 Muffle (Chamber) Furnace
(b) Varian Spectraa 250 Atomic Absorption Spectrometer
(c) Clay bowl furnace
(d) Optical microscope

### 3.2.1. Optical Micrography

Optical micrography may be described as a method which can be applied on metal objects to examine the structure of the metal and the mineral corrosion products formed in the metal. This technique can be used for the diagnostic purposes. Metallographic samples were prepared by polishing the surface and sometimes etching by chemicals. The samples were photographed and the characterization of the different microstructural properties were examined. The theory is based on the reflection of light from the grains and grain boundaries of the crystals (16). (Fig. 3.2.1)

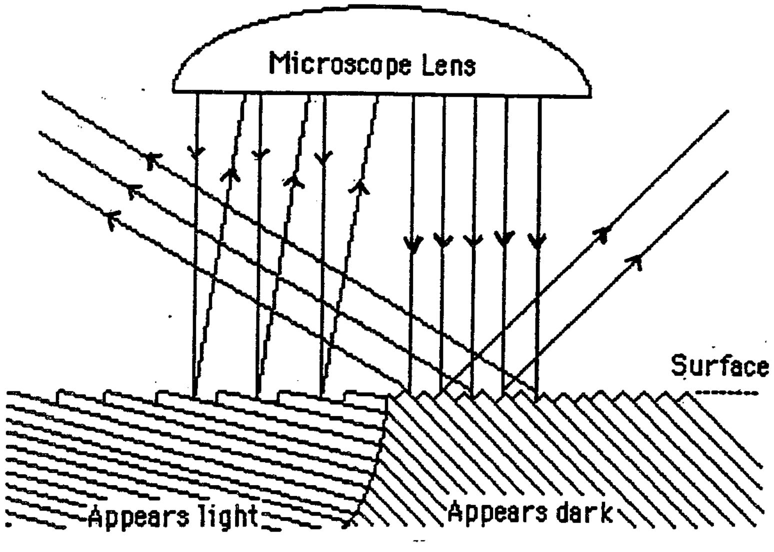


Figure 3.2.1 The theory of optical micrography

### 3.2.2. Clay Bowl Furnace

In order to follow, observe and control the conditions of the refining and alloying experiments, a clay bowl furnace was prepared. The bowl furnace is very similar to the primitive furnaces of the ancient times.

To prepare the furnace, a tin can which has a diameter of 30 cm was filled with sand and pieces of brick to the half of its height as it is shown in Figure 3.2.2. The pieces of brick was covered with a (2:1:1) mixture of clay, charcoal, and sand. Since the normal camp fire can only reach temperatures up to 600-700 °C, to increase the furnace temperature by air-blasting, a hole was opened on one side of the can through which a tuyere was placed.

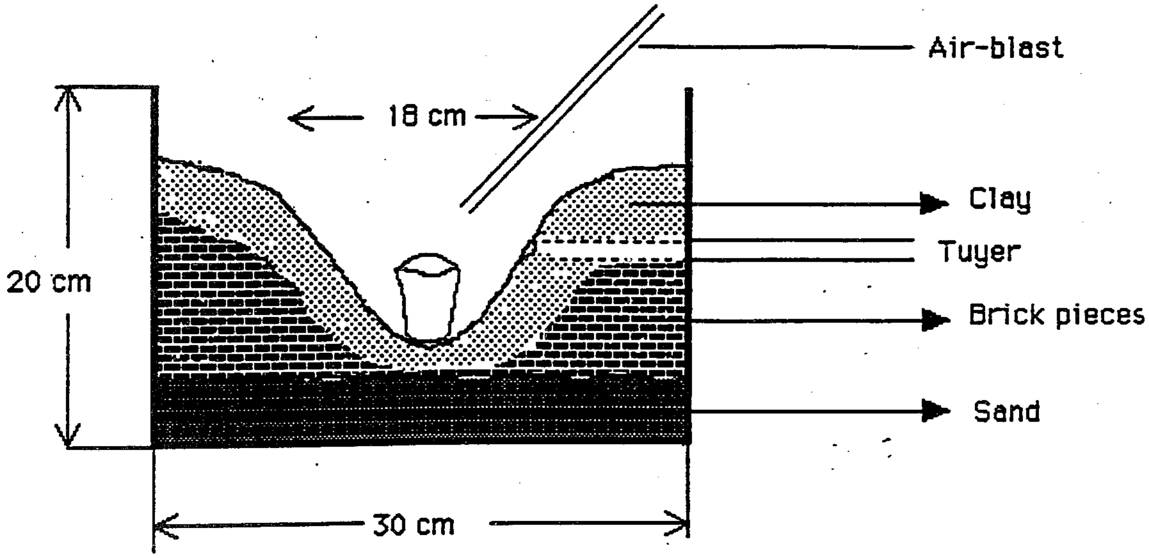


Figure 3.2.2 The diagramatic representation of a clay bowl furnace

## 3.3. Preparation of the Samples and Standards

### 3.3.1. Metallic Samples

(a) Weigh out nearly 15 mg of drilling sample in a 50 ml beaker.
(b) Add 5 ml of Aqua Regia to dissolve the sample and cover the beaker with a watch glass.
(c) Dilute the solution to 50 ml with 6 N $HNO_3$.

### 3.3.2. Nonmetallic Samples

(a) Weigh out nearly 20 mg of sample taken from a crucible slag and grounded to 200 mesh (75 μm) in a teflon beaker.
(b) Add 3 ml of HF and 1 ml of $HClO_4$ into the teflon beaker and heat to dryness.
(c) Add 5 ml of Aqua Regia and cover the beaker with a watch glass and heat gently for about 20 minutes.
(d) Dilute the solution to 50 ml with 6 N $HNO_3$.

### 3.3.3. Preparation of the Standards

A 1000 ppm stock solution is prepared by dissolving 1 g of the metal in 50 ml of acidic medium which is proper for the standard metal and diluted to 1 lt.

## 3.4. Atomic Absorption Spectroscopy

The theory is to present the analyte as an atomic vapour and to pass through it radiation of the right wavelength to excite atoms from the ground state to an excited atomic level. The light source radiates light of a frequency which is a characteristic of the element present in the vapour. Most common radiation source is the hollow cathode lamp and the atomization device is flame.

The degree of absorption is a quantitative measure for the concentration of the ground state atoms in the vapour. This is explained by the Beer-Lambert law. The extent of absorption of the radiation of particular frequency by an atomic vapour is a function of the pathlength of the absorption cell and the concentration of the absorbing atoms in the vapour.

$$I = I_o e^{-kbc} \tag{3.1}$$

where $I_o$ = intensity of the incident radiation of frequency $\nu$;
$I$ = intensity of the incident radiation after absorption;
k = absorption coefficient;
b = pathlength of the radiation through the vapour;
c = concentration of the absorbing analyte.

For analytical purposes the absorbance A is used. Thus, the absorbance is proportional to the concentration, such that,

$$A = \log I_o/I = abc \qquad (3.2)$$

where a is a constant for a given system.

Flame Atomic Absorption Spectrometry (FAAS) equipment is easy to operate. Little interference are encountered during analysis and they are usually easily controlled by background correction. FAAS is a single element technique that is ideal when one or a few elements must be determined in a large number of samples. It gives sensitive and reproducable results (32).

## 3.5. Alloying and Refining Experiments

Two sets of experimental were designed to achieve the objective of this study; preparation of bronze using tin that contains hard-head and to refine impure copper obtained from smelting of polymetallic sulphide ores.

### 3.5.1. Preparing Bronze Using Impure Tin

The common procedure used for the preparation of bronze is to melt the required amount of copper metal, in a crucible, refine it if necessary and then add the proper amount of pure tin metal to the molten copper in the crucible. Addition of tin lowers the melting point of the metal alloy which will increase the fluidity of the metal and improves its casting properties. In order to avoid contact with oxygen which will cause oxidation of the metal, the molten alloy should be poured into a mould to produce the desired objects without further delay.

If the tin used for making bronze is contaminated with iron, it should still be possible to use it to make bronze. It should be possible to refine the iron from the copper matrix without loosing any of the tin. When the tin-iron phase diagram is examined (Fig. 2.6.1), it can be seen that at 1200 °C, all tin-iron compounds are decomposed. At this temperature, copper will extract the tin and be converted to bronze. The rejected iron from the copper matrix can then be oxidized first by fire-refining and then eliminated from the molten bronze by drossing. Addition of silicates onto the molten bronze will react with the iron oxides and from iron silicates (fayalite like slags).

In the bronze making experiments, highly pure electrical wire is used as the source of copper metal which contained no iron and negligible impurities. Impure tin prills 70-1, 70-2, 70-3, 70-4, and 70-5 containing 10, 19, 25, 32, and 50 per cent iron (by weight), respectively, are prepared by fusing proper amount of commercially available tin metal and reagent grade iron metal in clay crucibles. Fusion of impure tin prills is achieved within 30 minutes in muffle furnaces kept at 1200 °C. During fusion in the muffle furnace the molten metals were covered with sodium carbonate flux to facilitate melting and with charcoal powder to prevent loss of any metal due to oxidation. Samples were drilled out from different regions of the tin-iron ingots and the places of these drilling points are shown in Table 3.5.1. The samples were dissolved according to the procedure in section 3.3.1. and the AAS analysis results of the samples drilled out from the cross-section of the tin-iron ingots are listed in Table 3.5.2. The second column in the Table 3.5.2 gives the total amounts of the tin and iron metals used for the preparation of the corresponding hard-head prills represented by numbers in the first column. The weights of the tin-iron ingots produced are listed in the third column. The recovery of the metals is almost 100 per cent meaning that the loss in the amounts of metals is negligible.

Table 3.5.1. The samples drilled out from hard-head prills

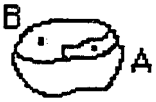
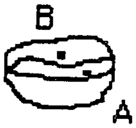
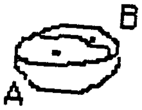
| Prill No. | Drilling Samples |
|---|---|
| 70-1 |  |
| 70-2 |  |
| 70-3 |  |
| 70-4 |  |
| 70-5 |  |

Table 3.5.2 The results of the AAS analysis of the drilling samples in Table 3.5.1

| Prill No. | Weight init.(g) | Weight final (g) | % Recovery | Drill. | Fe % theor. | Fe % calc. | Sn % theor. | Sn % calc. |
|---|---|---|---|---|---|---|---|---|
| 70-1 | 10.01 | 10.02 | 100.05 | A | 10.00 | 8.19 | 90.00 | 101.3 |
| | | | | B | 10.00 | 7.46 | 90.00 | 67.34 |
| 70-2 | 10.01 | 9.97 | 99.67 | A | 19.00 | 32.38 | 81.00 | 17.42 |
| | | | | B | 19.00 | 8.99 | 81.00 | 61.76 |
| 70-3 | 10.02 | 9.77 | 97.49 | A | 24.90 | 46.76 | 75.10 | 39.82 |
| | | | | B | 24.90 | 7.91 | 75.10 | 28.06 |
| 70-4 | 10.01 | 9.95 | 99.35 | A | 32.00 | 32.31 | 68.00 | 36.58 |
| | | | | B | 32.00 | 11.00 | 68.00 | 32.16 |
| 70-5 | 10.05 | 9.66 | 96.17 | A | 49.80 | 24.44 | 50.20 | 32.91 |
| | | | | B | 49.80 | 7.40 | 50.20 | - |

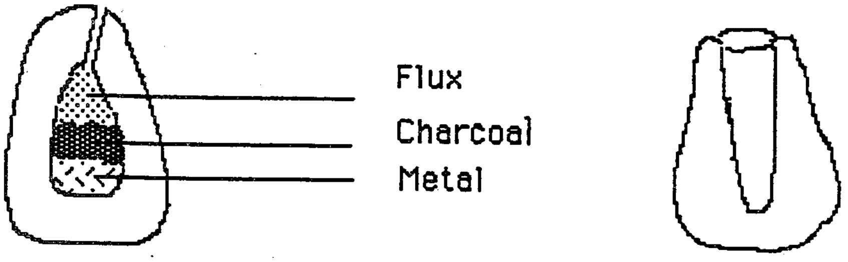
There are number of conclusions that can be made by examining Table 3.5.2. First of all there seem to be no loss or negligible loss of metal due to oxidation. After the prills are cooled, samples are removed from different parts of the prills by drilling. Second part of Table 3.5.2 shows the atomic absorption analysis of the samples for Fe and Sn content. As can be seen from the data the hard-heads produced are extremely heterogeneous. It is not possible to use sections of this prill in bronze making experiments since the amount of iron and tin added to copper cannot be estimated

Therefore smaller size (about 100 mg) prills were made. The complete hard-head prill will then be added to copper in the preparation of bronze. Since commercial porcelain and clay crucibles are too big to make prill of about 100 mg size, need for small size clay crucibles arouse.

### 3.5.2. Making Clay Crucibles

To prepare small (100 mg) hard-head prills, small crucibles were needed. These crucibles were made by using pure modeling clay. After adding the two metals, the flux and the charcoal, the top of the crucible is sealed and a small pin hole is opened so that the water vapor and the expanding gases could escape. (Fig. 3.5.1 (a) ) The early examples of these crucibles were small (about 1 1/2 cm in diameter and 2 cm in height) just enough to contain about 100 mg of Sn and Fe metals to prepare hard-head prills. After construction, the crucibles were dried in an oven for two hours at 115 °C. Unfortunately, these crucibles broke into many pieces as soon as they were placed in the muffle furnace that was preheated to 1200 °C. The most likely reason for this was either the clay was not dry enough or uneven and quick heating of the clay caused breakage.

The next set of crucibles which are prepared in similar way were left at room temperature overnight, and then further heated in an oven set at 115 °C for about 6-8 hours. When these crucibles were placed into the muffle furnace preheated to 1200 °C, again most of the crucibles broke.



(a) (b)

Figure 3.5.1 Hand-made sealed (a) and open (b) clay crucibles

It seems like plane modeling clay was not the right material for the construction of the crucibles. Therefore, new crucible construction material is prepared by mixing equal amounts (by volume) of modeling clay, clean sand and charcoal. The crucibles were kept at room temperature for four days and at 115 °C in an oven for three hours before being placed into the muffle furnace preheated to 1200 °C. Crucibles prepared by using this composition were extremely durable towards high temperatures. At these temperatures, carbon present in the clay matrix burned and produced a porous structure. This structure was able to withstand tensions build upon heating. The carbon also contributed in the creation of a reducing atmosphere in the crucible. The prills used in the bronze making experiments are prepared by using this type of crucible.

Initially mixture of 50/50 weight percent of $Na_2CO_3$ (mp 851 °C) and $K_2CO_3$ (mp 891 °C) was used as fluxing agent. However, $Na_2CO_3$ was just as successful and since $K_2CO_3$ is hydroscopic it was eliminated. The aim of adding fluxes was to lower the melting point of the hard-head and to obtain a liquid protective layer on the molten metal so that it will not react with any oxygen that may enter the crucible. Upon melting, the flux also acts like a glaze covering the clay crucible preventing metal loss and makes the crucible stronger.

Another experimental factor is the heating time. When the closed crucibles were heated for 10-15 minutes at 1200 °C in the muffle furnace, complete fusion of iron and tin was not generally observed. The charge has to be heated for about 30 minutes to form a single fused prill.

### 3.5.3. Preparation of Hard-Head Prills

After deciding the type of crucibles that should be used and the most suitable experimental conditions, many hard-head prills were prepared such as those listed in Table 3.5.3. Since major component of hard-head was $FeSn_2$ which contains about 19 per cent by weight iron, the composition Fe:Sn of hard-head prills in the bronze making experiments is kept at 20:80 per cent. The proper amounts of tin and iron were weighed out to prepare a 100 mg prill and are placed in a clay crucible with 200 mg of each charcoal and sodium carbonate. The crucibles were left at room temperature for two days and in an oven at 100 °C for six hours. After drying step, the crucibles were placed in the muffle furnace at 1200 °C for 25 minutes. First set of prill samples prepared by this procedure showed negligible loss in total mass. (Table 3.5.3) Thus it is concluded that the concentration of tin and iron in the prill is similar to the amounts placed initially into the crucible.

Table 3.5.3 Recovery of tin-iron "hard-head" prills

| Prill No. | Weight init. (g) | Weight final (g) | % Recovery |
|---|---|---|---|
| 29-1 | 0.1338 | 0.1334 | 99.70 |
| 29-2 | 0.1284 | 0.1281 | 99.77 |
| 29-3 | 0.1310 | 0.1300 | 99.24 |
| 31-1 | 0.1185 | 0.1137 | 95.95 |
| 31-2 | 0.1206 | 0.1178 | 97.68 |
| 31-3 | 0.1160 | 0.1156 | 99.66 |
| 34-2 | 0.1269 | 0.1263 | 99.53 |
| 34-3 | 0.1285 | 0.1234 | 96.03 |
| 34-4 | 0.1319 | 0.1247 | 94.54 |

### 3.5.4. Preparation and Refining of Bronze Prills Containing Impure Tin "hard-head"

In the experiments to prepare the bronze prills, proper amounts of Cu metal (about 1 grams) were used so that the ratio of Sn:Cu is kept at 10:90. Such a ratio of copper and impure tin should produce a bronze prill with an iron concentration of about 2 per cent, if no iron is lost. However, it is hoped that during the preparation of the bronze, tin will be absorbed by copper whereas, iron being not soluble in copper will be rejected. The rejected iron will then be oxidized and slagged out of the molten mass, completing the refinement experiment. Since the problem of heterogeneous prills may also take place, the complete prills are dissolved in acid and the concentration of tin and iron are determined to find the extend of refinement.

Different experimental conditions, crucibles, and different fluxing and slag forming ingredients are tried to find the best method of fire refining iron from the bronze prill.

**Trial (A)** In the first set of experiment to prepare hard-head containing bronze prills (Sample: 52-1, 52-2. 52-3, 52-4, and 52-5 in Table 3.5.4), porcelain crucibles were used. 100 mg Hard-head prill and 1 g Cu metal were weighed and placed in a porcelain crucible. The metals are covered with 500 mg of each of $Na_2CO_3$ and charcoal powder. The lids of the crucibles were closed and sealed with clay. The crucibles were placed in a muffle furnace that was preheated to 1200 °C for 45 minutes to complete fusion. At the end of heating period, it was seen that all of the clay seals were broken and two of the lids were also cracked. When the crucibles are cooled, it was seen that in crucibles with broken lids all of the carbon was combusted away and there was significant loss in the mass of the prills left in the crucible due to oxidation. The results of AAS analysis of these partially oxidized prills are shown in Table 3.5.4. It can be seen from the results that especially samples 52-4 and 52-5 with broken lids had the greatest loss in mass. Thus exposure of the metals at 1200 °C, to furnace atmosphere is not desirable, since both iron together with valuable tin is oxidized. It is decided to use sealed clay crucibles next time.

Table 3.5.4. Preparation of bronze using impure tin in porcelain crucibles

| Prill No. | Weight init. (g) | Weight final (g) | % Fe theor. | % Fe calc. | % Sn theor. | % Sn calc. |
|---|---|---|---|---|---|---|
| 52-1 | 1.47 | 1.35 | 1.83 | 0.95 | 7.29 | 2.63 |
| 52-2 | 1.42 | 1.45 | 1.75 | 0.83 | 7.38 | 7.22 |
| 52-3 | 1.44 | 1.43 | 1.74 | 1.05 | 7.27 | 5.39 |
| 52-4 | 1.39 | 1.24 | 1.84 | 0.01 | 7.19 | 1.21 |
| 52-5 | 1.37 | 1.31 | 1.90 | 0.01 | 7.19 | 4.46 |

**Trial (B)** Next set of alloying experiments were done by using crucibles made out of (1:1:1) mixture of clay, charcoal and sand. The crucibles were prepared similar to that of explained in section 3.5.2., but bigger in size. The hard-head prills and proper amount of Cu metal (about1 g) were placed in the crucible with $Na_2CO_3$ and charcoal. The crucibles were then closed and a small hole was opened on top of each crucible. After keeping the crucibles four days at room temperature and three hours at 115 °C in the oven, the crucibles were heated for 35 minutes at 1200 °C in muffle furnace. No crucibles were broken and the contents were not exposed to oxidizing atmosphere. Bronze prills samples 65-1, 65-2, and 65-3 are prepared by this procedure. The prills obtained were weighed and compared with the initial amounts. Table 3.5.5 shows the results of these experiments where almost 100 per cent metal recovery is observed. As expected the prills obtained were strongly attracted by a magnet. Since copper containing more than 1 per cent iron is attracted by magnet.

Table 3.5.5. Preparation of bronze using impure tin in closed clay crucibles

| Prill No. | Weight init. (g) | Weight final (g) | % Recovery |
|---|---|---|---|
| 65-1 | 1.2833 | 1.2702 | 99.85 |
| 65-2 | 1.2848 | 1.2848 | 100.00 |
| 65-3 | 1.3790 | 1.3769 | 99.85 |

**Trial (C)** In this set of experiments attempts were made to create oxidizing conditions in the crucibles so that iron can be refined. To achieve oxidizing conditions, open crucibles are used together with some fluxing agents. Modeling clay, charcoal and sand mixture is again used to make these open crucibles. First, proper amount of Cu metal was melted in a muffle furnace at 1200 °C in the crucible under a cover of charcoal powder-calcium oxide-powdered glass flux. As soon as Cu metal was melted, (generally in about 10 minutes) the hard-head prills were added into the crucibles and the crucibles were kept in the furnace for 10 more minutes for complete fusion to occur.

In these experiments for the first prill (Sample 76-5), only charcoal was used. For prills next (Samples 76-6 and 77-2), 2 g of (1:1:1) mixture of charcoal, CaO and powdered glass were used.

The difference between samples 76-6 and 77-2 is that in Sample 77-2, 800 mg of the flux mixture was added after the hard-head is placed over the molten copper. For the last prill (Sample 78-1), same experimental conditions as that for Sample 77-2 was used. However in this case natural fluxing agent such as powdered marble instead of CaO, and powdered river sand free of carbonates instead of glass were used. The prills were dissolved completely and analyzed by AAS and the results are tabulated in Table 3.5.6.

Table 3.5.6. Preparation of bronze using impure tin and to attempt to fire refining

| Prill No. | Weight init. (g) | Weight final (g) | % Fe theor. | % Fe calc. | % Sn theor. | % Sn calc. |
|---|---|---|---|---|---|---|
| 76-5 | 1.15 | 1.13 | 2.37 | 1.00 | 8.83 | 4.97 |
| 76-6 | 1.14 | 1.11 | 2.32 | 0.20 | 9.12 | 0.86 |
| 77-2 | 1.14 | 1.14 | 2.11 | 0.93 | 8.84 | 4.61 |
| 78-1 | 1.19 | 1.18 | 2.09 | 0.60 | 8.33 | 3.83 |

It can be seen in Table 3.5.6, that in almost all samples there were minimal loss in weight. However, together with iron, significant loss in tin content in almost all samples can be seen. Most likely before tin could be absorbed by copper, exposure of the molten metal to oxygen caused tin metal to oxidize also. The reason of the decrease in the amount of iron in the Samples 76-6, 77-2, and 78-1 is the slagging of iron oxide by silica.

**Trial (D)** To prevent the exposure of metal to the atmosphere of the muffle furnace, larger quantities of the fluxing agent and charcoal were used in this set of experiments. When the hard-head prill was added to the molten copper, the crucible was filled with further fluxing mixture. The composition of the fluxing agents used in this set of experiments are listed in Table 3.5.7. The heating temperature and duration was same as experimental conditions in Trial (C).

Table 3.5.7. Refining of bronze from iron by the addition of various flux mixtures

| Prill No. | Weight init. (g) | Weight final (g) | Flux used | Fe % theor. | Fe % calc. | Sn % theor. | Sn % calc. |
|---|---|---|---|---|---|---|---|
| 86-1 | 1.17 | 1.17 | Sand [b] | 2.37 | 2.23 | 9.28 | 9.05 |
| 86-2 | 1.19 | 1.20 | Charcoal<br>Sand [a] | 1.97 | 0.99 | 8.42 | 2.72 |
| 86-3 | 1.15 | 1.13 | Charcoal<br>Sand [b] | 2.11 | 0.31 | 8.99 | 7.29 |
| 88-1 | 1.16 | 1.15 | Marble<br>Sand [b] | 2.12 | 1.78 | 8.49 | 7.41 |
| 88-2 | 1.14 | 1.14 | Charcoal<br>Marble<br>Sand [a] | 2.22 | 1.14 | 8.93 | 6.04 |
| 88-3 | 1.11 | 1.08 | Charcoal<br>Marble<br>Sand [a,b] | 2.34 | 0.29 | 8.83 | 5.74 |
| 89-1 | 1.15 | 1.13 | Charcoal<br>Marble<br>Sand [a,b] | 2.17 | 0.46 | 9.00 | 8.40 |

a : Flux(es) was/were added before Cu was melted

b : Flux(es) was/were added after Cu was melted and Sn-Fe prills were added

The whole bronze prills obtained are then dissolved in acid and are analyzed by AAS to determine the Fe and Sn concentrations. The results are tabulated in Table 3.5.7. For the first prill (Sample 86-1), 800 mg of powdered sand was sprinkled after the addition of hard-head onto the molten mass of copper metal. The sand probably prevented the air contact of the molten mass completely. Therefore, both the loss of iron and tin is negligible. The fluxing of the next two prills (Samples 86-2 and 88-2) were done prior to melting of copper metal. The fluxing mixture probably has burned before the addition of the hard-head prills, causing the surface of the metallic molten mass exposed to air and the final amount of the tin was found to decrease considerably. The most satisfactory results are observed for the prill samples 86-3 and 89-1 where the flux mixture of (1:1) charcoal and sand and (1:1:1) mixture of charcoal, marble and sand, by weight are used respectively. It can be seen that the concentration of iron is decreased to mere 0.31 to 0.36 per cent without any significant loss in tin concentrations. The concentration of iron in most ancient copper objects believed to have been produced from copper obtained by the reduction of sulfidic ores contain around 0.5 per cent iron (12) (13). Under the melting conditions in open crucibles, iron is oxidized and reacts immediately with the silicates and forms the slag which can be mechanically removed from the top of the molten metal.

These experiments proved that it is possible to extract Sn from hard-head with Cu acting like a solvent and to remove the iron from the medium. Development of the technique makes unnecessary to refine Sn from Fe to make bronze, if tin is contaminated by iron

**Trial (E)** The best fluxing and alloying conditions used for prill 89-1 in part (D) were repeated for the preparation of another set of bronze prills. In these set of experiments, the slag formed after the addition of fluxing agents are also recovered. Prills and the crucible slags are dissolved according to the procedures presented in section 3.3 and the results are tabulated in Table 3.5.8. The results of the analyses of slags show that iron was almost completely oxidized by the flux and can be accounted for in the slag phase. It is also very satisfactory to see that tin loss from the metal is minimal and hardly any shows in the slag component. It was seen from the Table 3.5.8 that sum of the calculated iron percentages of the prills and that of the corresponding slag samples give the amount of iron which was used in preparing the prills.

Table 3.5.8 Analysis of the samples from slag of the refining experiment of bronze from iron,

| Sample No. | Weight init. (g) | Weight final (g) | Fe % theor. | Fe % calc. | Sn % theor. | Sn % calc. |
|---|---|---|---|---|---|---|
| 90-1 p | 1.10 | 1.08 | 2.24 | 0.29 | 9.45 | 9.13 |
| 90-2 p | 1.12 | 1.10 | 2.16 | 0.87 | 9.73 | 9.06 |
| 90-3 p | 1.17 | 1.17 | 2.12 | 0.36 | 8.18 | 6.28 |
| 90-1 s | 1.81 | 0.96 | - | 1.81 | - | 0.01 |
| 90-2 s | 2.11 | 1.16 | - | 1.39 | - | - |
| 90-3 s | 2.11 | 1.15 | - | 1.55 | - | 0.13 |

p = prill s = slag

**Trial (F)** In the final refining experiment fire refining method was attempted. For this experiment 20 g of copper is melted in a clay crucible under powdered charcoal which was placed to the bowl furnace as described in Figure 3.2.2. To the molten copper, 2 grams of hard head prill containing 20 per cent iron is added. The resulting alloy prill (Sample 116-5) was cooled for sampling. Three representative samples from different parts of the prill were drilled out and were analyzed for both iron and tin content prior to refining (Table 3.5.9). The prill was then placed into the crucible and heating was started. When the alloy was melted, a stream of air was blasted onto the surface of molten metal. In this experiment no fluxing agent was used. The formation of iron oxide was visiually seen on the surface of the molten alloy. The clay crucible provided the necessary silicates to form the slag.

AAS analysis of the resulting prill (Sample 116-5/1) is also given in Table 3.5.9. It can be seen that iron was effectively removed where its concentration was dropped to 0.17 per cent. On the other hand, there were only about 5 per cent loss in the amount of tin. However, considerable loss in the total mass of copper used was observed. Such loss of copper, however, could be minimized, if polling was applied or if resmelting of oxidized copper by charcoal was done after refining.

Table 3.5.9. Refining of bronze from iron by fire-refining method

| Prill No. | Weight (g) | Cu % theor. | Cu % calc. | Sn % theor. | Sn % calc. | Fe % theor. | Fe % calc. |
|---|---|---|---|---|---|---|---|
| 116-5 | 20.55 | 89.90 | 83.1 | 7.99 | 7.62 | 2.04 | 1.65 |
| 116-5/1 | 14.76 |  | 86.2 |  | 7.19 |  | 0.17 |

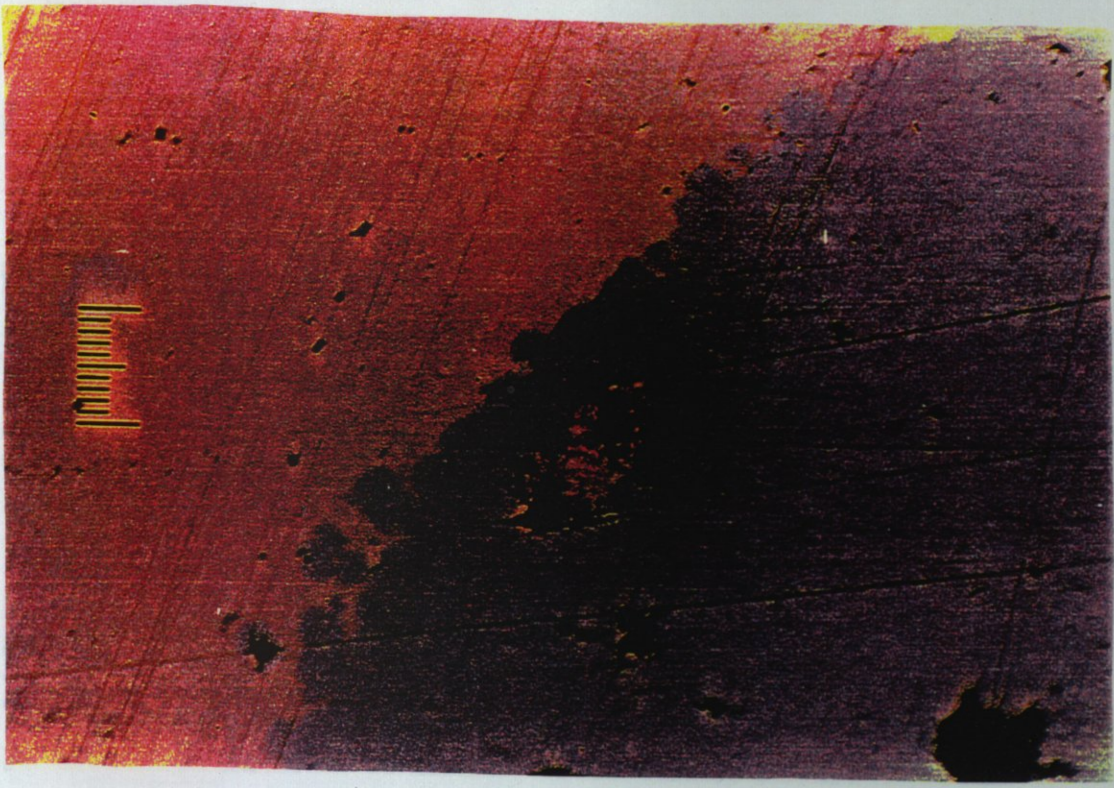
### 3.5.5. Structure of bronzes prepared by using tin contaminated by iron.

A set of experiments were done to observe the distribution of iron globules in the copper matrix of the bronze by examining the polished surface of bronze prills by optical microscope. Bronze ingots were prepared by heating of about 20 g Cu together with 2 g Sn-Fe alloy in clay crucibles. Bronze prills 43-2, 44-1, and 44-2 are prepared by the addition of Sn-Fe compounds that contain 30, 40, and 50 per cent iron, respectively. The metal charge was covered with $Na_2CO_3$ and charcoal powder to prevent the air contact and oxidation of the metals. The clay crucibles were put in the muffle furnace which was pre-heated to 1200 °C and kept in the furnace for 30 minutes. The prills were then cut into two pieces. One section was polished and its photomicrograph was taken. From the other section, two samples (A and B) were drilled out from different regions and analyzed by AAS.

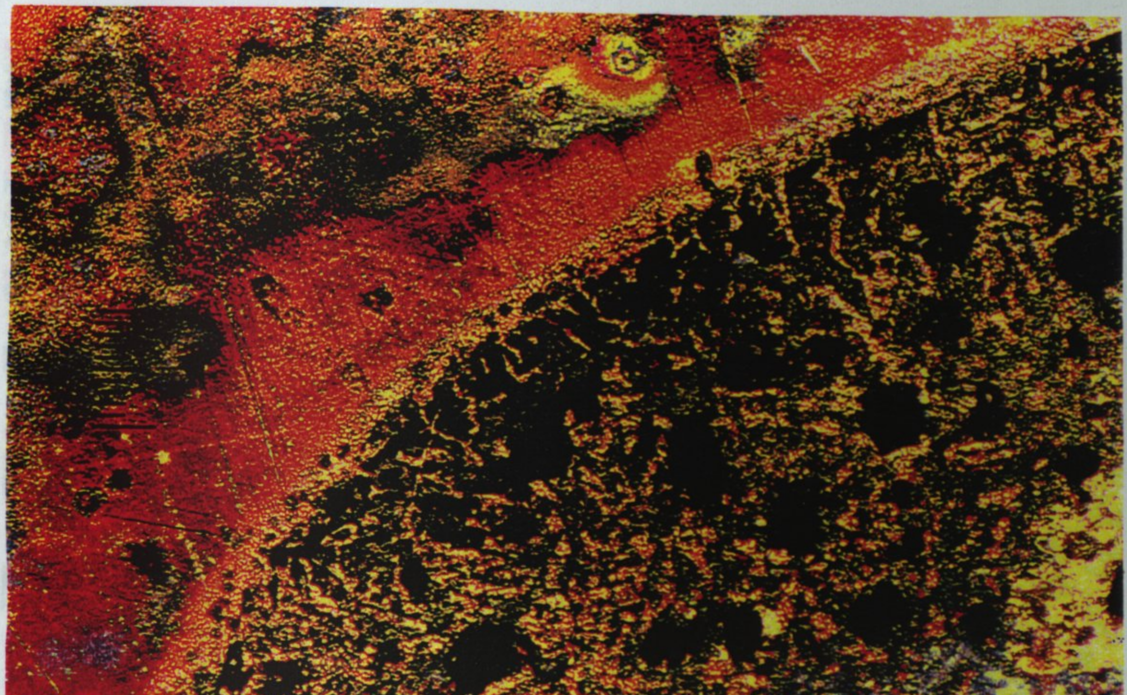
Table 3.5.10 AAS analysis results of prills prepared for optical micrography

| Sample No. | Weight (mg) | Fe % theor. | Fe % calc. | Sn % theor. | Sn % calc. |
|---|---|---|---|---|---|
| 43-2 A | 20.5 | 2.72 | 2.64 | 6.35 | 6.20 |
| 43-2 B | 20.8 | 2.72 | 16.63 | 6.35 | 5.50 |
| 44-1 A | 19.5 | 3.58 | 2.53 | 5.38 | 5.28 |
| 44-1 B | 20.6 | 3.58 | 2.39 | 5.38 | 4.74 |
| 44-2 A | 17.4 | 4.57 | 7.31 | 4.60 | 4.34 |
| 44-2 B | 15.0 | 4.57 | 2.39 | 4.60 | 4.70 |

The hard-head globules were clearly visible as white-grey colored inclusions in both faces of the cross section of the prills 43-2 and 44-2. These faces responded to hand magnet. Drilled out turnings from prills 43-2 B and 44-2 A were taken right from the hard-head regions. Their analysis results showed that the

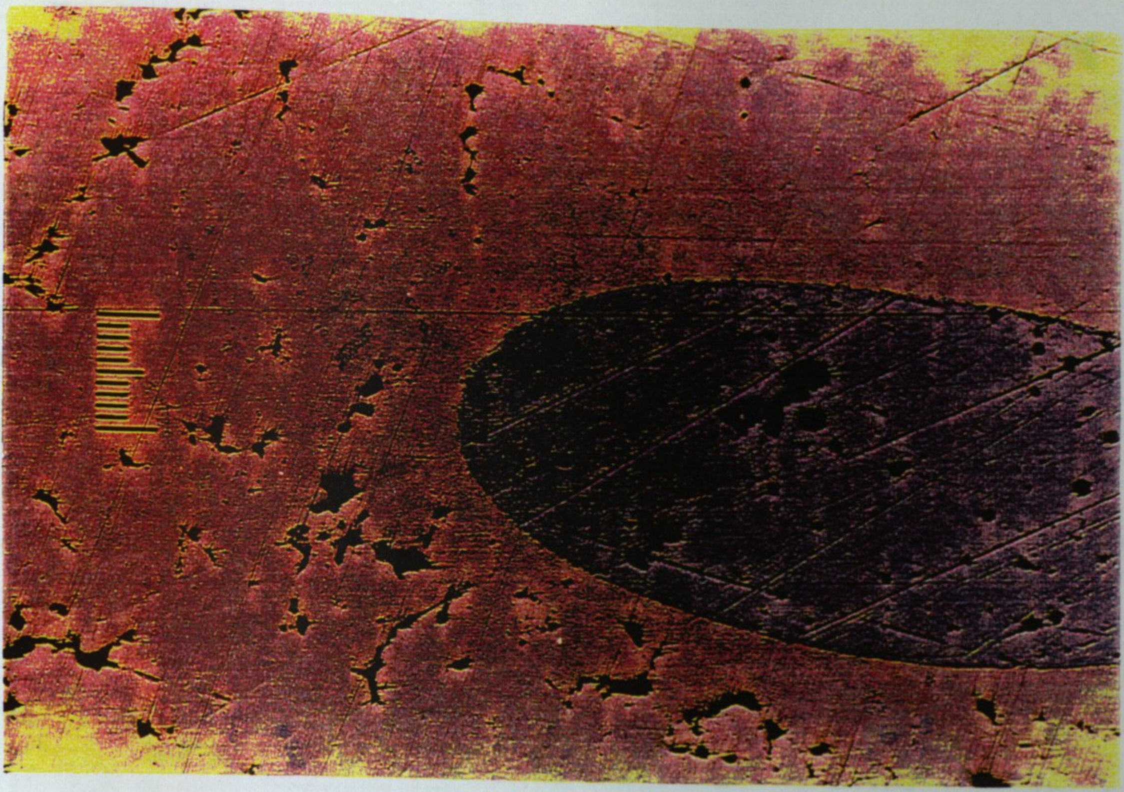


(a)



(b)

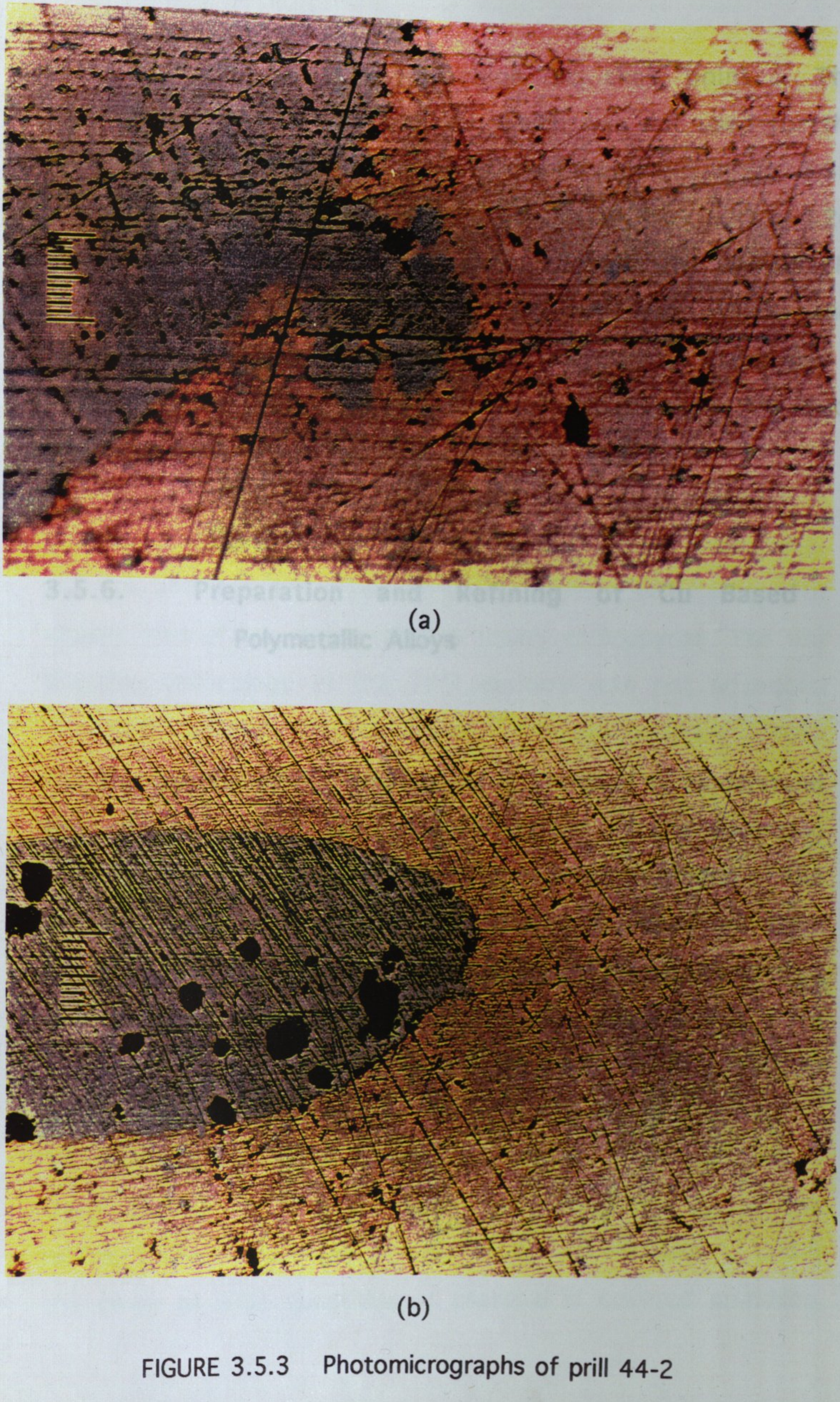
FIGURE 3.5.2 Photomicrographs of the prill 43-2



(c)

(d)

FIGURE 3.5.3 Photomicrographs of prill 44-2



(a)

(b)

FIGURE 3.5.3 Photomicrographs of prill 44-2 percentage of Fe was very high at that point. The photomicrographs of the sections, which was not used for the sampling, were taken□. The scales of the micrographs in Fig. 3.5.2 (a), (b), (c), (d),and Fig. 3.5.3 (a), (b) are 20, 50, 200, 200, and 20, 200 μm respectively. The white-grey regions in the micrographs Fig.3.5.2 (a), (b) and Fig. 3.5.3 (a), (b) are the globules of hard-head. The black inclusions in these micrograps are iron oxide diffused in hard-head. The micrographs Fig.3.5.2 (c) and (d) shows the black iron oxide inclusions in the copper matrix.

### 3.5.6. Preparation and Refining of Cu Based Polymetallic Alloys

This section of the experiments is designed to understand the copper refining technology practiced at the Bakırçay, Merzifon region during the 16th century. Carbon 14 dating of the charcoal inclusions obtained from the slag pieces are from 1453 - 1626 A.D. During the surveys in the region, number of prill samples are found among the slag piles which were extremely polymetallic in nature such as the one shown in Table 3.5.11.

Table 3.5.11 The composition of metallic prill from Bakırçay Slag Pile

| | Cu % | Fe % | Pb % | Sb % | As % | Zn % |
|---|---|---|---|---|---|---|
| Prill found | 56.2 | 5.07 | 19.2 | 6.86 | 5.77 | 1.69 |

These prills since found with the slags itself must be the impure product of smelting of polymetallic ores. The copper ores from the Bakırçay area is extremely polymetallic in character. Various ores such as pyrite, galena, sphalerite, stibnite and possibly arsenopyrite are closely associated with copper ores of the region which is mainly chalcopyrite. The ore dressing technology of the 16th century was not advanced enough to separate these ores prior to smelting. The evidence clearly shows that the ores reduced into a very complex metal without any prior ore dressing. The metal is then refined to obtain pure copper. Copper metal with the above composition would be very soft and cannot be used for most applications. Therefore, an extensive refining must have been applied.

Synthetic polymetallic copper based alloys were prepared by simultaneous heating of about 60 per cent Cu, 20 per cent Pb, 10 per cent Zn, 5 per cent Sb, 3 per cent Fe, and 2 per cent Ni together, covered with charcoal in a closed crucible in the muffle furnace preheated to 1200 °C for 30 minutes. Under the cover of large quantities of charcoal in covered crucibles, there were no loss in the mass of the metal due to oxidation. Number of prills are prepared in this way and are then used in the fire refinement experiments described by Agricola. The two examples (109-1 and 109-4) of these prills will be discussed in the following section.

The polymetallic prill is placed into a graphite crucible and melted in the bowl furnace. The reason for using a graphite crucible was to observe only the effect of air blast on the refinement of copper. No flux is used and silicates could come from clsy crucibles. When the metallic charge became molten completely, fire-refining was attempted by applying strong air blast in the bowl furnace for about one minute until solidification begins. This refinement process was repeated three times for the prill 109-1. The oxidized impurities remained on top of the molten mass and was removed after each refinement step. The remaining prill is taken out weighed and three samples were drilled out before and after each refinement and the mean of the analysis results gave the content of each refinement step 109-1/1, 109-1/2 and 109-1/3 which was tabulated below in the table 3.5.12 .

Table 3.5.12 Preparation and refining of polymetallic copper alloy 109-1

| Prill No. | Weight (g) | Cu % | Pb % | Zn % | Sb % | Ni % | Fe % |
|---|---|---|---|---|---|---|---|
| 109-1 | 20.2779 | 57.19▯ | 16.78 | 9.48 | 4.00 | 1.61 | 5.35 |
| 109-1/1 | 18.6203 | 64.24 | 16.72 | 7.97 | 4.29 | 1.58 | 1.79 |
| 109-1/2 | 14.5421 | 73.26 | 15.03 | 0.30 | 3.73 | 1.08 | 0.16 |
| 109-1/3 | 13.6227 | 78.15 | 10.87 | 0.05 | 3.43 | 1.07 | 0.08 |

After each fire refining step, weight of the prills decreased as expected mainly due to the oxidation of some of the copper. Fe and Zn showed the most dramatic refinement at the end of three refinement steps. High reactivity of iron with oxygen and its very low solubility in copper efficiently allowed it to be purified from copper. Zinc is removed due to volatilization sinc its boiling point is only 907 °C. The deposition of white Zn powder around the edge of the crucible was clearly visible. After the first application of air-blast, the crucible slag which was removed from the medium was strongly magnetic, most Fe, thus, was removed in the first step. Nickel and antimony showed only small amounts of refinement. Both of these elements form solid solutions with copper at the concentrations used in the experiment and were resistant to oxidation. This is the general trend since both nickel and antimony were considered to be elements useful for the provenance study of ancient copper objects. Most ancient copper and bronze objects contain nickel and antimony which results from the smelting of antimony and nickel containing copper ores and are not removed by refinement.

Pb metal showed the most resistantance to oxidation by air-blast. Only 35 per cent of the original lead could be oxidized and removed from the ally by simple air-blast oxidation. To remove th remaining lead probable suitable fluxes also shoud have been used.

The air blast refinement experiment as described above is repeated again with a new prill again a graphite crucible. In this experiment only two air blast refining steps are done. Similarly drilling samples were removed after each refining step and they are analyzed by AAS and the results are tabulated in Table 3.5.13. Again Fe and Zn are efficiently removed.

Table 3.5.13 Preparation and refining of polymetallic copper alloy 109-4

| Prills | Weight (g) | Cu % | Pb % | Zn % | Sb % | Ni % | Fe % |
|---|---|---|---|---|---|---|---|
| 109-4 | 20.1772 | 52.65 | 19.65 | 8.32 | 3.87 | 3.19 | 1.67 |
| 109-4/1 | 15.7080 | 69.09 | 21.17 | 3.79 | 4.50 | 1.60 | 0.41 |
| 109-4/2 | 13.1511 | 77.12 | 9.63 | 0.75 | 4.51 | 1.58 | 0.51 |

Final compositions of the prills 109-1and 109-4 are very similar to each other proving the reproducibility of the refining procedure

Figures 3.5.4 and 3.5.5 are the graphic representations of the data given in Tables 3.5.12 and 3.5.13 respectively, showing the relation between the number of refinement steps and the decreasing or increasing trend in the percentages of the constituents of the polymetallic alloys 109-1 and 109-4. Trials S1, S2, S3, and S4 stand for each step of fire-refining procedure.

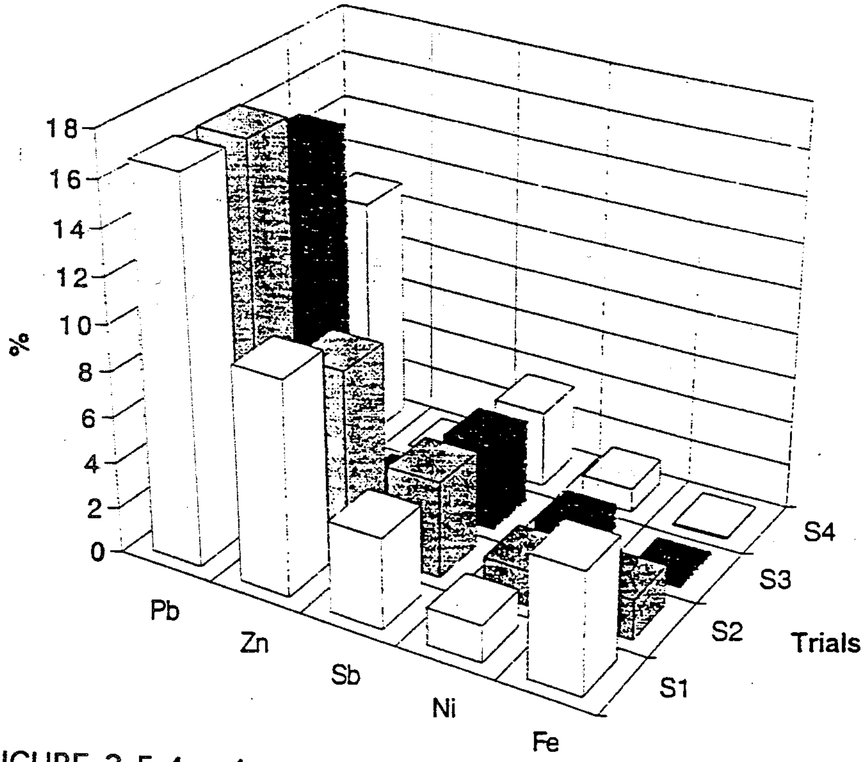


FIGURE 3.5.4 A graphic representation of refining of polymetallic copper alloy 109-1

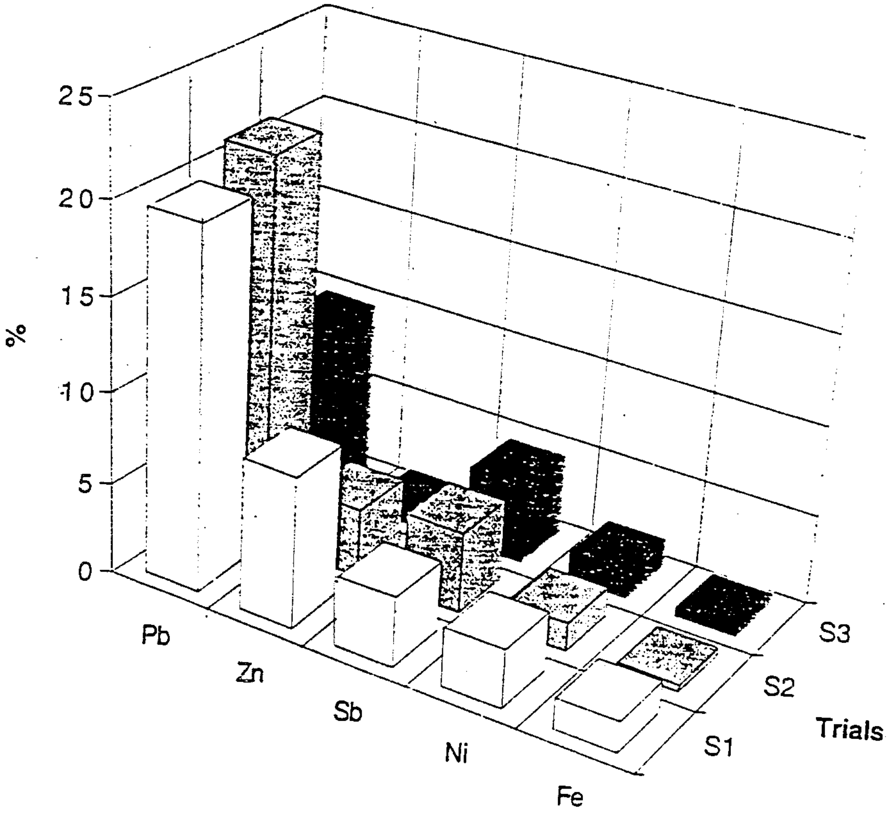


FIGURE 3.5.5 A graphic representation of refining of polymetallic copper alloy 109-4

# IV. CONCLUSION

Large amounts research have been conducted to determine the major, minor and trace elements present in ancient copper and bronze objects. The source of these impurities are mainly from the nature of polymetallic copper ores, fluxes and fuels utilized. Similarly smelting and refining operations had adverse effect on their concentration.

The type and the amounts of such impurities in copper have dramatic effects on the mechanical properties of the metal. Ancient metal smith were very quick to recognize such alloying effects without much knowledge on the structure of metals. Considerable experimentations must have been carried out by the ancient metal smith either to remove some of the unwanted impurities or to introduce certain metals on the long path to the invention of intentional alloys.

In this study similar ancient working conditions and techniques are utilized that are believed to have been performed by the ancient metal smith and it is proven that it is quite easy to change the concentration of various impurities in copper and purify it to desired quality.

In the first set of experiments, it was shown that it was possible to make good quality bronze using tin metal that contains considerable amounts of iron. Since tin was very scarce during the Bronze Age it must have been important for the ancient metal smith not to waste any portion of it. It is now proven that even tin-iron alloy (hard head) which cannot be further purified to obtain pure tin can be used to make bronze. It can be seen from the tin-iron binary phase diagram that at 1200°C iron and tin dissociate completely. When copper is added to this mixture at the same temperature, both iron and tin are solubilized in copper. Upon cooling, however, tin remains in copper forming the desired bronze where as insoluble iron is rejected from the alloy while tin is preferentially kept in copper. Iron oxide is then selectively fire refined and is slagged and removed by the addition of silicates.

Second important aspect of this study was to show if extremely polymetallic copper ores which could not be purified by simple ore dressing methods could be utilized as source of copper metal. Metallurgical debris found at Bakırçay, Merzifon region and dated to 15th century A.D. clearly indicated the utilization of such polymetallic ores. Copper prills found at Bakırçay contained considerable amounts of lead, iron, arsenic, antimony, and zinc. Such an alloy cannot be utilized without extensive refining.

In this work copper alloys of similar composition to those observed at Bakırçay were prepared. The alloys were then subjected to fire refining experiments using air blast. Analysis of the alloy at each purification step showed that iron and zinc were completely purified from the alloy. Antimony and nickel, on the other hand tend to form solid solution with copper at the present concentrations and were more resistant to refining. Lead was the major impurity in Bakırçay copper. Even though lead and copper do not form solid solution, it was not possible to remove all of the lead by simple fire refining method. Lead content of Bakırçay prills were as much as 20 per cent and extended fire refining also caused the loss of copper by oxidation. During the experiments removal of only half of the lead in the alloy were achieved by fire refining.

However, it should be possible to remove almost all of the lead from copper without any loss in copper. I believe further work on the refinement of lead from copper should be carried out possibly utilization of various fluxing agent that could accompany fire refining.

# APPENDIX A

Following section summarizes the experimental procedures of preparation and refining methods of hard-head and copper alloy prills. The amounts are given approximately.

For the prills 29-1, 29-2, 29-3, 31-1. 31-2, 31-3, 34-2, 34-3, 34-4:

Procedure : Preparation

Contents : 80 per cent Sn, 20 per cent Fe

Flux : Sodium carbonate, charcoal

Crucible Type : Closed clay

Heating Period : 25 minutes in 1200 °C

Furnace Type : Muffle

For the prills 43-2, 44-1, and 44-2:

Procedure : Preparation

Contents : 90 per cent Cu, 6 per cent Sn, 4 per cent Fe

Flux : Sodium carbonate, charcoal

Crucible Type : Closed clay

Heating Period : 30 minutes in 1200 °C

Furnace Type : Muffle

For the prills 52-1, 52-2, 52-3, 52-4, and 52-5:

Procedure : Preparation

Contents : 91 per cent Cu, 7.20 per cent Sn, 1.8 per cent Fe
Flux : Sodium carbonate, charcoal
Crucible Type : Porcelain
Heating Period : 45 minutes in 1200 °C
Furnace Type : Muffle

For the prills 65-1, 65-2. and 65-3:

Procedure : Preparation
Contents : 90 per cent Cu, 8 per cent Sn, 2 per cent Fe
Flux : Sodium carbonate, charcoal
Crucible Type : Closed clay
Heating Period : 25 minutes in 1200 °C
Furnace Type : Muffle

For the prills 76-5, 76-6, 77-2, and 78-1:

Procedure : Refining
Contents : 90 per cent Cu, 8 per cent Sn, 2 per cent Fe
Flux : Calcium oxide, powdered glass, charcoal
Crucible Type : Open clay
Heating Period : 20 minutes in 1200 °C
Furnace Type : Muffle

For the prills 86-1, 86-2, 86-3, 88-1, 88-2, 88-3, and 89-1:

Procedure : Refining
Contents : 90 per cent Cu, 8 per cent Sn, 2 per cent Fe
Flux : Powdered marble, powdered sand, charcoal
Crucible Type : Open clay

Heating Period : 20 minutes in 1200 °C
Furnace Type : Muffle

For the prills 90-1, 90-2, and 90-3:

Procedure : Refining
Contents : 90 per cent Cu, 8 per cent Sn, 2 per cent Fe
Flux : Calcium oxide, powdered glass, charcoal
Crucible Type : Open clay
Heating Period : 20 minutes in 1200 °C
Furnace Type : Muffle

For the prills 109-1 and 109-4:

Procedure : Preparation/Fire-refining
Contents : 60 per cent Cu, 20 per cent Pb, 5 per cent Zn,
5 per cent Sb,3 per cent Fe, 2 per cent Ni
Flux : None
Crucible Type : Graphite
Heating Period : 20 minutes for the preparation in 1200 °C
Furnace Type : Muffle for preparation/Clay bowl for fire refining

For the prill 116-5:

Procedure : Preparation/Fire-refining
Contents : 90 per cent Cu, 8 per cent Sn, 2 per cent Fe
Flux : None
Crucible Type : Open clay
Heating Period : 20 minutes in 1200 °C
Furnace Type : Muffle for preparation/Clay bowl for fire refining

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