THE EXAMINATION OF METAL WORKING TECHNOLOGY
IN KÜLTEPE
IN ASSYRIAN TRADE COLONIES PERIOD


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# ABSTRACT

## THE EXAMINATION OF METAL WORKING TECHNOLOGY
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Metal played important role in the social and economic development of societies since its discovery. It is so important that the some part of humankind historical development were designated by the type of metal which was extensively used depending upon the level of technology of that period enabling the processing of metal like bronze age and iron age.

In this frame, the rich metal deposits of Anatolia made this region a very important metal working and civilization center.

Kültepe where it was the center of the trade organization in Anatolia realized between Assur and Anatolia during 1945-1730 B.C called Assyrian Trade Colonies Period was one of the most important metal working center of Anatolia at that period.

In this thesis, it is aimed to make a contribution to understand the metal working technology in Kültepe by examining the uncovered metal artifacts dated to that period.

For this purpose, the metal artifacts uncovered from Kültepe Ancient Site belonging to Colonies Period which are exhibited in the Anatolian Civilization

Museum were examined by portable XRF (PXRF) to obtain the quantity of elements that constituted the artifacts without giving any harm to the artifact.

Besides the examination of exhibited artifacts in the Anatolian Civilization Museum, the uncovered metal artifact parts belonging to Colonies Period which are not suitable for exhibition and separated for studying were examined by energy dispersive X-ray unit of scanning electron microscope for elemental analysis and by X-ray diffraction for the analysis of minerals.

The microstructures of artifacts were examined by scanning electron microscope and optical microscope for revealing the operations on metal applied by ancient metalsmith.

In addition to analysis mentioned above, in order to make a contribution to understand the copper trade between Kültepe and its environs lead isotope analysis of some samples from the separated metal artifacts for studying was also performed.

As a result of all those analyses, it was concluded that Kültepe ancient metalsmiths in Colonies Period had the knowledge to smelt the copper and to pour molten metal into a mold to produce an object of desired shape. Moreover, they also discovered that the addition of some elements to copper hardens the structure. In this frame the bronze to be obtained by deliberately adding of tin to copper was attained.

In addition, they were aware of shaping the casted object by hammering. In the meantime, they had the knowledge of heat treatment that allows them forging the object many times till giving the desired shape without causing the fracture in the structure.

Keywords: Archaeometallurgy, Kültepe, Metal Working Technology, Corrosion, Lead Isotope Analysis, PXRF

# ÖZ

## ASUR TİCARET KOLONİLERİ ÇAĞINDA KÜLTEPE METAL İŞLEME TEKNOLOJİSİNİNİN INCELENMESİ

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Metal, kullanımının keşfinden bugüne toplumların sosyal ve ekonomik gelişimlerinde önemli bir rol oynamıştır. Bu önem, insanoğlunun tarihsel gelişiminin bir kısmının, dönemin teknolojik seviyesine bağımlı olarak kullanılan metalin niteliğine göre, bronz çağı, demir çağı olarak isimlendirilmesine yol açmıştır.

Bu çerçevede, Anadolunun zengin metal kaynakları bu bölgeyi önemli bir metal işleme ve uygarlık merkezi haline getirmiştir.

Asur Ticaret Kolonileri Dönemi olarak adlandırılan M.Ö. 1945-1730 tarihleri arasında, Asur Devleti ve Anadolu Krallıkları arasında gerçekleşen ticari organizasyonun Anadolu'daki merkezi olan Kültepe o dönemin Anadoludaki önemli metal işleme merkezlerinden biridir.

Söz konusu döneme ait çıkarılan metal eserlerin incelenerek, Kültepe'de metal işleme teknolojisini anlamaya yönelik bir katkı oluşturmak bu tezin amacını oluşturmaktadır.

Bu doğrultuda Koloni Dönemine ait Kültepe Arkeolojik Kazı Alanından çıkarılan ve Anadolu Medeniyetleri Müzesinde sergilenen metal buluntular, objelere herhangi bir zarar vermeden taşınabilir XRF (PXRF) cihazı ile incelenmiştir.

Bununla birlikte; kazı sırasında bulunan ve sergilemeye uygun olmayan Koloni Dönemine ait tasnif dışı etüdlük metal parçaların, element analizi için

elektron tarama mikroskobuna bağlı, X-ışını analizörü, minerallerin belirlenmesi için de X-ışını kırınım analiz cihazı kullanılmıştır.

Söz konusu örnekler üzerinde geçmiş dönem Kültepe metal ustalarının uyguladığı yöntemleri ortaya koyabilmek için gereken mikroyapı analizleri de optik mikroskop ve tarama elektron mikroskobu ile gerçekleştirilmiştir.

Yukarıda değinilen analizlere ek olarak, Kültepe ve çevresi arasındaki bakır ticaretini anlamaya katkı sağlamak amacıyla söz konusu etüdlük malzemelerin bir kısmının kurşun izotop analizi de yapılmıştır.

Tüm analizlerin sonucunda; Koloniler Dönemi Kültepe metal ustalarının bakırı eritip, erimiş metali bir kalıbın içerisine dökerek istedikleri şekildeki objeleri üretme bilgisine sahip oldukları anlaşılmıştır. Ayrıca, bakıra bazı elementler katarak yapıyı sertleştirmeyi de keşfetmişler ve bu çerçevede bakıra bilinçli bir şekilde kalay katarak bronzu elde etmişlerdir.

Ek olarak, dökümle elde edilmiş objelere dövme ile şekil verilebileceğinin ve aşırı dövmenin yapıda çatlamaya neden olduğunun farkında oldukları, aynı zamanda objeyi kırmadan istenilen şeklin verilmesine kadar dövmeyi sağlayacak ısıl işlem uygulama bilgisine de sahip oldukları anlaşılmıştır.


Anahtar Kelimeler: Arkeometalurji, Kültepe, Metal İşleme Teknolojisi, Korozyon, Kurşun İzotop Analizi, PXRF

# ACKNOWLEDGEMENTS

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# CHAPTER 1

# INTRODUCTION

Metal played important role in the social and economic development of societies since its discovery. It is so important that the some part of humankind historical development are designated by the type of metal which was extensively used depending upon the level of technology of that period enabling the processing of metal like bronze age and iron age.

The usage of metal has not appeared spontaneously. First, our ancestors have controlled fire and learned to use it in processing of many things in their life. In archaeological site, Chesowanja in Kenya dated by 1.5 million years, it is possible to find the evidence for usage of fire by human from magnetic measurements of burnt clay (Gowlett 1984).

While the direct ancestors of modern human were living in caves 10000-30000 years ago, the first steps towards the metallurgy appeared as drawing sketches belonging to their life by using materials like iron oxide.

The struggle of man with nature to survive made him explore his environment and find new materials which were superior compared to the used ones in terms of facilitating his life.

The most important one of these materials was copper which is relatively soft metal existed in nature in pure form, which enabled easily processing for new shapes.

Since iron and tin are both more difficult to be reduced to metallic state compared to copper, it is not surprising that copper was the first metal to be produced by man (Thompson 1958).

The earliest examples of metal objects uncovered in Anatolia were mainly malachite and native copper artifacts in the beginning of settled farming communities that is called Aceramic Neolithic dated 8th millennium B.C. (Yener 2000).

The first uncontested use of metallic copper dated to the the late eighth millenium has been come to light with more than fifty artifacts. Some of them showed the evidence of recrystallization which indicates that the objects had been annealed during the working stages on them at the aceramic Neolithic site of Çayönü Tepesi in southeastern of Turkey (Muhly 1986).

The intermediate period between the Stone Age and the Bronze Age has been called with a name deriving from the combination of materials to be used extensively at that periods; Chalcolithic Period, from the Greek *chalcos,* copper and *lithos,* stone.

The first copper tools were uncovered in Hacılar settlement dated to 5500 B.C. near Burdur. Therefore, Chalcolithic Age that copper appeared in production of some tools beside stone commenced at this date and prevailed between 5500 and 3000 B.C. in Anatolia (Akurgal 2000).

The efforts of man to obtain the better, opened the way to bronze which is the combination of copper with tin and/or arsenic, the right proportions resulting in significantly harder than copper.

The arsenic bronze was the pioneer of development of tin bronze and in Near East and Europe arsenic bronze was processed throughout approximately two millennia with the beginning in the late fifth and first half of the fourth millennia B.C. (Lechtman 1996).

Bronze appeared in Anatolia at the end of Chalcolithic Period. However, the usage of it in the production of pots and pans and tools has been observed at the beginning of 3000 B.C. (Akurgal 2000).

Bronze Age showed three stages progression in Anatolia (Akurgal 2000):

Early Bronze Age; (3000 – 2500 B.C.)

Middle Bronze Age; (2500 – 2000 B.C.)

Late Bronze Age; (2000 – 1200 B.C.)

Together with the fact that copper became very important material in the production of the essential tools and warfares of man's daily life, the consumption of copper increased and the native copper to be cropped out easily at the surface disappeared. This resulted in the efforts of man for extracting the copper from its ore by openning galeries below the surface.

As it is summarized above, considering the complex industry from mining operations to extracting the metal and from casting to hot, cold working processes behind the acquiring the tools made from metal, it is asserted that the history of human being can not be written without considering the influence of metal on the ancient socities as well as today's.

The availability of copper, arsenical copper, and later tin bronze made possible the production of tools which developed new crafts and revolutionized warfare with the development of weapons (Gale et al. 1985).

The appearance of metallurgy were especially encountered in the semiarid mineralized zones of the Anatolian and Iranian plateaus (Wertime 1964).

Since the metal is one of the essential commodites which contribute the wealth of societies, it has become one of the most important exchange material between the societies since ancient times.

In this respect, Anatolia appeared as attractive region which has plenty of mineral resources. Therefore the rich metal deposits and strategic geographical location of Anatolia made this region a very important metal supplier and metal working center.

As mentioned above, the fact that Anatolia has important metal resources and metal is a very strategic commodity in the wealth of societies in past as today enabled this geography as an intersection point of many ancient trade routes. The trade between Anatolia and Assyria to be located in North Mesopotamia was a very good example for the merchandise exchange mainly based on the metal.

The trade with Anatolia was very important for Assyrians since Assyria was devoid of essential mineral resources like the other parts of Mesopotamia (Dercksen 1996).

The basic pattern of the Old Assyrian trade was shipping of large quantities of tin and textiles from Assur to Anatolia for exchanging with silver and occasionaly gold besides the bronze was exported to Assur in the form of manufactured goods not as raw material (Larsen 1976).

Metal was the essential merchandise of this trade. Tin which is required to make bronze alloy by adding to copper was exported to Anatolia while silver and gold were conveyed to Mesopotamia by Asyrian merchants.

The trade period realized between Assur and Anatolia during 1945-1730 B.C. was called as Assyrian Trade Colonies Period which was based on the very high standard administrative rules.

## 1.1. Aim of the Study

Kültepe (ancient Kanesh) which is located at 21 km to the northeast of Kayseria (present Kayseri) the capital of the Kingdom of Cappadocia, was the administrative center of the ten colonial centers called Karum established by the Assyrians in Anatolia. All the other nine Karum were administered by Karum of Kanesh, which directly was affiliated with Assur. Kanesh was the centre which organizes the relations between the Anatolian Karums and the capital, Assur (Özgüç 2005).

Kanesh Colony established in the Kingdom of Kanesh has a very strategic position on the Anatolian plateau which was the first stop of the trade in Anatolia. Then the merchandises were distributed to Anatolia by commissioned agents (Larsen 1976).

Kültepe Archaeological Site, besides many tablets which include texts written in cuneiform script revealing how a great trade system of ancient world was organized have been uncovered there, at the same time, shelters many brilliant metallic artifacts of its age. This can be interpreted as the usual result of the position of the Kültepe in trade system.

It is understood from the sophisticated metal artifacts uncovered from the excavations that metal craftsmanship in Kültepe had reached high skilled level.

Therefore, it is thought that understanding of the technology that the ancient Kültepe metallurgist attained may provide new knowledge which is useful to link the metal working centers in Kültepe and with neighbors from the standpoint of archaeometallurgical studies in Anatolia

The detailed examination of metal processing in Kültepe has not been performed so far except Ufuk Esin's study which was published on the quantitative spectral analysis of some metal artifacts uncovered from many ancient sites of Anatolia including Kültepe.

This thesis has been initiated to make a contribution to understand the metal working technologies in Kültepe, which has not been realized in comprehensive manner till now. In other words, the objective of this study is to reveal all the processes applied on the metal to change it to a commodity by craftsmen in Kültepe where it was the center of the trade organization in Anatolia realized between Assur and Anatolia during 1945-1730 B.C called Colony Period by examining the uncovered metal artifacts dated to that period in Kültepe.

In this frame, this thesis is composed of six chapters:

With the introduction chapter; it is aimed to emphasize why it is attempted to make such a study in the frame of the selected region, Kültepe where it was the center of a trade organization in Anatolia, which was unique at that period and selected material, metal which is very strategic commodity in the wealth of societies in past as today.

The second chapter involves the brief explanation of ancient copper metallurgy which evolves from usage of native copper to processing copper as a result of a complex industry including mining, extracting and moulding.

The third chapter comprises the importance of Kültepe where its metal production capability was intended to be examined in Colony Period which is unique in terms of well documented trade system according to its age for Anatolian history.

The fourth chapter covers the identification of all the materials and their examination methods for accomplishing the aim of the study.

At the fifth chapter it has been focused on the results of examinations and related discussions with those.

Naturally, as the last chapter, chapter six has been the section which involves the conclusions to be arrived as a result of examinations and suggestions for further studies.

# CHAPTER 2

# ANCIENT COPPER METALLURGY

It is easily asserted that there has not been any material which is so important like metal to change and control his environment throughout the history of man.

It is so important that the some part of humankind historical development are designated by the type of metal which was extensively used depending upon the level of technology of that period enabling the processing of metal like bronze age and iron age.

## 2.1. Origins of Metallurgy

The usage of metal has not appeared spontaneously. First, our ancestors have controlled fire and learned to use it in processing of many things in his life.

In archaeological site, Chesowanja in Kenya dated by 1.5 million years, it is possible to find the evidence for usage of fire by human from magnetic measurements of burnt clay (Gowlett 1984).

The experience to be gained with daily life usage of fire throughout a very long period of life span of our ancestors enabled them to get the knowledge on the interaction of material which has existed in his environment with fire.

While the direct ancestors of modern human were living in caves approximately 10000-30000 years ago, the first steps towards the metallurgy commenced to appear by using materials like iron oxide to draw sketches belonging their life.

The main material that were used at that period was stone and therefore this age is called as paleolithic from the Greek paleo, old and lithos, stone.

Paralel to the development of knowledge in using available materials that man attained from his living environment, the effective use of fire has also been improved.

Fire-hardening of wooden spears and applying heat to stones for shaping into tools or weapons was the application of such developments.

## 2.2. The Usage of Native Copper

As mentioned above, the struggle of man with nature to survive made him explore his environment and find new materials which were superior compared to the used ones in terms of facilitating his life.

The most important one of these materials was copper which is relatively soft metal existed in nature in a pure form, which enabled easily processing for new shapes.

It is generally accepted that the first metals exploited by man were native variety, where these occur, the earliest would be the nuggets of gold to be seen in the gravels of river beds (Thompson 1958).

Therefore, it may be asserted that the first copper which man attained was also the native metal to be collected from the surface easily.

The brilliant and attractive colour of the native copper must have attracted the attention of early man wherever they cropped out at the surface (Thompson 1958).

Discovering of forming this new material into different shapes by hammering would not take too much time. Hammering of the metal provides hardness increasing and renders it brittle that means, when further working results in the development of cracks (Thompson 1958).

The ancient craftsmen learned to hammer for giving the desired shape resulted in increasing of hardening and brittleness of material. Since they had experience with pottery firing, heat treatment may have followed the cold hammering to reduce brittleness and to give the chance for reworking.

In fire-using industries such as the making of pottery and bricks and the glazing of ornamental objects, artisans had achieved temperatures well above the melting point of lead (327 $^0$C) and close to that of copper (1083 $^0$C) (Wertime 1964).

The next stage which is the melting of copper was the target for the ancient metalsmith. A temperature of 1083 $^O$C which is the melting point of copper can not be obtained in an ordinary fire without some form of forced draught.

The first uncontested use of metallic copper dated to the late eighth millenium was observed at the aceramic Neolithic site of Çayönü Tepesi in southeastern of Turkey. Some of over fifty artifacts made of metallic copper which were uncovered from that excavation showed the evidence of recrystallization indicating that the objects had been annealed during the working stages on them (Muhly 1986).

The intermediate period between the Stone Age and the Bronze Age has been called with a name deriving from the combination of materials to be used extensively at that periods; Chalcolithic Period, from the Greek *chalcos* 'copper' and *lithos* 'stone'.

This period was not short. It took a very long time that copper proved itself against common usage of stone and flint, while more and more deposits of copper ore were being found and while the technique of extractive metallurgy spreads in essentially lithic society (Tylecote 1992).

Chalcolithic Period prevailed in Anatolia between 5500 and 3000 B.C. (Akurgal 2000).

It has been argued that prior the third millennium B.C., the effect of metal was not considerable in the social and economic development of society and its role was limited with the local use of native metals within the regions that native metals like gold and copper were abundant (Muhly 1989).

Ancient metal workshops and any metal craftman's tools have not been encountered in the excavations in Mesopotamia which has no local sources of metal. They imported metal in the processed or semi-processed form from Turkey, Iran, Afghanistan and Oman before 2200 B.C. (Moorey 1986).

## 2.3 The Extraction of Copper From Ores

As stated above, at first the ancient metallurgists exploited the native-copper nuggets and they were not aware of the impurities in the copper which were used for processing according to their requirements. However with the increasing of the demand paralel to discovering of strong features of copper with respect to stone, the first early ore discoveries were worked out, they mined deeper, and began to reach first copper oxide and carbonate ores and then copper sulfide ores that were more difficult to smelt and less pure.

Where ore bodies crop out at the surface as a result of weathering they tend to become oxidized and to disintegrate. As the depth of mining increases, therefore, they not only tend to become harder but may also change radically in composition. Therefore, the first ores to be smelted were the oxide and carbonate ores such as cuprite ($Cu_2O$) and malachite [$Cu_2CO_3(OH)_2.H_2O$]. Since the sulphide ores require more advanced metallurgy and they are found in deep with respect to oxidized ores, it probably took some time to exploit them before necessary techniques were developed by ancient craftsmen (Thompson 1958).

Reduction of copper oxide and copper carbonate ores to the metal consists of only a heating process with charcoal to a temperature around 600 $^o$C while copper sulphide ores requires preheating process called roasting to reach oxide forms of copper before main heating process.

The smelting of sulphide ores presents additional problems as compared to the treatment of oxides and carbonates ores. Since cuprous sulphide cannot be reduced to metal by heating it with carbon unlike in case of oxide ores, the first stage for extracting of copper from sulphide ores is the roasting process which is simply the heating of heap to a relatively low temperature (Thompson 1958).

As a result of the change in copper source which means passing from oxide copper ores to sulphide ores, arsenical copper appeared in man's life. It is now generally agreed that arsenical copper was produced by the direct smelting of an arsenical copper ore. Therefore the amount of arsenic in the smelted copper completely depends on the arsenic content of the ore.

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If the ore includes arsenic and antimony, the oxidation of these elements to $As_2O_3$ and $Sb_2O_3$, respectively, results in these volatile compounds being carried away in the fumes from the heap. However some part of these elements are converted into the higher oxides $As_2O_5$ and $Sb_2O_5$, which combine with the metallic oxides to form much more stable arsenates and antimonates. These being non-volatile at the ordinary roasting temperatures are subsequently reduced with, and pass into the copper. The proportion of these elements present in the ore which ultimately enters the metal depends on the exact conditions under which the roasting is carried out. It will depend on such factors as the size of the pieces of ore, the way these are packed, the air supply, the time and the temperature reached, i.e. how well the lumps of ore are broken down, how loosely the heap is packed, and whether the wind is strong. Therefore, no direct correlation exists between impurities content of the ore and acquiring metal after smelting. As a result of these parameters, the metal composition attained after each smelting may have varied (Thompson 1958).

The extraction of the metal from pure cuprous sulphide ores presents no difficulty. Complete elimination of the sulphur and the conversion of the sulphide to the oxide was attained by roasting easily, followed by reduction as before with charcoal (Thompson 1958).

In the case of copper pyrites, a mixed sulphide of copper and iron, the operation is far more complex. As a result of the roasting the ore has been partially desulphurized and partly oxidized, and consists, at any rate for our purpose, of the sulphides of copper and iron together with oxide of iron in varying proportions depending on the exact nature of the roasting process. The extraction of the copper in a state of reasonable purity from this roast presents far greater difficulties than obtain with the reduction of carbonate or the pure sulphide ores since the amount of iron present normally far exceeds that of the copper, and it is the removal of this iron which is the real problem (Thompson 1958).

Copper arsenic alloys in varying arsenic content depending upon the produced ore, were the main metal composition produced and used throughout the Near East during the 4th millennium BC to the late Bronze Age, (Ryck et al. 2005).

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Local arsenic-bearing copper ores had been smelted by local Anatolian metal workers to produce arsenic bronze and caused to develop an important industry during the period 3400–2900 BC, which is earlier than the start of production of tin bronze in Mesopotamia (Yener 2000).

When considering the complex industry from mining operations to extracting the metal and from casting to hot, cold working processes behind the acquiring the tools made from metal, it is asserted that the history of human being can not be written without considering the influence of metal on the ancient societies as well as today's. In other words, the entrance of metal to man's life brought the very complex structure which involves very serious work branching and expertising behind it.

The production of metal artifacts requires a specific body of knowledge and skills which imply an efficient utilization comprising the stages: prospection, mining, beneficiation, smelting, or roasting and smelting, refining, alloying, and so on.

### 2.3.1 Prospection

Exploring of the ore that fulfills the metalsmith's requirement which means copper containing ore, needs a skilled person who learned many clues with experience like the colour and taste of water near a mineral source to prospect the exact ore. However, prospection for and the collection of minerals was not a new activity. There are many examples which indicate that mineral resources were known and exploited in the Palaeolithic and Neolithic periods (Ottaway 2001).

### 2.3.2 Mining

Early mining of copper consisted of the collection of outcropping pieces of ore that attracted man's attention with its different physical appearance compared to the material used until that day.

Together with the fact that copper became very important material in the production of the essential tools and warfares of man's daily life, the consumption of copper increased and the native copper to be cropped out easily at the surface disappeared. This resulted in the efforts of man for extracting the copper from its ore by openning galeries below the surface.

Ore extraction from the bedrock required stone hammers, antler and bone picks, sometimes with the aid of fire-setting to loosen the rock. These activities were all part of the existing technology which included, for instance, mining for flint and opal, quarrying for stone and flint, sinking shafts and building wells to obtain clear water (Ottaway 2001).

### 2.3.3 Beneficiation

After acquisition of ore, it needs serious efforts to prepare for smelting which may be called as ore concentration or beneficiation.

Copper-rich minerals were crushed and either hand-sorted to pick out the coloured and heavier minerals from the gangue or, in later periods, separated by gravity with the aid of wind or water. The hammerstones used for crushing, commonly smaller than those used for mining but with similar traces of wear, stone slabs. It is usually assumed that crushing and separation could be carried out by anyone. However, crushing involves skill, technique and the correct choice of tools. Beneficiation is so important that the more time that is spent on beneficiation, the less fuel is needed in the smelting process (Ottaway 2001).

### 2.3.4 Smelting

The application of heat to make some changes in the material feature was not a new knowledge which was applied to the hardening of clay figurines in the Palaeolithic, or the firing of clay to produce ceramics. The necessity to achieve consistently high temperatures and a reducing atmosphere to smelt the copper from its oxide or carbonate ore required the adaptation and refinement of the techniques. Smelting was carried out within a crucible, probably embedded in a small hearth-like oven. The heat was applied from above, since the whole crucible would not have withstood the high temperatures required to smelt the ore. The products indicate that the smelting process was incomplete - i.e. insufficiently high temperatures had been achieved to produce a liquid slag through which the molten copper could have fallen and collected at the bottom. This incomplete process led to the embedding of the copper prills in the solidified slag. Smelted copper was obtained by crushing the slag and removing the prills by hand. Interestingly, slag analyses indicated that process

temperatures and furnace conditions did not change significantly from the early to the late Bronze Age. In other words, the same sulphide copper, chalcopyrite with pyrites and quartz as gangue, was smelted throughout the whole Bronze Age by a method that did not alter much, even though the location of the smelting sites changed from the valley up to the mountains. The only difference was the increase in size of slag cakes from the early to the late Bronze Age - an increase from 2 - 3 kg to 5 - 6 kg in weight (Ottaway 2001).

### 2.3.5 Refining

Depending on the raw material and the smelting process used, the product of the smelting process could be copper prills, black copper - iron-contaminated copper from smelting copper oxide ores using a flux or matte - mixed iron and copper sulphide. All of these products had to be further processed, from simply remelting to refining, to prepare the copper for the next stage in the process. A crucible, ideally covered with charcoal to provide reducing conditions and thus to prevent the copper from oxidizing, could have been used. Perhaps later, small furnaces were used for this process. Achieving the right temperature while at the same time avoiding oxidation of the copper requires specialist knowledge (Ottaway 2001).

### 2.3.6. Alloying

As metals were reduced from ores impurities were also reduced, and these resulted in the fact that the coppersmith learned of the hardening property of alloying elements. This knowledge improved with experience and reached to the level which tin in proportions of one in ten was identified by 3000 B.C. as the ideal agent for improving the casting properties and hardness of copper (Wertime 1964).

With the exhaustion of outcrop ores, he turned sooner or later to the deeper, unweathered, less pure and more difficultly reducible ores of the pyritic type. In almost all cases such ores contain considerable proportions of impurities, some of which would find their way into the metal (Thompson 1958).

The earliest alloy in prehistoric Europe found prior to the Bronze Age was arsenical copper, also called arsenical bronze. By the Bronze Age, this was replaced by bronze, a tin-copper alloy. The advantages of an arsenical copper alloy against

pure copper are a lowering of the melting point, improved quality of the cast, increased hardness through cold-working, improved hot-workability and its changed aesthetic value through the creation of a more silvery colour. It is sometimes assumed that it was the silver colour of an object which persuaded prehistoric smiths to alloy copper with arsenic. Except for the silver colour, the advantages of tin bronzes are essentially the same as those of arsenical copper (Ottaway 2001).

There are no recorded finds of pure arsenic in any archaeological context. On the other hand uncovered metallic tin encountered in the excavations are steadily increasing.

# CHAPTER 3

# KÜLTEPE ARCHAEOLOGICAL SITE

The geopolitic position of Anatolia in the early second millennium B.C. was determined by more than a dozen city-states which exhibit more urban age compared to the past period (Sagona, Zimansky 2009). Meanwhile, Mesopotamia also showed a similar development which resulted in successful establishment of the city state system around royalty which dominated with its achievements, both militarily and economically.

Since northern Mesopotamia was devoid of essential mineral resources like the other parts of Mesopotamia, the unprecedented trade sytem for that age based on mainly metal exchange appeared between Anatolia and northern Mesopotamia (Dercksen 1996).

## 3.1. Old Assyrian and Anatolia Relations

Since Assur dominated the most important river route between northern and southern Mesopotamia; and it was also on the caravan routes that linked Anatolia to Iran, they established very strong and extensive commercial network with both southern Mesopotamia and Anatolia where the plenty of various minerals and its diverse agricultural and animal products were already well known to its neighbours (Özgüç 2005).

The geographical locations of the regions facilitated this commercial link between these two regions (Figure 3.1).

The trade realized between Assur and Anatolia was the result of reforms of King Erisum I who was in reign between 1974 and 1935 B.C. and Assur gained its

independency in his period. As a result of the reforms, state trade monopoly was removed and free trade organized by family firms was encouraged(Özgüç 2005).

The basic pattern of the Old Assyrian trade was shipping of large quantities of tin and textiles from Assur to Anatolia for exchanging with silver and occasionaly gold besides the bronze was exported to Assur in the form of manufactured goods not as raw material (Larsen 1976).

The trade period realized between Assur and Anatolia during 1945-1730 B.C. was called as Assyrian Trade Colonies Period which was based on the very high standard administrative rules.

The Anatolian kingdoms had developed political structures and the relations with Assyrians were based on aggreements in formal treaties which represent the essential equality of both sides (Larsen 2011).

The long distance trade occurred between Anatolia and Assur differentiated from short range trade, since the merchants who realized this commercial activity must reside in Anatolia. Therefore the Assyrians created a system in the form of "trade colonies" which were established as large towns called "Karum" mainly next to the the capital cities of indigenous kingdoms or important cities of central and southeastern Anatolia (Özgüç 2005).

There were ten Karum in Anatolia. Kültepe was the administrative center of these ten Karum of which only eight are known by name and two are identified: Kanishwith Kültepe and Hattusa with Boğazköy (Özgüç 2005).

### 3.2. Kültepe / Kanesh

Kültepe which means ash-mound is located at 21 km to the northeast of Kayseria (present Kayseri), the capital of the Kingdom of Cappadocia.

All the other nine Karum were administered by Karum of Kanesh, which directly was affiliated with Assur. Kanesh was the centre which organizes the relations between the Anatolian Karums and the capital, Assur (Özgüç 2005).

Figure 3.1 Ancient Turkey map showing important ancient civilization centers

Kültepe or with its ancient name Kanesh (the capital of the Kingdom of Kanesh) is at the center of a fertile, well irrigated plain at the foot of Erciyes mountain (Mount Argeus) besides the fact that it is also located at the intersection point of the ancient routes.

Kanesh became very attractive place because of these natural advantages in the ancient world of commerce and appeared as a brilliant international commercial and artistic center which linked Anatolia, Mesopotamia and Syria in the last quarter of the third millennium and the first quarter of the second millennium B.C. Moreover, Assur and Kanesh were very similar by virtue of their construction at the junction of caravan routes at a central and strategic region, and both were easily accessible from neighboring regions (Özgüç 2005).

Kanesh Colony established in the Kingdom of Kanesh has a very strategic position on the Anatolian plateau which was the first stop of the trade in Anatolia. Then the merchandises were distributed to Anatolia by commissioned agents (Larsen 1976).

Kültepe is composed of two parts (Figure 3.2): The city-mound of Kültepe where the Kings and the native population lived and the Karum which was established by Assyrian merchants. The mound is one of the largest central Anatolian mounds which is 21 m higher than the surrounding plain with dimensions of 550 m north-south and 500 m east-west (Özgüç 2005).

Excavations on the mound revealed that the city-mound had a long history and contains 18 cultural levels commenced from the earliest phase of the Early Bronze Age (Özgüç 2005).

The Karum of Kaniş (Figure 3.3) comprises four building levels: Level IV is built on virgin soil, and level III belongs to the very beginning of the Middle Bronze Age (2000-1950 B.C.), level II and level I dated to Colony Period. First level shows two phases designated by la and lb (Özgüç 2005).

The lower city of Kanesh (Karum) with 2 km in diameter which surrounds the Kültepe Mound was settled for about 250 years and building levels X to VI

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unearthed on the mound and levels II to Ia-Ib at lower city represent the "Assyrian Trade Colonies Period" (Özgüç 2005).



Figure 3.2. Aerial Photograph of Kültepe Mound

As a result of the excavations in Kültepe, 23500 tablets were uncovered. 23000 of these tablets were from level II and 500 were from level Ib and no tablet from Ia at which no evidence for trade was observed (Özgüç 2005).

Kültepe has become very important settlement center which host many civilization and moreover, the informations obtained from excavations made great contributions to understand the ancient Anatolian history.

Kültepe showed the features of great urban culture not only in Assyrian Trade Colonies Period. The monumental buildings erected in Early Bronze Age and the production of pottery with potter's wheel are few of many evidences which reveal the fact that Kültepe was large and developed city also before "Colonies Period" (Kutlu 2011).

Figure 3.3 General view of lower city (Karum)

Kültepe Archaeological Site, besides many tablets which include texts written in cuneiform script revealing how a great trade system of ancient world was organized have been uncovered there, at the same time, shelters many brilliant metallic artifacts of its age. This can be interpreted as the usual result of the position of the Kültepe in trade system.

### 3.3. The Metal Production in Kültepe in Colonies Period

It is understood from the sophisticated metal artifacts uncovered from the excavations that metal craftsmanship in Kültepe had reached high skilled level.

This situation is not unexpected result. Since Anatolia has various types of metal resources, metal working has shown brilliant progress at each stage of its history.

In this respect, Kültepe was also an important metal working center besides being the administrative center which manages the large quantities of metal circulation in Anatolia at "Colonies Period".

However, Assyrian merchants also carried their local metal product traditions to Anatolia. These metal weapons and tools were commenced to manufacture by Anatolian metalsmiths of that age (Yıldırım 2011).

Several workshops were unearthed in Karum of Kültepe. One of these was the highly developed workshop including an oven and hearth, pot bellows, tuyeres, crucibles and moulds amongst ancient Anatolian metal workshops (Dercksen 2011).

Workshops have similar architectural plans with the other houses. These workshops were also the residence of ancient metalsmiths, who were also Assyrian people besides the native ones (Yıldırım 2011).

The majority of metal objects in Kanesh graves are various types of weapons. Stone moulds (Figure 3.4 and Figure 3.5) for casting were also discovered in the workshops of levels II and Ib. The weapons consist of arrowheads, daggers, flat axes, lugged axes, crescentic axes, fenestrated axes, shaft-hole axes, battle axes, two and three pronged forks and swords (Özgüç 2005).



Figure 3.4 Stone moulds to produce flat axe

Most of the open or two-piece stone moulds for weapons or tools were used in this age.Tools and weapons like flat or lugged axes, chisels daggers and knives were produced by open moulds (Yıldırım 2011).



Figure 3.5 Stone mould to produce chisels

The moulds in workshops and the burial gifts obtained from excavations revealed that the residents of Kanesh produced and used extensively all types of bronze weapons (Özgüç 2005).

Since copper was not obtained from ore in Kültepe, the copper used for casting was the ingots which were produced in different regions of Anatolia and exported to Kültepe.

Various copper, silver and gold ingots were discovered in the private houses and workshops of the Karum and in a destroyed temple at the city-mound. The majority of the moulds for copper ingots are bar or disk shaped, but for gold and silver ingots they are usually irregular, and sometimes in the shape of a bun or a disk. Pure silver ingots weighing two kg were recovered from a bowl in a Karum workshop of level II (Özgüç 2005).

The products of several mining or processing centres were represented by the settlement names nearby the mines or processing place like Haburata, Kunanamit, Tuphiya, etc. Since it was not profitable to transport and sell poor copper, naturally, the merchants preferred to purchase the high purity copper for easy exchange. The terminology distinguishing the purity of metal in the documents, the copper which included high amount of impurities was called bad or black copper. The best quality copper was called refined (washed) copper (Dercksen 2011).

The Assyrians were extremely active in the copper trade. Even though, the Assyrian administration restricted the trade of native textiles considering the competition risk with their own products, the copper trade was strongly supported. The purpose was to transfer gold and silver from Anatolia to Assur. The merchants exchanged their goods with low-grade copper, which was subsequently exchanged with high-grade purified copper which then was used in exchange of silver. The value of copper depended on the quality of the ore and purification level. High grade copper was 1/45 the price of silver, but low-grade copper could be 3 or 4 times cheaper. Moreover, the native kings participated in copper trade and exchanged low-grade copper from their storehouses with high-grade ore (Özgüç 2005).

Tin was used to make payment for caravan expenditures and taxes like money. Copper was also used as money by the natives, but the primary form of currency was silver ingots. Although Anatolian silver is generally uniform in quality, there are also types of silver qualified according to the names of two specific cities. The merchants sent their silver earnings to Assur wrapped in sealed packs weighing 3 to 15 kg by their relatives or by trusted couriers. The silver and gold trade was subject to taxation for both the sending country and the receiving country with the exception of gifts sent to Assur for the temples, for supporting cult practices etc. The merchants could leave their silver ingots at the palace for safe-keeping for which they paid a certain amount of rent. The merchants lent money to native Anatolians in the form of silver at high rates of interest (Özgüç 2005).

Silver ingots weighing 2 kg each, cut in various shapes and marked, were discovered in a bowl in the Karum while small many bronze and copper tools to be examined in this study were also uncovered from Karum (Figure 3.6).

The capital of the firms of the wealthy Assyrians in Assur was based on gold As with silver, gold was sent to Assur by special couriers, in small and sealed packs each weighing 1/2 or 1kg. Garelli gives an exchange rate of 8 1/4 shekels of silver par 1 shekel of gold or more, but Larsen states that the rate of exchange for gold changes from 7 to 9 shekels of silver for one shekel gold (Özgüç 2005).



Figure 3.6 The trench MK-34 where some of the studied samples were found

# CHAPTER 4

# MATERIALS AND METHODS

As stated before, the objective of the thesis is to endeavor to understand the metal working technologies in Kültepe Archaeological Site by examining the uncovered metal artifacts belonging to Colony Period of Kültepe (1945-1730 B.C.).

In the frame of this objective, the material examined and the methods used for examinations have been explained in this chapter.

## 4.1. The Metal Artifacts Examined

The uncovered metal artifacts from Kültepe Excavation Site belonging to Colony Period, which are exhibited in the Anatolian Civilization Museum (4.1.1) and which are not suitable for exhibition and separated for studying (4.1.2) were examined. All samples were designated with number in sequence according to study sequence and with a prefix "Kt" representing Kültepe.

### 4.1.1. The Metal Artifacts from Anatolian Civilization Museum

There are many metal artifacts belonging to Colony Period of Kültepe in the inventory of Anatolian Civilization Museum in Ankara. Thanks to the permission taken from Ministry of Culture and Tourism in the frame of study with Chairmanship of Kültepe Excavation Site, it was possible to make the examinations of the artifacts which are stored in the depots of museum.

Analysis of thirtythree artifacts shown in Figures 4.1 - 4.33 were realized by portable X Ray Fluorescence Spectrometer (PXRF) to obtain the elements composition of the artifacts without giving any harm to them. The numbers written on the Figures 4.1 - 4.33 are the points where PXRF analysis was carried out.

Some informations about the materials studied are given in Table 4.1.

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Table 4.1. The metal artifacts studied with PXRF in Anatolian Civilization Museum

| Sample No | Museum Inventory No | Object |
|---|---|---|
| Kt-01 | 126-57-64 | Spearhead (Fig. 4.1) |
| Kt-02 | 126-61-64 | Spearhead (Fig. 4.2) |
| Kt-03 | 125-8-64 | Spearhead (Fig. 4.3) |
| Kt-04 | 125-25-64 | Spearhead (Fig. 4.4) |
| Kt-05 | 122-45-64 | Spearhead (Fig. 4.5) |
| Kt-06 | 123-16-64 | Spearhead (Fig. 4.6) |
| Kt-07 | 122-23-64 | Spearhead (Fig. 4.7) |
| Kt-08 | 130-81-64 | Spearhead (Fig. 4.8) |
| Kt-09 | 125-55-64 | Spearhead (Fig. 4.9) |
| Kt-10 | 94-55-64 | Flat axe(Fig. 4.10) |
| Kt-11 | 117-94-64 | Flat axe (Fig. 4.11) |
| Kt-12 | 123-19-64 | Shaft-hole axe (Fig. 4.12) |
| Kt-13 | 1-40-95 | Shaft-hole axe (Fig. 4.13) |
| Kt-14 | 1-47-2000 | Shaft-hole axe (Fig. 4.14) |
| Kt-15 | 94-55-64 | Flat axe (Fig. 4.15) |
| Kt-16 | 131-3-64 | Rivetted dagger (Fig. 4.16) |
| Kt-17 | 71-2-66 | Dagger (Fig. 4.17) |
| Kt-18 | 71-9-60 | Dagger (Fig. 4.18) |
| Kt-19 | 94-71-64 | Chisel (Fig. 4.19) |
| Kt-20 | 177-16-74 | Fork weapon (Fig. 4.20) |
| Kt-21 | 94-33-64 | Sickle blade (Fig. 4.21) |
| Kt-22 | 126-23-04 | Sickle blade part (Fig. 4.22) |
| Kt-23 | Kt.n/k132 | Ring (Fig. 4.23) |
| Kt-24 | Kt.01/k98 | Ring (Fig. 4.24) |
| Kt-25 | 126-46-64 | Bracelet (Fig. 4.25) |
| Kt-26 | 1-27-99 | Finger cymbal (Fig. 4.26) |
| Kt-27 | Kt 97/k478 | Drinking cup (Fig. 4.27) |
| Kt-28 | 126-90-64 | Drinking cup (Fig. 4.28) |
| Kt-29 | Kt.01/k23 | Drinking cup (Fig. 4.29) |
| Kt-30 | 1-7-93 | Small bowl (Fig. 4.30) |
| Kt-31 | 1-107-03 | Small shovel (Fig. 4.31) |
| Kt-32 | 127-23-04 | Fired tube piece(Fig. 4.32) |
| Kt-33 | 127-22-61 | Small animal sculpture (Fig. 4.33) |

Figure 4.1 Spearhead (Kt-01)
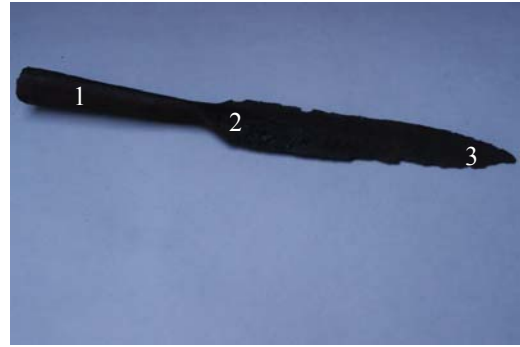


Figure 4.2 Spearhead (Kt-02)



Figure 4.3 Spearhead (Kt-03)



Figure 4.4 Spearhead (Kt-04)



Figure 4.5 Spearhead (Kt-05)



Figure 4.6 Spearhead (Kt-06)

Figure 4.7 Spearhead (Kt-07)



Figure 4.8 Spearhead (Kt-08)



Figure 4.9 Spearhead (Kt-09)



Figure 4.10 Flat axe (Kt-10)



Figure 4.11 Flat axe (Kt-11)



Figure 4.12 Flat axe (Kt-12)

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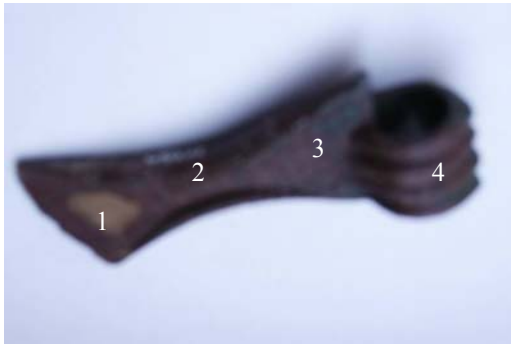
Figure 4.13 Shaft-hole axe (Kt-13)



Figure 4.14 Shaft-hole axe (Kt-14)



Figure 4.15 Shaft-hole axe (Kt-15)
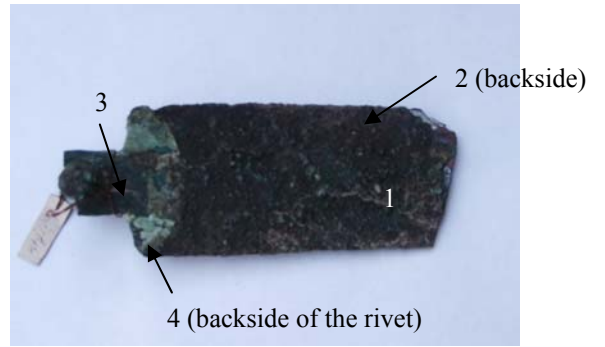


Figure 4.16 Rivetted dagger (Kt-16)



Figure 4.17 Dagger (Kt-17)



Figure 4.18 Dagger (Kt-18)

Figure 4.19 Chisel (Kt-19)
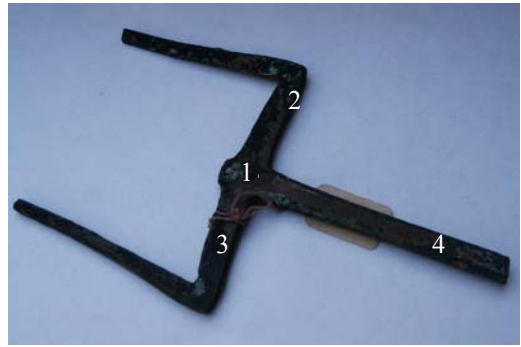


Figure 4.20 Fork weapon (Kt-20)



Figure 4.21 Sickle blade (Kt-21)
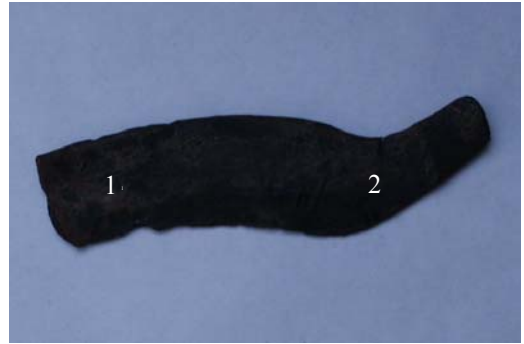


Figure 4.22 Sickle blade fragment (Kt-22)



Figure 4.23 Ring (Kt-23)



Figure 4.24 Ring (Kt-24)

Figure 4.25 Bracelet (Kt-25)



Figure 4.26 Finger cymbal (Kt-26)



Figure 4.27 Drinking cup (Kt-27)



Figure 4.28 Drinking cup (Kt-28)



Figure 4.29 Drinking cup (Kt-29)



Figure 4.30 Small bowl (Kt-30)

3 (Bottom side)
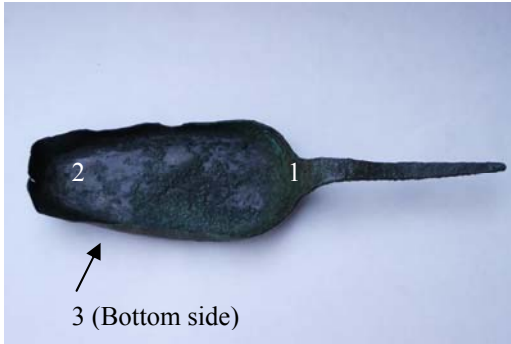
Figure 4.31 Small shovel (Kt-31)



2 (Dross from inner part)
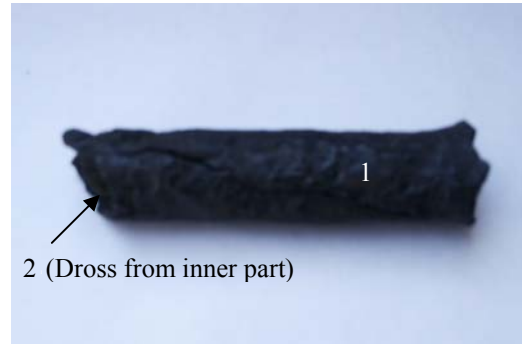
Figure 4.32 Fired tube fragment (Kt-32)



Figure 4.33 Small animal sculpture (Kt-33)

### 4.1.2. The Metal Artifacts from Kültepe Excavation Site

Besides the examination of exhibited artifacts in the Anatolian Civilization Museum, the uncovered metal artifact parts belonging to Colony Period which are not suitable for exhibition and separated for studying in Kültepe Excavation Site were examined in the frame of permission of Chairmanship of Kültepe Excavation Site.

Thirtytwo artifacts fragments shown in Figures 4.34 – 4.65 are composed of mainly cutter and piercing tools (chisel and pin fragments) that are suitable to use at dailylife. Apart from these, a ring, a small plate fragment and a small bowl fragment are inside the examined pieces.

The analysis of these thirtytwo artifacts were performed as elemental analysis and microstructural evaluation by using Scanning Electron Microscope-coupled with Energy Dispersive X-Ray Spectrometer (SEM-EDS), and optical microscope. In addition to analysis mentioned above, X-Ray Diffraction Method (XRD) was applied to two selected samples (Kt-34, Kt-36).

Some informations about the samples studied are given in Table 4.2.

Table 4.2. The studied artifacts which are not suitable for exhibition

| Sample No | Object |
|-----------|--------|
| Kt-34 | Chisel Fragment (Fig. 4.34) |
| Kt-35 | Pin Fragment (Fig. 4.35) |
| Kt-36 | Chisel Fragment (Fig. 4.36) |
| Kt-37 | Plate Fragment (Fig. 4.37) |
| Kt-38 | Pin Fragment (Fig. 4.38) |
| Kt-39 | Pin Fragment (Fig. 4.39) |
| Kt-40 | Chisel Fragment (Fig. 4.40) |
| Kt-41 | Pin Fragment (Fig. 4.41) |
| Kt-42 | Pin Fragment (Fig. 4.42) |
| Kt-43 | Pin Fragment (Fig. 4.43) |
| Kt-44 | Pin Fragment (Fig. 4.44) |
| Kt-45 | Bowl Fragment (Fig. 4.45) |
| Kt-46 | Pin Fragment (Fig. 4.46) |
| Kt-47 | Pin Fragment (Fig. 4.47) |
| Kt-48 | ChiselFragment (Fig. 4.48) |
| Kt-49 | Chisel Fragment (Fig. 4.49) |
| Kt-50 | Ring Fragment (Fig. 4.50) |
| Kt-51 | Pin Fragment (Fig. 4.51) |
| Kt-52 | Pin Fragment (Fig. 4.52) |
| Kt-53 | Pin Fragment (Fig. 4.53) |
| Kt-54 | ChiselFragment (Fig. 4.54) |
| Kt-55 | Pin Fragment (Fig. 4.55) |
| Kt-56 | Pin Fragment (Fig. 4.56) |
| Kt-57 | Pin Fragment (Fig. 4.57) |
| Kt-58 | Chisel Fragment (Fig. 4.58) |
| Kt-59 | ChiselFragment (Fig. 4.59) |
| Kt-60 | Pin Fragment (Fig. 4.60) |
| Kt-61 | Pin Fragment (Fig. 4.61) |
| Kt-62 | Pin Fragment (Fig. 4.62) |
| Kt-63 | Pin Fragment (Fig. 4.63) |
| Kt-64 | Chisel Fragment (Fig. 4.64) |
| Kt-65 | Pin Fragment (Fig. 4.65) |

Figure 4.34 Chisel Fragment (Kt-34)



Figure 4.35 Pin Fragment (Kt-35)



Figure 4.36 Chisel Fragment (Kt-36)



Figure 4.37 Plate Fragment (Kt-37)



Figure 4.38 Pin Fragment (Kt-38)



Figure 4.39 Pin Fragment (Kt-39)

Figure 4.40 Chisel Fragment (Kt-40))



Figure 4.41 Pin Fragment (Kt-41))



Figure 4.42 Pin Fragment (Kt-42))



Figure 4.43 Pin Fragment (Kt-43)



Figure 4.44 Pin Fragment (Kt-44)



Figure 4.45 Bowl Fragment (Kt-45)

Figure 4.46 Pin Fragment (Kt-46)



Figure 4.47 Pin Fragment (Kt-47)



Figure 4.48 Chisel Fragment (Kt-48)



Figure 4.49 Chisel Fragment (Kt-49)



Figure 4.50 Ring (Kt-50)



Figure 4.51 Pin Fragment (Kt-51)

Figure 4.52 Pin Fragment (Kt-52))



Figure 4.53 Pin Fragment (Kt-53)



Figure 4.54 Chisel fragment (Kt-54)



Figure 4.55 Pin Fragment (Kt-55)



Figure 4.56 Pin Fragment (Kt-56)



Figure 4.57 Pin Fragment (Kt-57)

Figure 4.58 Chisel Fragment (Kt-58)



Figure 4.59 Chisel Fragment (Kt-59)



Figure 4.60 Pin Fragment (Kt-60)



Figure 4.61 Pin Fragment (Kt-61)



Figure 4.62 Pin Fragment (Kt-62)



Figure 4.63 Pin Fragment (Kt-63)

Figure 4.64 Chisel Fragment (Kt-64)        Figure 4.65 Pin Fragment (Kt-65)

## 4.2. The Methods of Analyses

If the metal working technologies of a certain place of a certain age is intended to reveal over a metal artifact, the first thing that has to be done is to determine the elemental composition of the metal artifacts representing the place at focused age. The elemental composition may provide us some informations about the classifications of artifacts depending on their usage purpose and the additives to be included in the composition of the alloy that they are mixed deliberately or not.

The later stage following the obtaining the elemental composition of the metal artifact has to be detailed microstructural examination to reveal all processes to be applied on the metal by ancient metalsmith.

In addition to analyses stated above, the next attempt is to try to have the information for the provenance of the metal ore from which that artifact was produced. Lead Isotope Analysis (LIA) besides the chemical analysis may be helpful method to estimate the origin of metal. In addition the estimation of provenance of the metal may provide information about the trade route used in that period.

In this study, the same sequence was followed.

The composition determinations of metal artifacts of this study were performed by Portable X-Ray Fluorescence Spectrometer (PXRF) and Scanning

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Electron Microscope coupled with Energy Dispersive X-Ray Spectrometer (SEM-EDS).

The microstructural analysis for understanding which processes were applied on the metal like cold and/or hot working and heat tretment was carried out by optical microscope and scanning electron microscope.

In order to make an estimation for provenance of metal ore used by Kültepe metalsmith, LIA of ten artifacts which contain relatively more lead (Kt-37, Kt-41, Kt-42, Kt-46, Kt-49, Kt-50, Kt-54, Kt-57, Kt-59, Kt-64) were performed in Thermal Ionization Mass Spectrometer (TIMS).

LIA of samples were carried out in Central Laboratuary of Middle East Technical University.

The detailed explanation about the methods and instruments used in this study was given in the following paragraphs.

### 4.2.1 Element Analysis by Using Portable XRF

X-Ray fluorescence analysis (XRF) is widely used multi-elemental analysis technique especially in applications requiring nondestructive analytical methods.

The objective of XRF analysis is to get accurate analytical data about the composition of a specific material by using X-rays which are electromagnetic waves with a wavelength of 0.01 nm to 10 nm (Figure 4.66).

XRF spectrometry is based on the principle that primary X-rays (from an X-ray tube or radioactive source) are incident upon a sample and create inner shell (K, L, M) vacancies in the atoms of the surface layers. These vacancies de-excite by the production of a secondary (fluorescent ) X-rays whose energies are characteristics of the elements present in the sample. Some of these characteristic X-rays escaped from the sample are counted and their energies are measured. Comparison of those energies with known values for each element allow the elements present in the sample to be identified and quantified (Pollard et al. 2006).
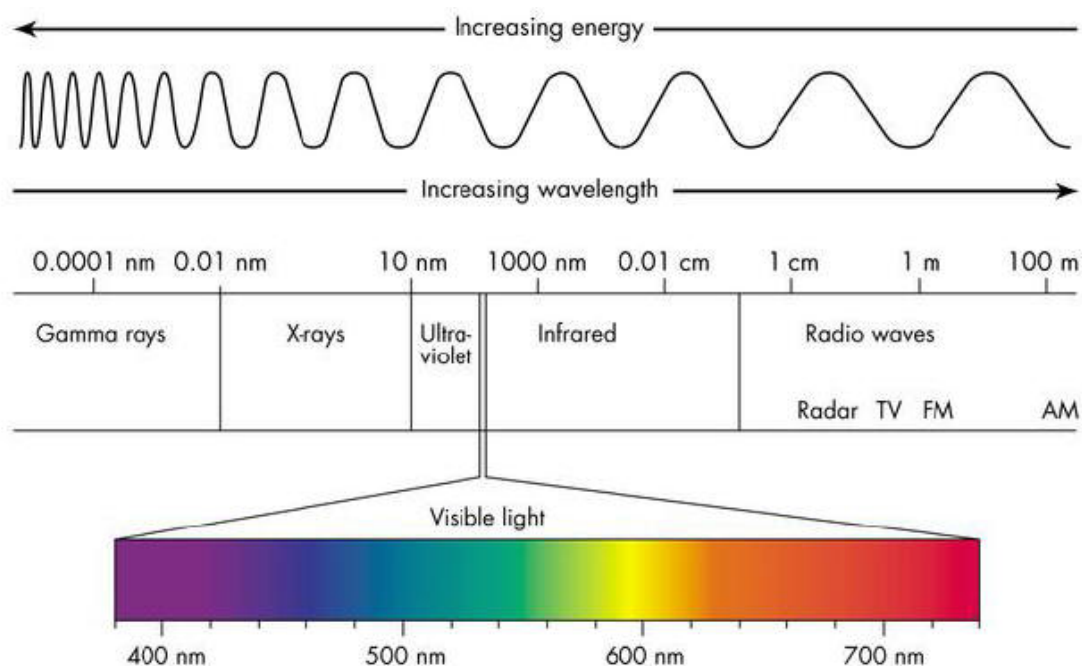
Figure 4.66 The schematic representation of Electromagnetic Spectrum

X-rays can easily permeate materials and as the atomic number of the atoms in the material get smaller that strength increases. When the X-ray passes through the material, the material is ionized and a flourescent X-ray surface is generated.

When primary X-rays strike the sample two processes take place; scattering and absorption which is usually the dominant process. Scattering may be elastic (coherent or Rayleigh scattering), in which case the scattered ray has the same wavelength as the primary beam, or inelastic (incoherent or Compton scattering), which results in longer wavelength (lower energy) X-rays. Coherent scattering results in the primary spectrum of the X-ray tube being ''reflected'' into the detector, which is why the lines characteristic of the X-ray tube target material appear in the resulting spectrum (Pollard et al. 2006).

XRF Spectrometer is composed of X-ray generator, detector and analyzer.

X-ray is generated by X-ray tube which is a vacuum tube produces a continuum of primary X-rays up to a maximum energy defined by the operating voltage of the tube.

X-ray tube emits the electrons from the heated filament cathode by a high positive potential and accelerated towards the target anode which is made from a suitable metal (often rhodium, tungsten, or molybdenum) having a capability of emitting X-rays efficiently when bombarded with electrons in an electric field created by a positive potential of the anode relative to the cathode. They strike the anode target, interact with its atoms and lose their energy through a number of processes (Beckhof et al. 2006).

The fluorescent X-ray generated from the sample is detected by the Si (Li) semiconductor detector. The X-ray is then converted into a pulse that is held by the peak voltage relative to the energy. This pulse is amplified through the pre-amp and liner-amp and sent to the multichannel analyzer.

As stated above, fluorescent X-rays are created when a substance, irradiated by primary X-rays, gives off secondary X-rays. Each X-ray energy has a value that is characteristic of a certain element.

If the energies of the fluorescent X-rays are known, the composition of the material can be determined. There are two methods used to separate the energies:wavelength separation and energy separation.

### 4.2.1.1 Wavelength Dispersive XRF (WDXRF)

In WDXRF the detection and energy measurement processes are separated.The secondary X-rays are regarded as electromagnetic waves whose wavelength is characteristic of the atom from which they came. The atoms of the sample emit their characteristic X-rays,which are directed onto a dispersion device. The dispersion device separates the secondary radiation into its component wavelengths and a detector records the intensity of radiation as a function of wavelength (Pollard et al. 2006).

The detection system of this method is comprised of an analyzing crystal and slit and the X-ray is handled as an electromagnetic wave. When the X-ray comes in contact with the analyzing crystal, the light is separated into seven colors using a prism and the energy (wavelength) is separated. If the analyzing crystal is rotated or

the detector moved, only the X-ray that has the target energy is captured. If a slit is inserted in front of the detector, only a narrow energy area can be detected.

### 4.2.1.2 Energy Dispersive XRF (EDXRF)

In this method, the detector itself has the ability to separate the energies. For the detector, the semiconductor detector (SSD), scintillation counter, or proportional counter with their differing qualities can be used.

In EDXRF the secondary X-ray emitted by the excited atom is considered to be a particle (an X-ray photon) whose energy is characteristic of the atom whence it came. The major development which has facilitated this technique is the solid state semiconductor diode detector. An EDXRF system consists of a solid state device which provides an electronic output that is proportional to the energy spectrum of the X-rays emitted by the unknown sample, simultaneously measuring the energy of the incident photon and counting the number of photons with known energies (Pollard et al. 2006).

The ability of the detector to separate the energies of the X-ray is called energy separation ability. When the X-ray of energies extremely close together can be separated the energy resolution is said to be high.

The Portable XRF Spectrometer (Figure 4.67) used in the artifacts exhibited in Anatolian Civilization Museum in this study is Energy Dispersive type and belongs to Turkish Atomic Energy Authority (TAEK). Analysis were performed by the expert of TAEK.

### 4.2.2 Element Analysis by Using SEM-EDS

The metal artifacts taken from Chairmanship of Kültepe Excavation Site have been heavily corroded. The corrosion of those metal artifacts is expected since they stayed under the soil approximately 4000 years.

However, the corrosion has been progressed so that the metal core that corrosion has not reached yet was too small. Therefore it has not been possible to make analysis by Portable XRF which requires a certain test area on the specimen for having accurate results which reflects the original metal content.

Figure 4.67 Portable XRF

Therefore the analysis of the specimens which have been heavy corroded has been possible by EDS unit of Scanning Electron Microscope.

Since the method for analyzing by EDS is the same as XRF, it is thought that there is no need to repeat the explanation of the method.

### 4.2.3 X-Ray Diffraction Analysis (XRD)

X-ray diffraction uses X-rays of known wavelengths to determine the lattice spacing in crystalline structures and therefore directly identify chemical compounds. Powder XRD, the simplest of the range of XRD methods, is the most widely applied method for structural identification of inorganic materials, and, in some cases, can

also provide information about mechanical and thermal treatments during artifact manufacture (Pollard et al. 2006).

In powder X-ray diffraction measurements, the solid sample is irradiated by a collimated beam of monochromatic X-rays of known wavelength. A proportion of these are diffracted at angles which depend on the crystal structure of the specimen. The wavelength of the incident radiation must be of the same magnitude as the distance between the scattering points and a typical choice of X-ray wavelength. The X-rays are reflected in a manner which appears similar to the reflection of light from a mirror. Therefore, a crystalline specimen will produce a series of reflected X-ray intensity maxima (a diffraction pattern) at angles determined by the spacings between crystal planes of its constituent minerals. The diffraction pattern is characteristic of the minerals present, and can be used to identify them. The power of the diffracted beam is dependent on the quantity of the corresponding crystalline material in the sample and therefore relative amounts of different minerals can also be determined. The processes in XRD are identical to those of wavelength dispersive detection in XRF, except that in XRD the wavelength of the X-rays is known and the lattice spacings are to be determined, whereas in WDXRF the lattice spacing is known and the wavelengths of the secondary X-rays are to be determined (Pollard et al. 2006).

XRD analysis requires powder samples in our case. Therefore a small amount of sample, typically 5–10 mg, is removed from the artifact by scraping the surface. Following this, The sample was powdered in an agate mortar and XRD analysis was performed by using Cu Kα X-rays. Scanning was carried out with 2θ values 0 to 90 degree.

XRD Analysis was carried out using Rigaku brand X-ray diffractometer in Metallurgical and Materials Engineering Department of METU (Figure 4.68).

Figure 4.68 Rigaku brand X-Ray Diffractometer

### 4.2.4 Determination of Metal Working Technology by Using Optical Microscope and Scanning Electron Microscope (SEM)

Determination of metal working technology by examining the microstructure of the processed metal, which is called as metallography is the science dealing with the constitution and structure of metals and alloys as revealed by optical microscopy, electron microscopy.

Metallography is an important tool which enables us to understand the ancient metalsmith knowledge to be reflected on a metal artifact which was shaped by them.

It is possible to determine the grain size and the size, shape, and distribution of various phases and inclusions which have a great effect on the mechanical properties of the metal. The microstructure will reveal the mechanical and thermal treatment of the metal, and it may be possible to predict its expected behaviour under a given set of conditions (Avner 1986).

Metallographic examination shows the phases which have been formed in a metallic sample and also their state (Sperl 1980). It is possible to have a knowledge of manufacturing method, heat treatment applied through the manufacturing process, the nature of corrosion and so on.

The success in microscopic study depends on the preparation of the specimen which is expected to have a flat, scratch-free, mirrorlike surface.

#### 4.2.4.1 Specimen Preperation

The steps required to prepare a metallographic specimen properly are covered in the following sections.

#### 4.2.4.1.1 Sampling

From the artifacts without giving any harm to them, very small pieces in the range of a few mm were cut in proper sections. Some of the material to be studied is very small, the section for microscopic examination was obtained by manual hacksawing, while a few of them has larger thickness compared to others, abrasive cutting machine was needed to take proper section in such samples (Figure 4.69).

The specimen was kept cool during cutting operation. Otherwise, heat taken place in cutting due to the friction may cause microstructural changes.



Figure 4.69 Abrasive cutoff machine      Figure 4.70 Mounting Press

### 4.2.4.1.2 Mounting

Mounting of a specimen is performed to provide convenient handling for the subsequent steps of metallographic preparation and examination.

When working with bulk samples, mounting may not be necessary. However, if the section is very small especially like in archaeological samples, mounting of thin sections in a suitable material is inescapable to prepare the specimen for metallographic analysis (Voort 2004).

Synthetic plastic materials are used to mount the thin sections to obtain a uniform size for handling in subsequent polishing operation in a special mounting press (Avner 1986).

The material used for mounting in this study is bakelite which is the most common thermosetting resin. Under heat and pressure applied by mounting press (Figure 4.70), the section embedded to bakelite was obtained (Figure 4.71).

Figure 4.71 Mounted section          Figure 4.72 Polishing operation

### 4.2.4.1.3 Polishing

The specimen was moved perpendicular to a series of emery papers containing successively finer abrasives starting from No 180 and successively No 320, No 600 and finally No 1000 (Figure 4.72) This vertical movement facilitate recognition of the stage when the deeper scratches have been replaced by shallower ones characteristic of the finer abrasive. Using water as lubricant prevents overheating the sample, minimizes smearing of soft metals, and also provides a rinsing action to flush away surface removal products so the paper will not become clogged.

### 4.2.4.1.4 Fine Polishing

The final approximation to a flat scratch-free surface was obtained by use of a wet rotating wheel covered with a special cloth that is charged with carefully sized abrasive alumina particles (Figure 4.73).

### 4.2.4.1.5 Etching

In order to make visible of the many structural characteristics of the examined polished surface, etching process was applied

Etching is nothing but a controlled corrosion process by means of a chemical etchants which produce metallographic contrast either by crystal faceting which produces steps at grain boundaries and reflectivity differences or by grain or phase-boundary etching (Voort 1999).

4.73 Fine polishing operation                Figure 4.74 Etching operation

Chemical etchants have three main components which are a corrosive agent, a modifier for reducing the ionization, and an oxidizer (Voort 1999).

By applying etching reagent, contrast is obtained and grain boundaries are made visible because of the differences in the rate at which various grains are attacked by the reagent. This difference in the rate of attack is mainly associated with the angle of the different grain sections to the plane of the polished surface. As an etching reagent for bronze materials, 10 mg $FeCl_2$, 20 ml concentrated HCl and 100 ml water composition was prepared and used.

### 4.2.4.2 Microscopy

The microscope is by far the most important tool of the metallographic study from both the scientific and technical standpoints (Avner 1986).

Microscopy is the study of the fine structure and morphology of objects with the use of a microscope. Microscopes range from optical microscopes, which resolve details on the micrometer level, to transmission electron microscopes that can resolve details less than one nanometer across. Resolution and contrast are key parameters in microscopy. Resolution is the minimum distance between two object features at which they can still be seen as two features. The contrast of a feature is the fractional change in image brightness that it causes (Sawyer, Grubb 1987).

### 4.2.4.2.1 Optical microscopy

Although the transmission electron microscope (TEM) and the scanning electron microscope (SEM) overcome the resolution and depth of field limitations of optical microscope, they have not reduced the importance of light microscope which is widely used tool in metallography (Voort 2004).

In the optical microscopy, an image is produced by the interaction of light and an object under investigation.

The microscopes can be equipped for both transmitted and incident light. In transmitted light techniques a light beam passes from a condenser lens system through the specimen and into the imaging system, the objective and eyepiece lenses. Opaque materials or samples too thick like metals to provide information by transmitted light techniques can be imaged using incident light. Here the light passes through the objective lens and is reflected from the specimen surface back into the objective. (Sawyer, Grubb 1987).

The metallurgical microscope (Figure 4.75) illuminates the specimen with incident (reflected light), on the contrary, biological and mineralogical microscopes are designed for illumination with transmitted light (Voort 2004).

In optical microscope, the image can reveal fine detail in or on the specimen at a range of magnifications from X2 to X2000. Resolution in the order of 0.5 micrometer is possible, limited by the nature of the specimen, the objective lens and wavelength of light (Avner 1986).

The prepared specimen is placed perpendicular to the optical axis of the microscope and is illuminated through the objective lens by light from the source, which is focused by the condenser into a beam that is made approximately parallel to the optical axis of the microscope by the plane glass reflector. The light is then reflected from the surface of the specimen. This light reflected from the specimen surface will be magnified in passing through the objective lens and will continue upward through the plane glass reflector and gets magnified again by the eyepiece.

Figure 4.75 Metal Microscope
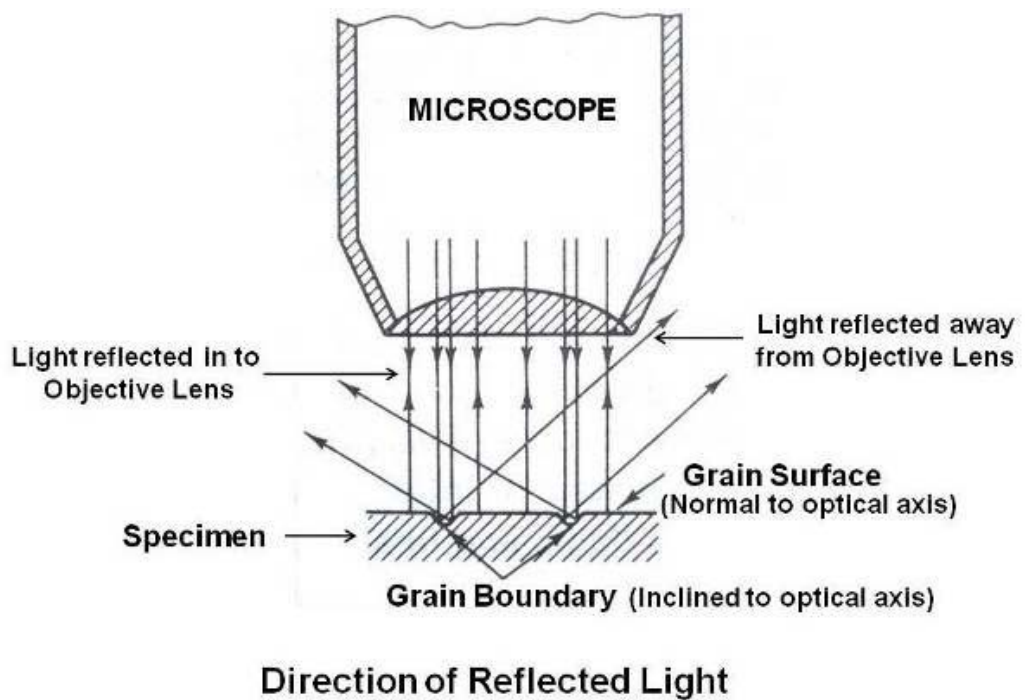


Figure 4.76 Schematic illustration of the microscopic appearence of grain boundaries as dark lines (Avner 1986)

The direction of light reflected from specimen depends on specimen's surface condition like surface of grain, grain boundary, etc. (Figure 4.76).

The final image of the specimen is bright for reflected light normal to the optical axis and dark for reflected light inclined to the optical axis. In this way, the various micro-structural features of a metallographic specimen such as grain boundaries that have been etched to produce grooves with inclined edges, precipitate particles and inclusions that have either been etched or polished in such a way that their edges are inclined are revealed.

In this study, microstructural examinations were carried out with an optical microscope (SOIF XJP-6A) in Metallurgical and Materials Engineering Department in METU with a magnification range of X100, X200 and X300. The microscope is equipped with a computer unit enabling to take many photographs of microstructure of samples easily (Figure 4.77).



Figure 4.77 Metal Microscope and attached computer unit for image analyser

**4.2.4.2.2 Scanning Electron Microscopy**

The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructural characteristics of solid objects. The primary reason for the SEM's usefulness is the high resolution which can be obtained when bulk objects are examined. Another important feature of the SEM is the three dimensional appearance of the specimen image, direct result of the large depth of field.

In principle the electron microscope is similar to the light microscope. In electron microscope, light rays are replaced by a beam of electrons which provides a basic magnification range of X1400 to X32000, which may be extended to X200000 with accessory lenses.

Analytical electron microscopy combines the high image resolution of the electron microscope with analysis of the characteristic X-rays produced when the sample is bombarded with electrons. This combination produces a very powerful method of chemical analysis, particularly suitable for analysis of small regions of a solid, and for the detection of spatial variation in composition (Pollard et al. 2006).

In a simple electron microscope, a primary beam of electrons is produced using a conventional electron gun, where a heated cathode, maintained at ground potential, emits electrons which are drawn out by a positive potential (typically 30kV) to form a high energy electron beam. This beam is easily electrostatically and/or magnetically focused (since electrons are charged particles) to a few microns across, and can be directed to any point on the sample by a series of magnetic lenses. The system must be evacuated to reduce attenuation and scatter of the electron beam (Pollard et al. 2006).

When an electron beam from the electron gun encounters a specimen in the specimen chamber, several important kinds of emissions take place (Fig. 4.78). The most useful emissions are emissions of backscattered electrons, secondary electrons, photons and X-rays.
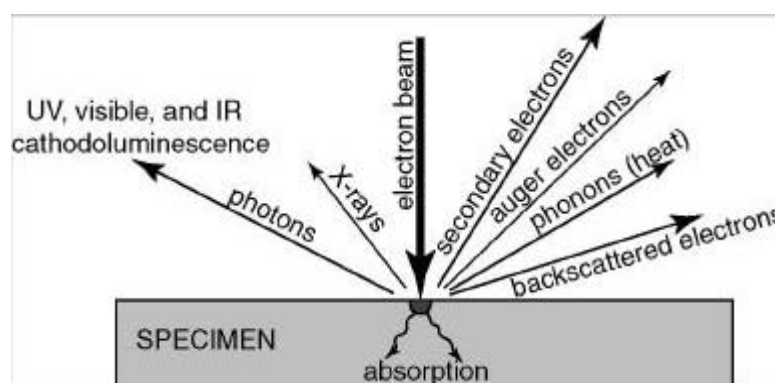
Figure 4.78 The schematic representation of dispersion of electron beam

Three important signals from the specimen are backscattered electrons, secondary electrons and X-rays. Backscattered electrons are primary beam electrons which have been elastically scattered by nuclei in the sample and escape from the surface. The fraction escaping varies from 0.06 for carbon to 0.5 for gold so a backscattered electron image (BEI) has compositional contrast. Backscattered electrons have a high energy and they can come from depths of 1 micrometer or more within the specimen. They leave the surface from a wide area, and this means that the resolution in BEI is low, only about 1 micrometer. BEI combined with x-ray microanalysis is a powerful method of determination of the local chemical composition of a material. Backscattered electrons travel in straight lines after leaving the specimen, so a detector to one side will give topographic contrast. The usual solid state detectors for BEI are placed directly above the specimen to increase collection efficiency. Split into halves or quarters, these detectors provide atomic number contrast by adding the signals from all sectors, and topographic contrast by subtraction of signals.

Secondary electrons are emitted from the specimen with low energy, less than 50 eV, so they come from the top few nanometers of the material. If the beam falls on a tilted surface or onto an edge, more secondaries will escape from the specimen.

When a high energy electron beam impinges upon a specimen, x-rays photons are produced. They fall into two classes. Characteristics X-rays have well defined energies which are characteristic of the atoms in the specimen. These X-rays

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form sharp peaks in the X-ray energy spectrum and contain analytical information. They are emitted by atoms in the specimen as they return to their ground state, after an inner shell electron has been removed by an interaction with a high energy beam electron. Continuum X-rays have a wide range energies and are the background in the X-ray energy spectrum, with no useful information. They are produced when incident high energy electrons are slowed by scattering near the atomic nucleus.

The essential feature of a scanning microscope is that the image is formed point by point, by scanning a probe across the specimen. The probe of a SEM is a focused electron beam and a detected signal is displayed as a TV type image. The electron beam in the display tube moves in synchrony with the probe on the specimen (Goldstein 1981).

Since Analytical SEM provides the researchers, simpler calculation of quantitative results, small analytical spot size whose location can be controlled combination of imaging and analysis, and improved detection levels over XRF, it continues to remain the one of the most important tools in examining the material (Pollard et all).

In this frame, most of the samples taken from Kültepe Excavation Site and examined in this study has been heavily corroded and the remaining metal core is too small to realize the element analysis reflecting the original used metal, all specimens were examined by using a scanning electron microscope equipped with energy dispersive X-ray analysis system (Figure 4.79) in Metallurgical and Materials Engineering Department in METU.

In this way, microstructure examination of samples at higher magnifications and element composition of many sections from the samples were realized.

The JSM-6400 basic unit consists of an electron optical column mounted on the main console, a control and display system, a power supply unit, and a pump box.

The main console incorporates a vacuum system, and the control and display system incorporates the control panels, keyboard, and display system. The basic SEM is connected to an EDS unit, which allows a characteristic X-ray spectrum to be displayed .
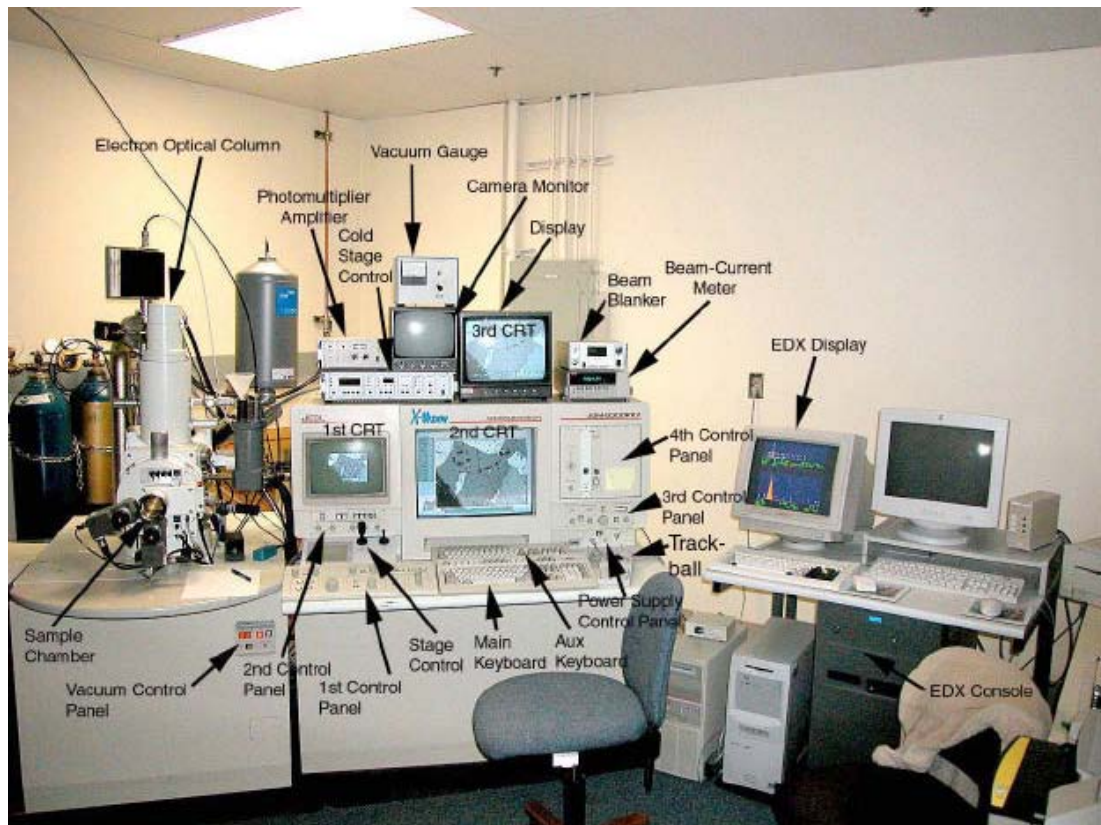
Figure 4.79 JEOL-6400 brand SEM unit and auxiliary equipments

### 4.2.5 Provenance Analysis by Using Lead Isotope

The use of ''chemical fingerprinting'' to trace metal objects back to their parent ore source has been one of the main goals of archaeological chemistry since the 1930's. To determine from which metalliferrous ore a metal object is produced by using the trace element composition of metal is very complicated by factors such as variations in partitioning due to process and temperature, mixing of ores from different sources, deliberate or accidental addition of metals to modify the working or visual properties of the finished product, and the likely recycling of scrap metal (Pollard et al. 2006).

The discovery in the late 1960s that the lead isotope ratios in an archaeological metal object give an indication of the ore source and are apparently unaffected by anthropogenic processing made this technique attractive(Pollard et al. 2006).

Lead is unique among all the metals in having variations among mining districts in the relative abundances of its stable (non-radioactive) isotopes. Lead has four stable, non-radioactive isotopes (atomic weights 204, 206, 207 and 208) and the relative amounts of each of these four, the isotopic composition (IC), varies among ore bodies. The general principle that is responsible for this variation is that the isotopes of lead which constitute an ore reflect the geological age of that ore body, the age of the Earth at the time when the ore body formed .(Rabinowitz 1995).

The principle lead ore is galena, the sulfide of lead. It often contains some bismuth, cadmium or silver as impurities, but practically no uranium or thorium. So once the ore is formed it is separated from its parent elements, and its isotope ratios will not change. Thus, ore formed 2.5 billion years ago had more primordial lead and relatively less decay products compared with ores formed only 500 million years ago, which will also include lead formed in the intervening 2 billion years. Uranium-235 decays to lead-207 with an apparent half life of 0.7 billion years, U-238 decays to lead-206 more slowly, a 4.5 billions year half life.Thorium-232 decays to lead-208 with a 14 billion year half life. Lead-204 is not created by radioactive decay, and what is now present is primordial.The net result is that older lead ores will have lower 206/204, 206/207, and 206/208 ratios than more recently formed lead ores (Rabinowitz 1995).

In this frame, it is thought that realizing of LIA to some samples uncovered from Kültepe in this study may provide a contribution to understand Kültepe metallurgy in terms of metal exchange also.

Therefore, LIA was applied to ten samples (Kt-37, Kt-41, Kt-42, Kt-46, Kt-49, Kt-50, Kt-54, Kt-57, Kt-59, Kt-64).

As stated above LIA was carried out in Central Laboratuary of METU.

In Central Laboratary, Pb was extracted from each sample using the following procedure:

A quantity of each sample was placed into an individual, pre-cleaned, Savillex vial and dissolved in about 1 ml 16 M $HNO_3$ by heating to 80°C overnight. The $HNO_3$ was evaporated to dryness and 1 ml of 1 M HBr was added to each vial.

The samples were then left to stand (cold) overnight. Separation of the Pb from the dissolved fraction was achieved using ion exchange methods. Five drops of cation exchange resin (AG1-X8) were added to pre-cleaned polypropylene columns, each fitted with a 35μm polyethylene frit. The resin was cleaned by eluting three times with onecolumn volume (CV) of Teflon-distilled 6 M HCl, followed by 1 CV Milli-Q water. The resin was then pre-conditioned by addition of Teflon-distilled 1 M HBr. The sample was then added to the column. Any Pb present in the sample forms stable bromide complexes with the preconditioned column surface; other elements present in the sample matrix are eluted off the column by washing with 1.5 CV of 1 M HBr. The isolated Pb fraction was then eluted off the column by washing with 1 CV 6 M HCl. This fraction was collected into a pre-cleaned Savillex beaker and 1 ml Teflon-distilled 16 M $HNO_3$ was added to each individual sample. Each sample was then dried at 100°C overnight (Weeks et al. 2009).

Consequently, the isotopes of the lead obtained from samples were measured in Thermal Ionization Mass Spectrometer (TIMS).

# CHAPTER 5

# RESULTS AND DISCUSSIONS

Since the main issue in this thesis is to understand the metal working technologies accomplished in Colony Period of Kültepe, the analysis of the uncovered metal artifacts belonging to Kültepe in terms of elemental composition and microstructure constitutes the backbone of the study.

In this respect, the metal artifacts uncovered from Kültepe Ancient Site belonging to Colony Period which are exhibited in the Anatolian Civilization Museum and which are not suitable for exhibition and seperated for studying in excavation site were examined.

## 5.1. The Analysis of Artifacts Exhibited in Anatolian Civilization Musuem

The many bronze artifacts uncovered from Kültepe excavations are exhibited in the Anatolian Civilization Museum. The analysis of artifacts exhibited in the museum representing the various type of implements from arm to daily life without giving any damage were performed by using portable XRF.

The analysis taken from the sections represented by numbers in their photographs (Fig. 4.1 to 4.33) of these thirtythree metal artifacts were given in Table 5.1 and explanations are at the following pages.

Table 5.1 Elemental composition of Kültepe excavations artifacts exhibited in the Anatolian Civilization Museum

| Artifact No | Object | Cu (%) | Sn (%) | As (%) | Sb (%) | Pb (%) | Fe (%) | Ni (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|---|
| Kt-01 | Spearhead (Section 1) | 99.03 | | 0.59 | | 0.17 | 0.21 | | |
| | Spearhead (Section 2) | 99.72 | | 0.14 | | 0.14 | | | |
| | Spearhead (Section 3) | 99.17 | | 0.50 | | 0.12 | 0.21 | | |
| Kt-02 | Spearhead (Section 1) | 98.70 | | 0.83 | | 0.14 | 0.32 | | |
| | Spearhead (Section 2) | 99.49 | | 0.23 | | 0.19 | 0.08 | | |
| | Spearhead (Section 3) | 99.32 | | 0.44 | | 0.13 | 0.12 | | |
| Kt-03 | Spearhead (Section 1) | 97.91 | | 1.03 | | 0.09 | 0.50 | | 0.46 |
| | Spearhead (Section 2) | 97.76 | | 1.03 | | 0.20 | 0.47 | | 0.53 |
| | Spearhead (Section 3) | 97.40 | | 1.12 | | 0.18 | 0.54 | | 0.76 |
| Kt-04 | Spearhead (Section 1) | 95.78 | | 1.98 | | 0.20 | 1.72 | | 0.32 |
| | Spearhead (Section 2) | 96.74 | 0.65 | 1.48 | | 0.32 | 0.48 | | 0.32 |
| | Spearhead (Section 3) | 97.51 | 0.36 | 1.01 | | 0.18 | 0.36 | | 0.59 |
| Kt-05 | Spearhead (Section 1) | 98.43 | 0.43 | 0.20 | | 0.32 | 0.13 | | 0.48 |
| | Spearhead (Section 2) | 98.00 | 0.49 | | | 0.38 | 0.08 | | 1.04 |
| | Spearhead (Section 3) | 97.89 | 0.35 | 1.02 | | 0.24 | 0.07 | | 0.42 |

Table 5.1 continued

| Artifact No | Object | Cu (%) | Sn (%) | As (%) | Sb (%) | Pb (%) | Fe (%) | Ni (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|---|
| Kt-06 | Spearhead (Section 1) | 99.05 | 0.46 | | | 0.23 | 0.25 | | |
| | Spearhead (Section 2) | 99.12 | | 0.23 | | | 0.22 | 0.20 | |
| Kt-07 | Spearhead (Section 1) | 97.39 | 0.63 | 1.14 | | 0.61 | 0.23 | | |
| | Spearhead (Section 2) | 97.37 | 0.52 | 0.99 | | 0.90 | 0.23 | | |
| | Spearhead (Section 3) | 94.92 | 0.71 | 3.50 | | 0.30 | 0.40 | 0.17 | |
| Kt-08 | Spearhead (Section 1) | 95.37 | | | | 3.48 | 0.65 | | |
| | Spearhead (Section 2) | 90.74 | | | | 8.92 | 0.31 | | |
| Kt-09 | Spearhead (Section 1) | 95.64 | | 2.19 | | 0.34 | 1.66 | 0.18 | 0.52 |
| | Spearhead (Section 2) | 96.82 | | 1.96 | | 0.42 | 0.62 | 0.18 | |
| | Spearhead (Section 3) | 95.50 | | 2.48 | | 0.55 | 0.76 | 0.18 | |
| Kt-10 | Flat axe (Section 1) | 97.91 | | 1.35 | | 0.21 | 0.53 | | |
| | Falt axe (Section 2) | 97.86 | | 1.31 | | 0.23 | 0.61 | | |
| Kt-11 | Flat axe (Section 1) | 98.51 | | 0.99 | | 0.13 | 0.37 | | |
| | Flat axe (Section 2) | 98.33 | | 1.20 | | 0.10 | 0.30 | | |

Table 5.1 continued

| Artifact No | Object | Cu (%) | Sn (%) | As (%) | Sb (%) | Pb (%) | Fe (%) | Ni (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|---|
| Kt-12 | Flat axe (Section 1) | 97.75 | | 1.49 | | 0.19 | 0.56 | | |
| | Flat axe (Section 2) | 97.84 | | 1.43 | | 0.23 | 0.50 | | |
| Kt-13 | Shaft-hole axe (Section 1) | 83.20 | 16.20 | 0.29 | | 0.17 | 0.15 | | |
| | Shaft-hole axe (Section 2) | 84.25 | 15.16 | 0.31 | | 0.09 | 0.18 | | |
| | Shaft-hole axe (Section 3) | 92.20 | 7.60 | 0.14 | | 0.06 | | | |
| | Shaft-hole axe (Section 4) | 90.94 | 8.78 | 0.22 | | 0.06 | | | |
| Kt-14 | Shaft-hole axe (Section 1) | 78.66 | 16.73 | 1.25 | | 2.53 | 0.54 | 0.30 | |
| | Shaft-hole axe (Section 2) | 83.23 | 12.71 | 0.59 | | 2.89 | 0.33 | 0.25 | |
| Kt-15 | Shaft-hole axe (Section 1) | 86.04 | 10.67 | 1.59 | | 0.77 | 0.92 | | |
| | Shaft-hole axe (Section 2) | 83.38 | 13.97 | 1.80 | | 0.45 | 0.39 | | |
| | Shaft-hole axe (Section 3) | 87.22 | 11.07 | 0.79 | | 0.70 | 0.21 | | |
| Kt-16 | Rivetted dagger (Section 1) | 97.92 | | | | | 2.08 | | |
| | Rivetted dagger (Section 2) | 98.32 | | 0.07 | | | 1.60 | | |
| | Rivetted dagger (Section 3) | 98.74 | | 0.07 | | | 1.19 | | |
| | Rivetted dagger (Section 4) | 98.22 | 0.79 | | | 0.10 | 0.90 | | |

Table 5.1 continued

| No | Object | Cu (%) | Sn (%) | As (%) | Sb (%) | Pb (%) | Fe (%) | Ni (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|---|
| Kt-17 | Dagger (Section 1) | 92.81 | | 4.91 | | 0.31 | 1.97 | | |
| | Dagger (Section 2) | 92.94 | | 5.56 | | 0.30 | 1.20 | | |
| Kt-18 | Dagger (Section 1) | 98.51 | | 0.73 | | 0.30 | 0.46 | | |
| | Dagger (Section 2) | 95.77 | | 0.77 | | 2.65 | 0.82 | | |
| | Dagger (Section 3) | 56.88 | | | | 41.05 | 2.07 | | |
| Kt-19 | Chisel (Section 1) | 96.69 | | 2.91 | | 0.25 | 0.16 | | |
| | Chisel (Section 2) | 95.65 | | 3.79 | | 0.26 | 0.16 | 0.14 | |
| | Chisel (Section 3) | 96.12 | | 3.52 | | 0.19 | 0.16 | | |
| Kt-20 | Fork weapon (Section 1) | 84.33 | 11.51 | 0.31 | | 3.69 | 0.16 | | |
| | Fork weapon (Section 2) | 93.48 | 4.84 | | | 1.68 | | | |
| | Fork weapon (Section 3) | 93.27 | 5.26 | | | 1.46 | | | |
| | Fork weapon (Section 4) | 78.48 | 16.97 | 1.33 | | 2.77 | 0.44 | | |
| Kt-21 | Sickle blade (Section 1) | 98.98 | | 0.87 | | 0.08 | 0.07 | | |
| | Sickle blade (Section 2) | 99.06 | | 0.78 | | 0.09 | 0.08 | | |

Table 5.1 continued

| No | Object | Cu (%) | Sn (%) | As (%) | Sb (%) | Pb (%) | Fe (%) | Ni (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|---|
| Kt-22 | Sickle blade part (Section 1) | 98.73 | | 0.60 | | 0.41 | 0.08 | 0.18 | |
| | Sickle blade part (Section 2) | 98.59 | | 0.65 | | 0.53 | | 0.23 | |
| Kt-23 | Ring (Section 1) | 97.09 | | 0.42 | | 1.00 | 1.49 | | |
| | Ring (Section 2) | 97.19 | | 0.23 | | 0.61 | 1.97 | | |
| Kt-24 | Ring (Section 1) | 90.34 | | 6.14 | | 1.31 | 2.21 | | |
| | Ring (Section 2) | 88.88 | | 8.61 | | 0.61 | 1.90 | | |
| Kt-25 | Bracelet (Section 1) | 92.95 | 4.87 | 0.23 | | 0.10 | 0.46 | | 0.43 |
| | Bracelet (Section 2) | 93.62 | 5.23 | 0.29 | | 0.11 | 0.37 | | 0.37 |
| Kt-26 | Finger cymbal (Section 1) | 97.84 | 0.52 | 0.97 | | 0.57 | 0.10 | | |
| | Finger cymbal (Section 2) | 96.87 | | 2.29 | | 0.41 | 0.43 | | |
| Kt-27 | Drinking cup (Section 1) | 92.46 | 7.09 | 0.10 | | | 0.35 | | |
| | Drinking cup (Section 2) | 92.80 | 6.41 | 0.13 | | | 0.65 | | |
| Kt-28 | Drinking cup (Section 1) | 84.77 | 11.17 | 0.91 | 0.94 | 0.79 | 0.49 | | 0.93 |
| | Drinking cup (Section 2) | 85.35 | 11.29 | 0.91 | 0.81 | 0.78 | 0.21 | | 0.65 |

Table 5.1 continued

| No | Object | Cu (%) | Sn (%) | As (%) | Sb (%) | Pb (%) | Fe (%) | Ni (%) | Zn (%) |
|---|---|---|---|---|---|---|---|---|---|
| Kt-29 | Small bowl (Section 1) | 88.25 | | 9.52 | | 0.49 | 1.74 | | |
| | Small bowl (Section 2) | 94.13 | | 4.87 | | 0.43 | 0.57 | | |
| Kt-30 | Drinking cup (Section 1) | 93.40 | 6.55 | 0.06 | | | | | |
| | Drinking cup (Section 2) | 96.40 | 3.55 | 0.05 | | | | | |
| Kt-31 | Small shovel (Section 1) | 95.72 | | 2.40 | | 0.61 | 0.76 | | 0.30 |
| | Small shovel (Section 2) | 98.46 | | 0.90 | | 0.36 | 0.28 | | |
| | Small shovel (Section 3) | 97.73 | | 1.44 | | 0.50 | 0.33 | | |
| Kt-32 | Fired pipe piece (Section 1) | 97.10 | | 1.57 | | 0.37 | 0.57 | | 0.39 |
| | Fired pipe piece (Section 2) | 88.18 | | | | 2.98 | 8.19 | | |
| Kt-33 | Small animal sculpture (Section 1) | 98.86 | | 0.06 | | 0.07 | | | |
| | Small animal sculpture (Section 2) | 95.27 | | 0.32 | | 0.36 | 3.18 | 0.25 | 0.62 |
| | Small animal sculpture (Section 3) | 95.94 | | 0.42 | | 0.39 | 1.87 | | 1.39 |
| | Small animal sculpture (Section 4) | 99.77 | | 0.11 | | 0.12 | | | |

Those thirtythree artifacts can be subdivided into two groups as warfare tools (20 samples) and daily utensils (13 samples). Warfare tools are composed of spearheads, flat axes, shaft-hole axes, daggers, a chisel and a fork weapon (Figure 4.1 - 4.20) while daily utensils include sickle blades, rings, drinking cups, a bracelet, a finger cymbal, a small bowl, a small shovel, a fired pipe piece and a small animal sculpture (Figure 4.21 – 4.33).

Each group in warfare tools and daily utensils is examined individually in terms of elemental composition to understand whether the specific composition is used or not.

All nine spearheads are mainly copper with the percentages changing from 90.74 to 99.72, average being 97.39.

Second important element is arsenic with an amount varying between 0.14% and 3.50% average being 0.96%. Arsenic exists in all spearhead samples except Kt-08.

Lead and iron are present in all spearhead samples. Lead value is between 0.09%and 8.92%average being 0.75%, while iron percentage in spearhead samples varies from 0.08 to 1.72, average being 0.41.

In some spearheads, zinc is also present with a percentage of varying 0.32 to 1.04, average being 0.22.

The interesting point observed in spearhead samples is that the much of lead content of Kt-08 artifact with the amount of 3.48% at handle end and 8.92% at sharp end. This lead proportion may be the indicator of deliberately adding it to copper.

Three flat axe samples (Fig. 4.10 – 4.12) have copper percentages varying from 97.75 to 98.51, average being 98.03%.

Arsenic content is between 0.99% - 1.49%, average being 1.29% while lead is present in the percentage of 0.10 to 0.23, average being 0.18 and iron exists in the range of 0.30 – 0.61, average being %0.48.

The analysis results of these three flat axes show a homogeneous element composition.

The another type of axe is the shaft hole axe and there are three artifacts to have the opportunity of making element analysis from this axes (Figure 4.13 – 4.15).

Copper is the main constituent with a varying proportion between 78.66%and 92.20% average being 85.46%.

The second important element in this type of axes is tin with a content of 7.60% to 16.73%, aveage being 12.54%.

Arsenic exists in this type of artifacts in the range of 0.14% - 1.59%, average being %0.77, while lead content is between 0.06% and 2.89%, average being 0.86% and iron varies in the range of 0.15% - 0.92%, average being 0.3%.

Nickel exists in Kt-14 only with an average quantity of 0.28%.

The most striking feature observed in this type of axes is the existence of tin with amount of 7.60% and over which imply that tin is deliberately added to copper to have tin bronze.

Another artifact in warfare classification is dagger and there are three daggers one of them is rivetted type which was examined in this study (Figure 4.16 – 4.18).

All daggers are mainly copper with the percentages changing from 56.88 to 98.74 average being 92.23%.

Arsenic exists with an amount varying between 0.07% and 5.56%, average being 1.34%.

However, lead and iron are present in all dagger samples. Lead value is between 0.1% and %41.05 while iron percentage varies 0.9 – 2.08, average being 1.36%.

The first point that may be underlined is the higher arsenic content of the sample Kt-17 with the average of 5.23%.

The second important point is the higher iron content of the daggers with average of 1.36% compared to both 0.51% of warfare group and 0.67% of overall samples.

The third point is the very big increase in lead content of section 3 of Kt-18.

The other sections, 1 and 2 do not show the same results. The copper content of section 1 and section 2 are 98.51% and 95.77% respectively. There seems to be a joining of two different alloys which constitute the metal artifact. The fact that no arsenic was found in section 3 although section 1 and 2 comprise appreciable proportions as 0.73% and 0.77% respectively, and iron content is too much in section 3 with 2.07% compared to section 1 and 2 with amounts of 0.46% and 0.82% respectively, also can be interpreted as the evidence of joining two different parts.

Since it is not possible to make microstructural study on the sample belonging to museum, the study was limited with the elemental analysis and so it is difficult to arrive at the exact conclusion.

There is one chisel sample with average copper content of 96.15%, average arsenic content of 3.40%, average lead content of 0.23% and average iron content of 0.16% which shows usual metal composition of that period.

The last object under warfare tool classification is fork weapon which seems the joining of two pieces as being at dagger sample (Kt-18).

The elemental composition from the sections 1 and 4 of handle part and the elemental composition from the sections 2 and 3 of fork part show remarkable difference. Average copper percentage is 81.4% at handle part while it is 93.37% at fork part. In addition to this, average tin content is 14.24% at handle part while it is 5.05% at the fork part. At handle part arsenic was present with the amount of 0.82% but at fork part no arsenic was found.

When the remaining constituents lead and iron are examined, the same situation was observed. Iron is present with the average of 0.30% at handle part, while no iron is present at fork part and lead exists with the average of 3.23% at handle part while 1.57% at the fork part.

Daily utensils of samples are thirteen pieces. Main element of this group is also copper.

Sickle blades (Kt-21, Kt-22) show the similar pattern as examined samples above with the copper varying between 98.59% and 99.06%, average being 98.84%.

Arsenic content of sickle blades is in the range of 0.60% and 0.87%, average being 0.72% while lead exists between 0.08% and 0.53%, average being 0.28% and iron is present with a very small amount of 0.06%. In addition, nickel is observed at sample Kt-22 as average being 0.20%.

There are two ring samples (Kt-23, Kt-24) which mainly differ from each other with their arsenic contents. Kt-23 sample includes average 97.23% copper, 0.33% arsenic, 0.8% lead, 1.73% iron while Kt-24 sample has average 89.61% copper, 7.38% arsenic, 0.6% lead and 2.1% iron.

The most striking point here is the arsenic content of sample Kt-24. The amount of 7.38% is by far big compared to the arsenic content of the other samples of which average is 1.28%.

The ring samples have an appreciable iron also with an average quantity of 1.89% compared to average iron amount of all samples that is 0.68%.

There is one sample to be considered in the frame of jewellery piece. This is sample Kt-25, bracelet. It is composed of average 93.25% copper, 5.05% tin, 0.26 % arsenic, 0.96% lead, 0.41% iron.

The most discernible point in this element composition is the high tin content which gives hardness to the structure not to be needed for a piece of jewellery.

The element composition of the sample Kt-26 supposed to be a finger cymbal is 93.29% copper, 0.26% tin, 1.63% arsenic, 0.49% lead and 0.27% iron which represent very harmonious composition with the general copper based products of that period.

There are three samples (Kt-27, Kt-28, Kt-29) to be considered as drinking cup.

All three drinking cups are mainly copper with the percentages changing from 84.77 to 96.40, average being 90.86% .

Second important element is tin with an amount varying between 3.55% and 11.29%, average being 7.68%.

Arsenic content of drinking cups varies between 0.05% and 0.91%, average being 0.36% while lead, antimony and zinc exist with an average amount of 0.79%, 0.87% and 0.79%, respectively only in sample Kt-28.

Iron is observed at samples Kt-27 and Kt-28 varying between 0.21% and 0.65%, average being 0.42%.

The presence of tin in appreciable quantities in all of drinking cups is the interesting point that can be investigated in another similar cups of that period to make a generalization.

There is a small bowl (Kt-30) which has average 91.20% copper, 7.20% arsenic, 0.46% lead, 1.15% iron as elemental composition.

The high arsenic content of small bowl like ring sample (Kt-24) differentiate it from other samples of which average arsenic content of all is 1.28%.

The element composition of the small shovel designated by Kt-31 is 97.30% copper, 1.58% arsenic, 0.49% lead, 0.46% iron and 0.10% zinc as average values which represent very harmonious composition with the general copper based products of that period.

A small tube (Kt-32) supposed to be exposed to fire is another interesting sample which was examined in this study. Since the outer part of the tube was cleaned in the museum, the elemental composition of inner and outer sections of sample showed the difference.

The copper content of outer layer is 97.10% while inner part's has 88.18%. Iron is 0.57% at outer layer, 8.19% at inner while lead is 0.37% at outer layer, 2.98% at inner layer.

The last sample from museum for elemental examination by PXRF is a small animal sculpture which was designated by Kt-33.

It has average 97.46% copper, 0.23% arsenic, 0.23% lead, 1.26% iron, 0.06% nickel and 0.50% zinc which shows harmonious composition with the general copper based products of that period.

Average elemental composition of each group and overall samples are given in Table 5.2.

Table 5.2 Comparison for Average Elemental Composition of All Groups

| Elements | Warfare Group Average | Daily Utensils Group Average | All Samples Average |
|---|---|---|---|
| Cu (%) | 93.93 | 94.64 | 94.17 |
| Sn (%) | 2.80 | 1.95 | 2.51 |
| As (%) | 1.12 | 1.58 | 1.28 |
| Sb (%) | - | 0.06 | 0.02 |
| Pb (%) | 1.47 | 0.48 | 1.14 |
| Fe (%) | 0.52 | 0.98 | 0.68 |
| Ni (%) | 0.03 | 0.02 | 0.03 |
| Zn (%) | 0.10 | 0.17 | 0.12 |

As it is seen from table, there is not remarkable differences in composition of groups. However, tin and lead amounts are higher in warfare group with respect to daily utensils group. Especially lead exists in warfare group about three times of daily utensils group's. This difference should be investigated by further study whether lead is deliberately added to the certain group of tools.

Tin as an important alloying element which increases the hardness of the copper seems to appear especially in the production of warfare tools which is expected to have a higher strength.

Apart from these, the existence of other elements existed in the structure may be interpreted as impurities passing from ore during smelting process.

### 5.2. The Analysis of Artifacts Fragments

Besides the examination of exhibited artifacts in the Anatolian Civilization Museum, the uncovered small fragments of metal artifacts which are not suitable for exhibition and separated for studying in Kültepe Excavation Site were examined by using Scanning Electron Microscope coupled with Energy Dispersive X-Ray Spectrometer (SEM-EDS) and optical microscope.

Thirtytwo artifacts fragments shown in Figures 4.34 – 4.65 are composed of mainly cutter and piercing tools (chisel and pin fragments) that are suitable to use at daily life. Apart from these, a ring, a small plate fragment and a small bowl fragment are inside the examined pieces.

### 5.2.1 The Elemental Analysis of Artifacts Fragments by SEM-EDS

There are mainly two groups; cutter tool (chisel fragments) and piercing tool (pins). Each group was examined individually in terms of element composition to understand whether the specific composition is used or not.

The element analysis of these thirtytwo samples were performed by SEM-EDS. The results are given in Table 5.2 and related explanations are at the following pages.

Chisel and pins are classified especially according to their size and crosss-sections. Chisel parts are bigger and their cross-sections are rectangular or square while the cross-section of the pins are generally circular.

All nine chisel samples (Kt-34, 36, 40, 48, 49, 54, 58, 59, 64) are mainly copper with the percentages changing from 86.59 to 98.41, average being 93.31%.

Second important element is tin which exists at six of nine samples with an amount varying between 0.45% and 9.83%, average being 3.80%. Tin content were 9.83%, 8.57%, 7.28%, 6.24% for Kt-49, Kt-64, Kt-34 and Kt-59, respectively which imply deliberately adding of tin with copper. Samples Kt-36, Kt-54 and Kt-58 do not have tin while Kt-40 and Kt-48 have 1.85% and 0.45%, respectively which may result from the smelted copper to be used for production of these chisels.

Table 5.3 Elemental composition of artifacts fragments uncovered from Kültepe excavations

| Sample No | Object | Cu (%) | Sn (%) | As (%) | Pb (%) | Fe (%) | Ag (%) | Au (%) | Ni (%) | Cl ( %) | Mg (%) | Si (%) | Sb (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Kt-34 | Chisel Fragment | 90.70 | 7.28 | 0.74 | - | 0.09 | - | 1.04 | - | - | - | 0.15 | - |
| Kt-35 | Pin Fragment | 97.64 | 0.54 | 0.83 | - | 0.41 | - | - | - | - | - | 0.18 | 0.40 |
| Kt-36 | Chisel Fragment | 94.38 | - | 3.16 | - | 0.20 | - | - | - | 1.91 | 0.35 | - | - |
| Kt-37 | Plate Fragment | 98.32 | - | 0.86 | 0.07 | 0.05 | 0.14 | 0.47 | - | - | 0.09 | - | - |
| Kt-38 | Pin Fragment | 97.61 | 0.11 | 0.91 | - | 0.15 | 0.15 | - | - | 0.83 | 0.24 | - | - |
| Kt-39 | Pin Fragment | 97.20 | - | 1.31 | - | 0.57 | 0.07 | - | - | 0.81 | | 0.04 | |
| Kt-40 | Chisel Fragment | 93.10 | 1.85 | 1.19 | 0.29 | 0.27 | 0.10 | - | 0.99 | 1.44 | 0.07 | 0.18 | 0.52 |
| Kt-41 | Pin Fragment | 96.34 | - | 1.37 | - | 1.19 | - | 0.65 | - | - | 0.24 | 0.15 | 0.06 |
| Kt-42 | Pin Fragment | 95.71 | 0.37 | 1.73 | 0.25 | 0.40 | - | - | - | 0.95 | 0.42 | 0.13 | 0.04 |
| Kt-43 | Pin Fragment | 89.19 | 0.35 | - | - | 0.48 | - | - | - | - | - | - | 0.33 |
| Kt-44 | Pin Fragment | 93.82 | 1.14 | 1.32 | - | 0.77 | 0.56 | - | - | 1.07 | 0.72 | 0.05 | 0.55 |
| Kt-45 | Bowl Fragment | 86.15 | 11.43 | 0.23 | - | - | - | - | - | 1.01 | - | 0.55 | 0.63 |
| Kt-46 | Pin Fragment | 96.18 | 0.40 | - | 0.58 | 0.10 | - | - | - | 2.43 | - | 0.31 | - |
| Kt-47 | Pin Fragment | 99.03 | - | 0.28 | - | - | 0.25 | - | - | - | - | 0.18 | 0.26 |
| Kt-48 | Chisel Fragment | 97.36 | 0.45 | 0.58 | - | 0.08 | 0.24 | 0.60 | - | 0.65 | - | 0.04 | - |
| Kt-49 | Chisel Fragment | 86.59 | 9.83 | 1.04 | 0.42 | 0.41 | - | 1.41 | - | 0.28 | - | 0.02 | - |

Table 5.3 continuied

| Sample No | Object | Cu (%) | Sn (%) | As (%) | Pb (%) | Fe (%) | Ag (%) | Au (%) | Ni (%) | Cl ( %) | Mg (%) | Si (%) | Sb (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Kt-50 | Ring Fragment | 93.90 | - | 2.66 | 0.79 | 0.79 | - | 0.52 | - | 1.11 | 0.23 | - | - |
| Kt-51 | Pin Fragment | 98.15 | - | 1.24 | 0.16 | 0.45 | - | - | - | - | - | - | - |
| Kt-52 | Pin Fragment | 97.09 | 0.33 | 0.76 | - | 0.67 | 0.42 | 0.62 | - | - | - | 0.08 | 0.03 |
| Kt-53 | Pin Fragment | 96.06 | 0.33 | 1.72 | - | 0.62 | - | 0.67 | - | - | - | 0.10 | 0.50 |
| Kt-54 | ChiselFragment | 97.43 | - | 0.09 | 0.82 | 0.24 | - | - | - | 1.31 | - | 0.11 | - |
| Kt-55 | Pin Fragment | 96.76 | 0.17 | 0.58 | - | 0.55 | 0.34 | - | - | 0.98 | - | 0.50 | 0.12 |
| Kt-56 | Pin Fragment | 97.23 | 0.26 | 1.00 | 0.03 | 0.61 | 0.04 | - | - | 0.30 | 0.04 | 0.36 | 0.13 |
| Kt-57 | Pin Fragment | 97.94 | - | 0.38 | 0.11 | 0.05 | 0.25 | - | - | - | - | 0.18 | 1.09 |
| Kt-58 | Chisel Fragment | 98.41 | - | 0.46 | - | 0.66 | - | - | - | - | - | 0.08 | 0.39 |
| Kt-59 | ChiselFragment | 92.10 | 6.24 | 0.66 | 0.43 | 0.17 | - | - | - | - | 0.16 | 0.24 | - |
| Kt-60 | Pin Fragment | 98.78 | 0.16 | 0.37 | - | 0.28 | 0.27 | - | - | - | - | 0.14 | - |
| Kt-61 | Pin Fragment | 96.73 | - | 0.83 | 0.29 | 1.12 | 0.23 | - | - | - | - | 0.10 | 0.70 |
| Kt-62 | Pin Fragment | 97.79 | - | 0.79 | - | 0.23 | - | 1.04 | - | - | 0.11 | 0.04 | - |
| Kt-63 | Pin Fragment | 95.77 | - | 2.19 | 0.62 | 1.14 | 0.04 | - | - | - | - | 0.24 | - |
| Kt-64 | Chisel Fragment | 89.70 | 8.57 | 0.55 | 0.23 | 0.25 | - | 0.05 | - | - | | 0.23 | 0.42 |
| Kt-65 | Pin Fragment | 96.06 | - | 1.75 | 0.33 | 1.37 | 0.15 | - | - | - | 0.18 | - | 0.16 |

Since chisel requires hardness to perform the task expected from it, the ancient Kültepe metalsmiths seem to learn adding tin to obtain tin bronze which has better mechanical properties compared to copper itself.

Arsenic exists in all chisels with an amount varying between 0.09% and 3.16% average being 0.94%. The presence of arsenic may result from the copper ingot which was produced from ores including arsenic.

However, iron is present in all chisel samples with a value between 0.09% and 0.66%, average being 0.26%, while lead exists in five of nine samples with the amount varying between 0.23% and 0.82%, average being 0.24%.

One of the interesting points observed in some chisel samples is the presence of gold and silver. Samples Kt-34, Kt-38 and Kt-49 have 1.04%, 0.6% and 1.41% gold, respectively.

Another remarkable point is that only the sample Kt-40 includes nickel with 0.99% amongst all samples, not just chisels, while antimony exists in three samples; Kt-40, Kt-58, Kt-64 with the values of 0.52%, 0.39%, 0.42%, respectively.

As stated above, all these fragments stayed beneath the soil approximately 4000 years. Naturally all of them were exposed to the chemistry of soil and attacked by corrosive effects of moist soil. Therefore the elements observed in the chisel samples like chlorine, magnesium and silicone existed in soil are mainly the result of corrosion mechanism which proceeded from outer surface to the inside of the metal.

The other main group examined in this study is pins. There are twenty samples (Kt-35, 38, 39, 41, 42, 43, 44, 46, 47, 51, 52, 53, 55, 56, 57, 60, 61, 62, 63, 65) belonging to this group.

All twenty pin samples have copper as main element with the percentages changing from 89.19 to 99.03 average being 96.55%.

Arsenic appears as second important element which exists in all pin samples except Kt-43 and Kt-46 in appreciable quantities. The arsenic percentage varies between 0.28 and 2.19, average being 0.97%. On the contrary to chisel group, the deliberate addition of tin to the copper in pin group is not observed. Tin exists in

eleven of twenty samples (Kt-35, 38, 42, 43, 44, 46, 52, 53, 55, 56, 60) in small amounts between 0.11% and 1.14%, average being 0.21%.

However, iron is present in all pin samples like in chisel group with a value between 0.05% and 1.37%, average being 0.56% except Kt-47.

Lead exists in eight of twenty samples varying between 0.03% and 0.62%, average being 0.12%.

The same situation about the presence of gold and silver observed in some chisel samples exists in pin group also. Twelve of twenty samples include silver with a value between 0.04% and 0.56%, average being 0.14% and gold is present in four samples with a quantity between %0.62 and %1.04, average being 0.15%.

All except seven of the samples include antimony in small quantities changing between 0.03% and 1.09%, average being 0.22%, while the elements related with the corrosion like chlorine, magnesium and silicon exist in small quantities. Exception to this, there are two samples (Kt-43 and Kt-46) with high chlorine presence of 9.65% and 2.43%, respectively. Especially in sample Kt-43, corrosion attacked all metal matrice so that chlorine appears too much even though the analysis is performed from the core by EDS unit of SEM.

There are three samples not to be classified into these two groups. These are a plate fragment (Kt-37), a bowl fragment (Kt-45), and a ring (Kt-50).

A plate fragment has a typical element composition with 98.32% copper, 0.86% arsenic, 0.47% gold, 0.14% silver, 0.08% magnesium, 0.07% lead and 0.05% iron.

However, a bowl fragment differs with its tin content of 11.43% representing typical tin bronze. Arsenic quantity is low with %0.23 compared to the 0.99% average content of all samples. The other three elements observed in the sample are chlorine with 1.01%, silicon with 0.55% and antimony with 0.63%.

The last sample examined in this study is a ring which has a composition of 93.9% copper, 2.66% arsenic, 0.79% lead, 0.79% iron, 0.52% gold, 1.11% chlorine and 0.23% magnesium, which shows similarity in terms of element composition.

The average quantity of elemental composition of all sample and that of groups are given in Table 5.4.

Table 5.4 Comparison for Average Elemental Composition of All Groups

| Elements | Chisel Group Average | Pin Group Average | Other Three Sample Average | All Samples Average |
|---|---|---|---|---|
| Cu (%) | 93.31 | 96.55 | 92.79 | 95.29 |
| Sn (%) | 3.80 | 0.21 | 3.81 | 1.56 |
| As (%) | 0.94 | 0.97 | 1.25 | 0.99 |
| Pb (%) | 0.24 | 0.12 | 0.29 | 0.17 |
| Fe (%) | 0.26 | 0.56 | 0.28 | 0.45 |
| Ag (%) | 0.04 | 0.14 | 0.05 | 0.10 |
| Au (%) | 0.34 | 0.15 | 0.33 | 0.22 |
| Ni (%) | 0.11 | 0.00 | 0.00 | 0.03 |
| Cl (%) | 0.62 | 0.85 | 0.71 | 0.77 |
| Mg % ) | 0.06 | 0.10 | 0.11 | 0.09 |
| Si (%) | 0.12 | 0.14 | 0.18 | 0.14 |
| Sb (%) | 0.15 | 0.22 | 0.21 | 0.20 |

As it is seen from Table 5.4, there is no remarkable difference in amount of copper content between groups.

The main discernible feature is the tin amount. Especially the high amount of tin in chisel group may be interpreted as the fact that the ancient Kültepe metalsmiths seem to learn adding tin to obtain tin bronze which has better mechanical properties compared to copper itself.

## 5.2.2 The Corrosion Analysis on Some Samples by SEM-EDS

As stated in many part of this thesis, the samples examined in this study belong to the Colonies Period of Kültepe dated 1945-1730 B.C. which means that all of this artifact fragments stayed beneath the soil approximately 4000 years till they were uncovered in the frame of excavation study.

Naturally, during a span of 4000 years, all metal artifacts were exposed to the oxidation, humidity and soluble salts such as alkaline and alkaline earth chloride, nitrate, sulphate, carbonate, phosphate and etc. in the environment (Table 5.5). Therefore, the elements observed in the chisel samples like chlorine, magnesium, silicon and etc. existed in soil are mainly the result of corrosion mechanism which proceeded from outer surface to the inside of metal.
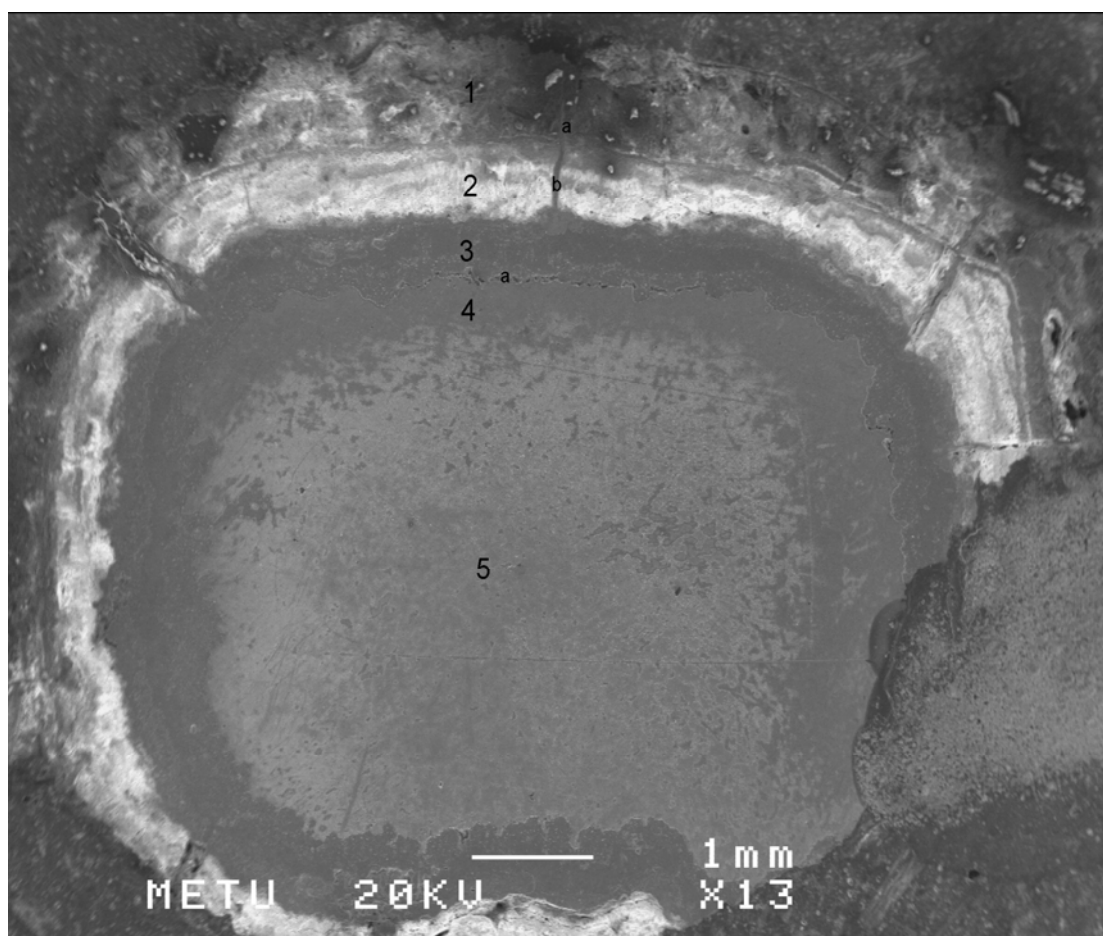


Figure 5.1 SEM micrograph of sample Kt-36 cross-section

To study corrrosion mechanism sample Kt-36 was selected, due to the fact that it is relatively big and examination of corrosion layers of the sample reveals the corrosion mechanism clearly under the SEM observation.

The cross-section micrograph of sample which shows all corrosion layers how proceeded inside from outer surface was given in Figure 5.1.

The elemental analysis of each section shown by numbers was carried out in SEM-EDS unit. The results are given in Table 5.5.

The elemental composition of the outest layer (layer-1) shows that the metal buried under soil during a long time produced compounds with the soil elements. The silicon content of 26.97%, magnesium content of 1.44%, aluminium content of 2.75%, sulphur content of 2.99%, potassium content of 0.88%, calcium content of 1.29%, iron content of 1.19% and chlorine content of 5.93% prove the interaction of metal with soil elements.

Figure 5.2 and Figure 5.3 show the micrograph taken from layer-1 and EDS spectrum belonging to this area, respectively.

Corrosion is essentially an electrochemical process resulting in part or all of the metal being transformed from the metallic state to the ionic one. Corrosion requires a flow of electron between certain areas of a metal surface through an electrolyte. An electrolyte is any solution that contains ions (Avner 1986).

There is a tendency for metals to react chemically to form compounds. Therefore most metals exist in nature in the combined state as, oxides, sulfides, carbonates or silicates, since their energy in combined state is lower (Smith 1990).

Since humid soil is a good environment, metal under soil will have a tendency to make compounds according to the composition of soil.

In all corrosion reactions, it should be considered that copper is oxidized accompanying oxidizing agent. Here in our case it is most probable that the oxidizing agent is oxygen present in soil as dissolved gas.

The reaction between oxygen and copper can be written as follow.

$$4\,Cu\,(s) + O_2\,(g) + 2\,H_2O \longrightarrow 4\,Cu^+ + 4\,OH^-$$
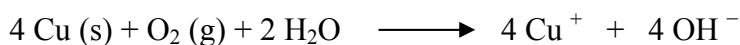
The $Cu^+$ produced may react with ions present around in soil to form a salt. Here the most expected ions are $Cl^-$, $CO_3^{2-}$ which have a great tendency for copper to make compounds.

When the deeper layer into metal core is examined, soil effect disappears. The elemental composition of layer-2 is 78.92% copper, 20.05% chlorine, 0.55% gold, 0.14% zinc, 0.10% silver.

Figure 5.4 and Figure 5.5 show the micrograph taken from layer-2 and EDS spectrum belonging to this area, respectively.

In layer-3, diffusion of chloride seems to grow with 9.15% increase and it reaches 29.20% while copper amount reduces to 69.87%.

Figure 5.6 and Figure 5.7 shows the micrograph taken from layer-3 and EDS analysis belonging to this area, respectively.

In Figure 5.6 the small island in main structure differing with its brighter colour with respect to main matrix (designated by a) was analyzed. The result shows that this regions are attacked by chloride. The elemental composition is 68.19% copper, 30.85% chlorine, 0.46% tin, 0.35% zinc and 0.15% iron.

The layer-4 has elemental composition as 78.74% copper, 18.88% chlorine, 1.86% sulphur and 0.52% iron. The diffusion of chloride seems to decrease in this region.

Figure 5.8 and Figure 5.9 show the micrograph taken from layer-4 and EDS analysis belonging to this area, respectively.

The layer-5 which is expected to be the metal core differs with its bright colour with respect to the outer layers which contain appreciable amount of corrosive agents.

Figure 5.10 and Figure 5.11 shows the micrograph taken from layer-5 and EDS analysis belonging to this area, respectively.

Table 5.5 The elemental composition of shown sections of sample Kt-36

| Section | Cu (%) | Sn (%) | As (%) | Ca (%) | Fe (%) | Ag (%) | Au (%) | S (%) | Cl ( %) | Mg (%) | Si (%) | K (%) | Al (%) | Zn (%) |
|---------|--------|--------|--------|--------|--------|--------|--------|-------|---------|--------|--------|-------|--------|--------|
| 1 | 56.21 | - | - | 1.29 | 1.19 | - | - | 2.99 | 5.93 | 1.44 | 26.97 | 0.88 | 2.74 | 0.36 |
| 1-a | 98.00 | 0.23 | - | - | 0.10 | - | - | - | 1.67 | - | - | - | - | - |
| 1-b | 98.05 | - | - | - | - | - | - | - | 1,95 | - | - | - | - | - |
| 2 | 78.92 | - | - | - | 0.24 | 0.10 | 0.55 | - | 20.05 | - | - | - | - | 0.14 |
| 3 | 69.87 | - | - | - | - | - | 0.93 | - | 29.20 | - | - | - | - | - |
| 3-a | 68.19 | 0.46 | - | - | 0.15 | - | - | - | 30.85 | - | - | - | - | 0.35 |
| 4 | 78.74 | - | - | - | 0.52 | - | - | 1.86 | 18.88 | - | - | - | - | - |
| 5 | 94.38 | - | 3.16 | - | 0.20 | - | - | - | 1.91 | 0.35 | - | - | - | - |
| 5-a | 52.14 | - | - | 7.78 | - | - | 1.95 | 1.64 | 27.68 | 1.84 | 0.93 | 3.39 | 2.33 | 0.32 |
| 5-b | 68.92 | 0.62 | 0.29 | - | 0.18 | - | 0.71 | - | 29.28 | - | - | - | - | - |

The elemental composition of layer-5 is 94.38% copper, 3.16% arsenic, 1.91% chlorine, 0.35% magnesium and 0.20% iron.

The most striking point here is that arsenic which exists in main structure with the amount of 3.16% disappeared in the regions to be attacked by corrosion. The reason of this phenomenon may be the formation of various compounds of arsenic which are generally volatile.

The second interesting point is that chlorine is stil present with appreciable amount of 1.91% in relatively deeper region of sample that corrosion is not expected to reach. This may be due to high mobility of chloride ions.

In Figure 5.10 the small precipitations in main structure differing with its darker colour with respect to main matrix (designated by "a" and "b") was also analyzed. The elemental analysis of "a"region is 52.14% copper, 27.68% chlorine, 7.78% calcium, 3.39% potassium, 2.33% aluminium, 1.95% gold, 1.84% magnesium, 1.64% sulphur, 0.93% silicon, 0.32% zinc.

In order to estimate the structure in "a"; It is suitable to make following approach;

Copper has molar weight of 63 and chlorine has 35.5 g/mol. If their moles in 100 g of sample are calculated; copper has 52.14/63=0,83 mol, chlorine has 27.68/35.5=0.78 mol. 0.78 mol chlorine corresponds to 0.78 mol of CuCl which is the salt supposed to be formed here. 0.78 mol CuCl also corresponds to 0.78 mol Cu corroded. As a result, it may be suggested that (0.78/0.83)X100= %94 of region "a" corresponds to CuCl salt formation. Here, CuCl salt formation was supposed to be in this case since it is insoluble salt in humid environment.

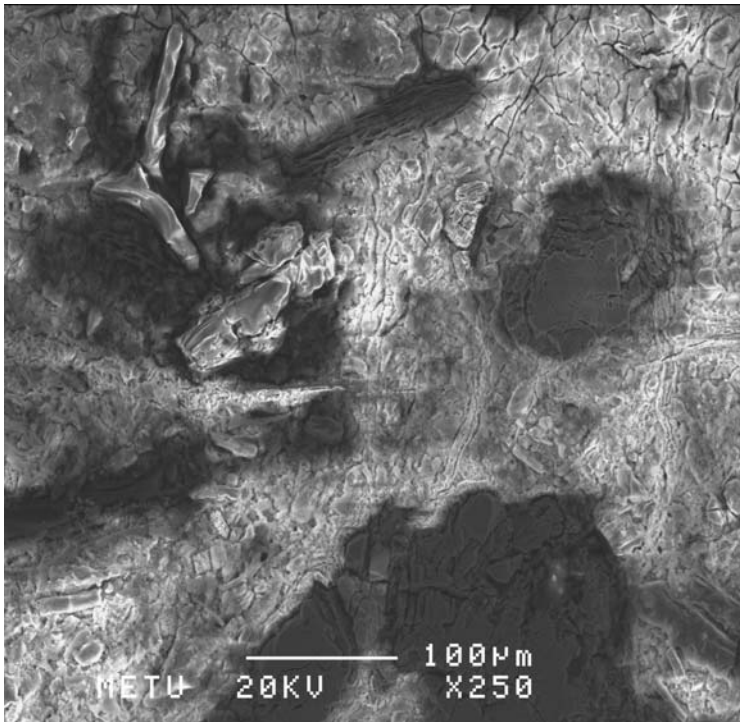The same things may be suggested for region"b" also.

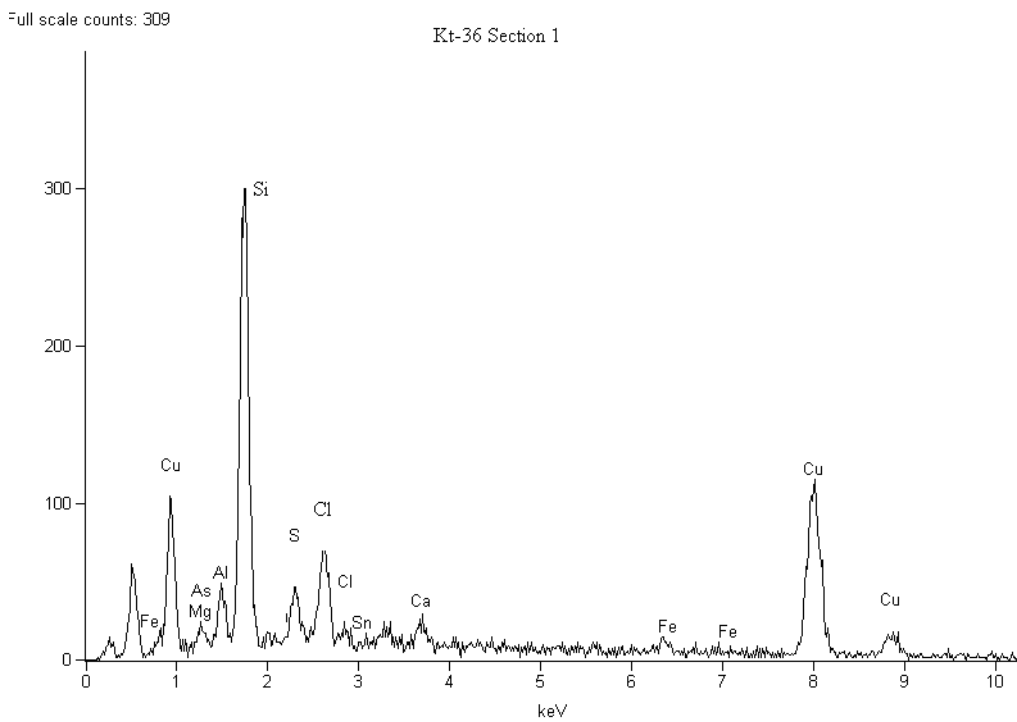Figure 5.2 SEM micrograph of section 1 of sample Kt-36



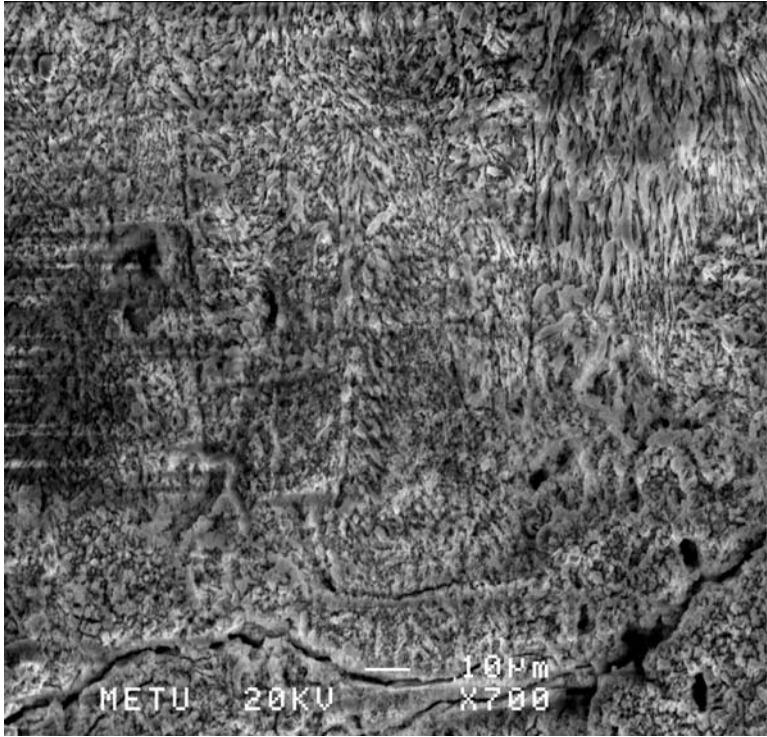Figure 5.3 EDS spectrum of section 1 of sample Kt-36

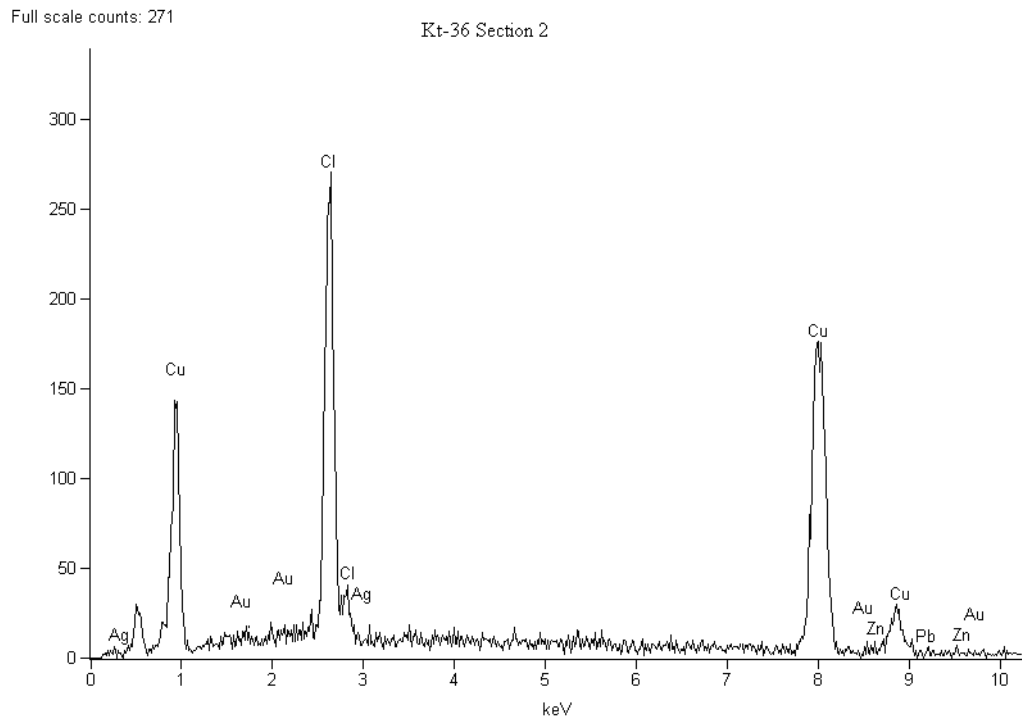Figure 5.4 SEM micrograph of section 2 of sample Kt-36



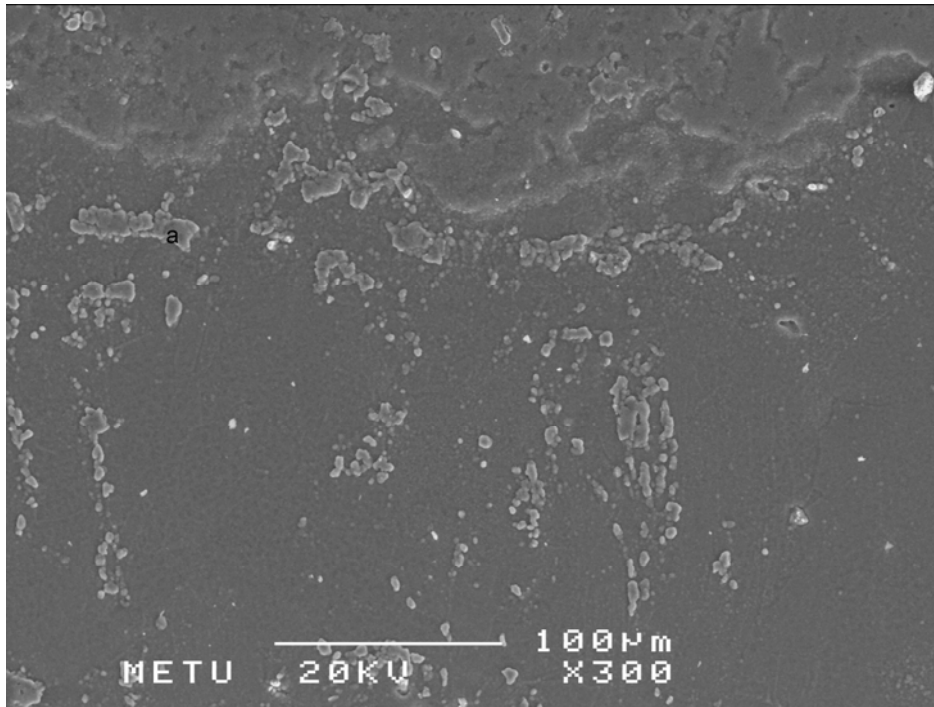Figure 5.5 EDS spectrum of section 2 of sample Kt-36

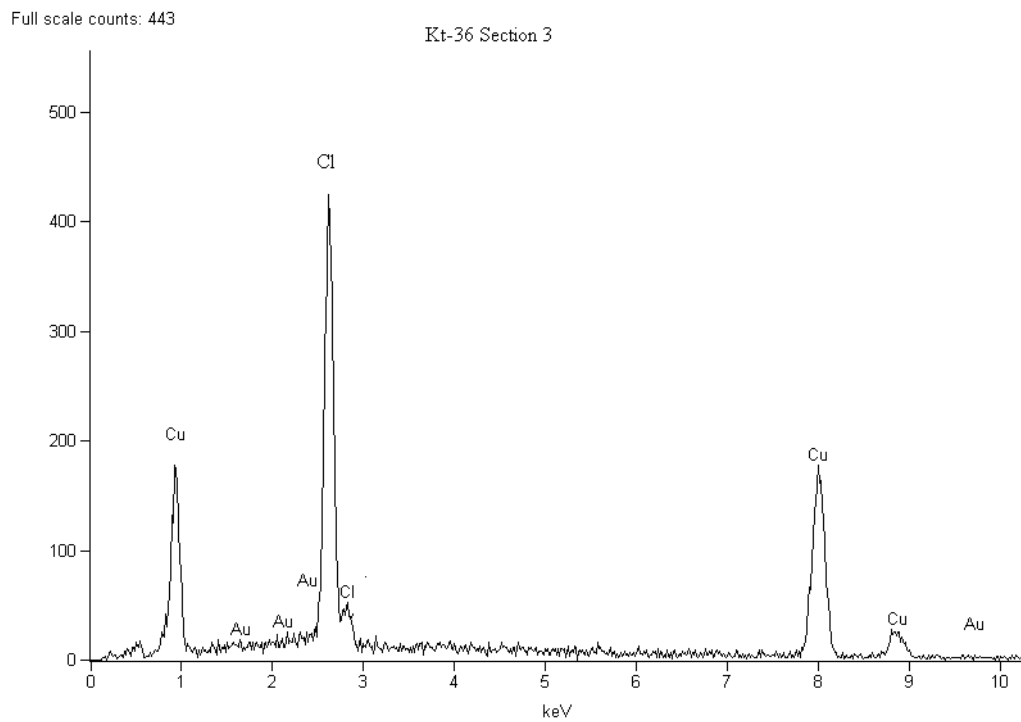Figure 5.6 SEM micrograph of section 3 of sample Kt-36



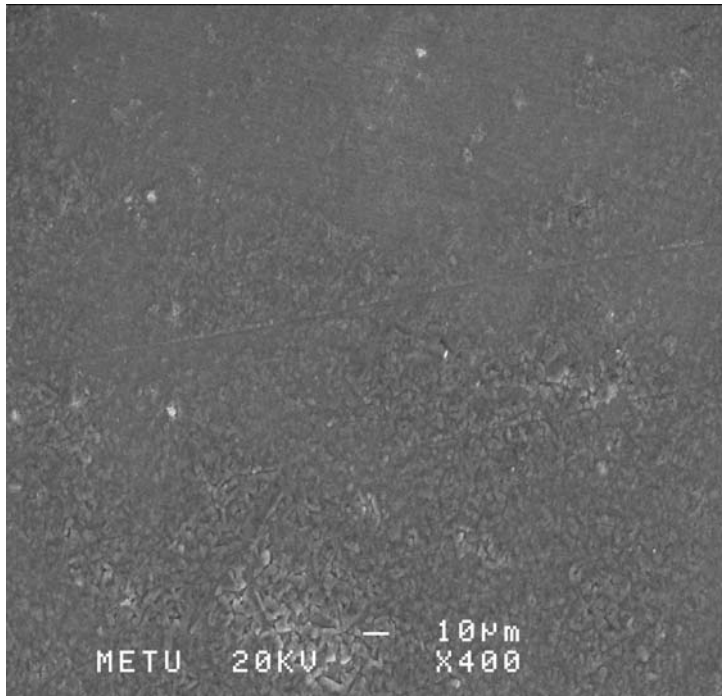Figure 5.7 EDS spectrum of section 3 of sample Kt-36

Figure 5.8 SEM micrograph of section 4 of sample Kt-36
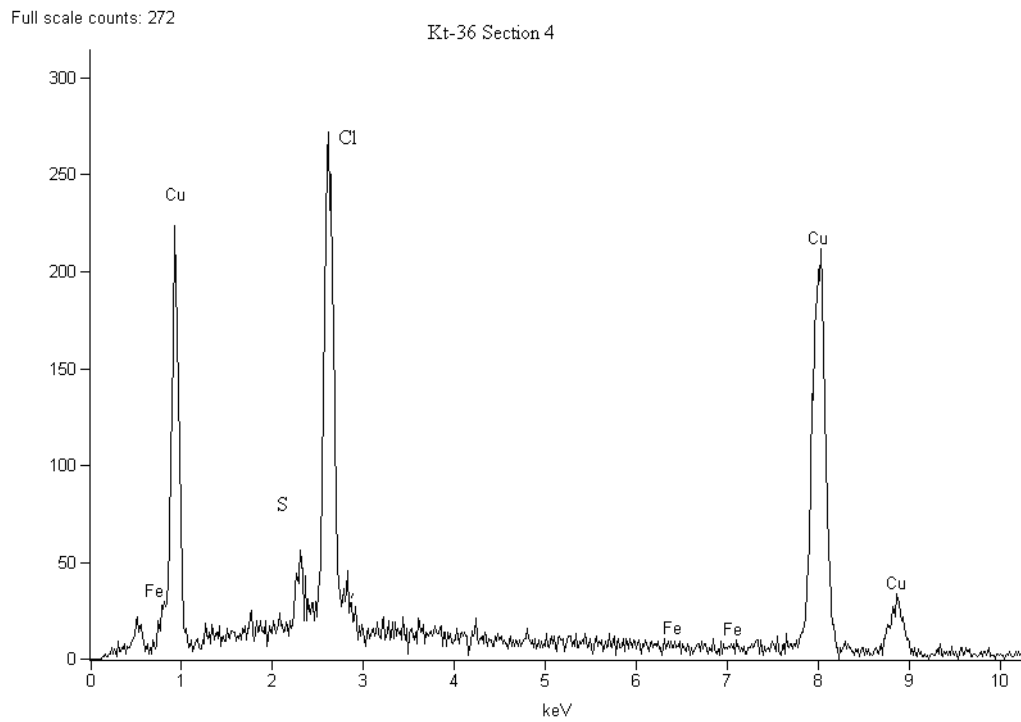


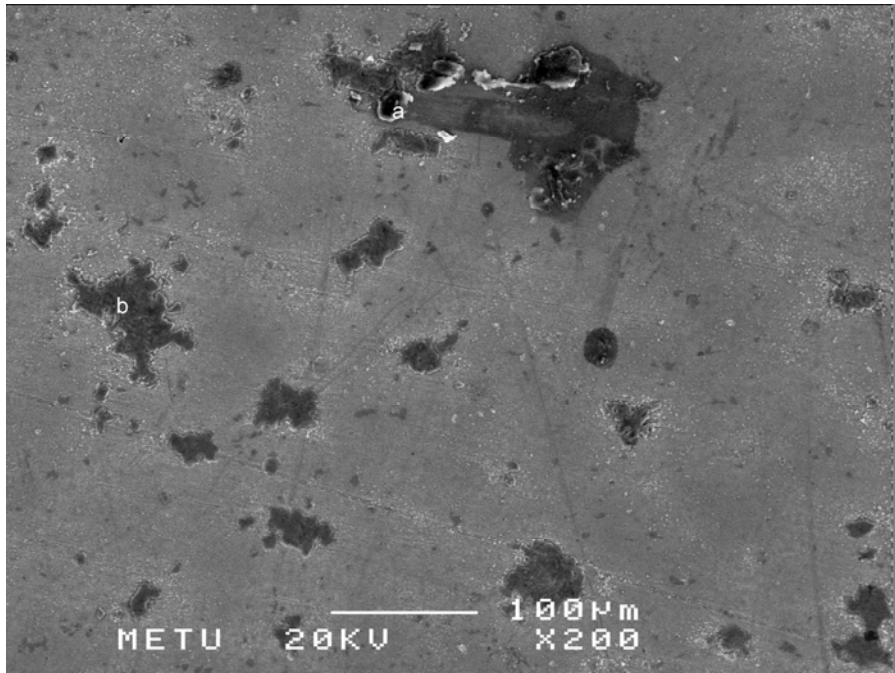Figure 5.9 EDS spectrum of section 4 of sample Kt-36

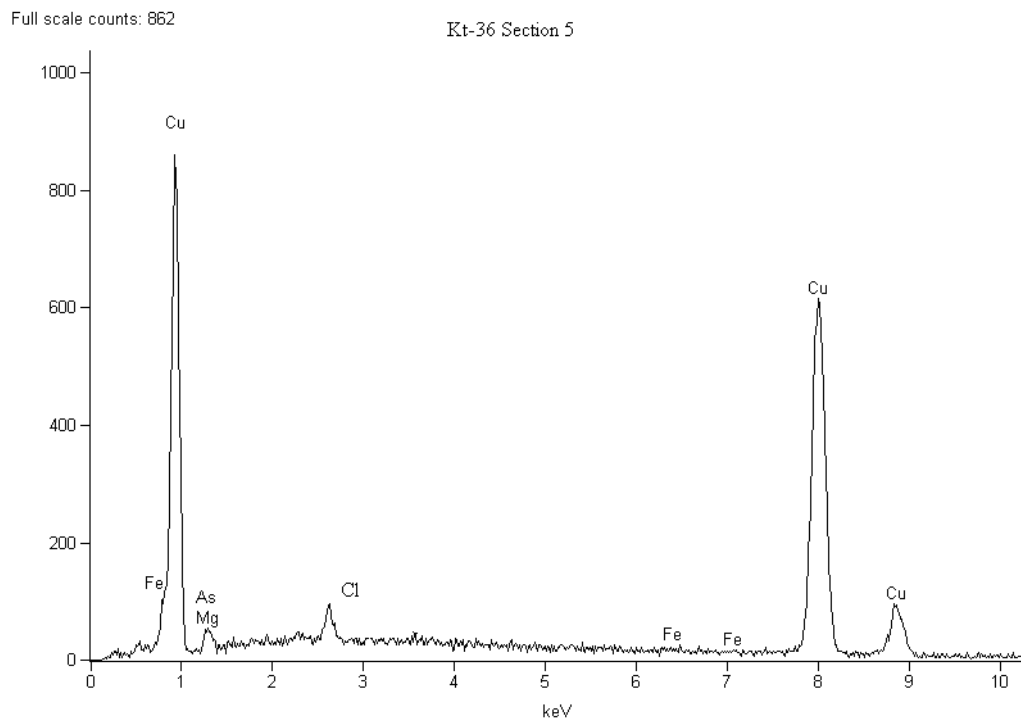Figure 5.10 SEM micrograph of section 5 of sample Kt-36



Figure 5.11 EDS spectrum of section 5 of sample Kt-36

Since the main constituents of corrosive layers of bronze are copper-based compounds, bronze patinas is supposed to be very similar to pure copper patinas and so surface layer consists of copper (II) salts (malachite in soil), which covers a red cuprous oxide layer that is in contact with the metal core (Constantinides et al. 2002).

In arsenical copper, well-separated three corrosion layers from outer to inner starts with a hydrated copper carbonate, malachite [$Cu_2CO_3(OH)_2.H_2O$, green)], the sandwiched cuprite layer ($Cu_2O$, red) and inner nantokite layer (CuCl, pale gren) (Constantinides et al. 2002).

High soil carbonate levels seems to behave as protective agent by forming a layer around the metal core (Gerwin, Baumhauer 2000).

The corrosion of copper-based alloys in an aerobic environment is dependent not only on the chemistry of copper in chloride media but also on the behaviour of major alloying elements such as tin, lead and zinc and trace elements such as arsenic and antimony. The corrosion products found on copper artifacts on the sea-bed generally consist of an outer layer of a green-blue basic copper (II) chloride overlying a red-brown layer of the copper (I) oxide, cuprite. Characterization of the many blue-green materials generally showed that the patterns did not match the natural mineral XRDs of atacamite and paratacamite but rather corresponded to atacamite syn.(synthetic), which has the formula $Cu_7CI_4(OH)_{10}.H_2O$, and to paratacamite syn. (25-1427), which has the 'standard formula', $Cu_2(OH)_3Cl$ (MacLeod 1991).

In addition to revealing the element composition in all layers of sample Kt-36 in SEM-EDS, the corresponding compounds formed were investigated in samples Kt-34 and Kt-36 by using XRD analysis.

The X-ray diffraction raw data for samples Kt-34 and Kt-36 were obtained from Rigaku brand X-ray diffraction device. The diffractogrammes of these data were plotted by CMPR software (Figure 5.12, Figure 5.13). The raw data of samples were also converted the GSAS format by means of the same software. GSAS is a structure analysis programme which uses linear least square method for the refinement of     X-ray raw data and determining the phase fractions.

As stated in above studies, corrosion products of copper to be expected are malachite [$Cu_2CO_3(OH)_2.H_2O$], paratacamite $Cu_2(OH)_3Cl$, nantokite (CuCl), cuprite ($Cu_2O$).

From the XRD traces of sample Kt-34, cuprite ($Cu_2O$) with the ratio of 56.36%, paratacamite [$Cu_2(OH)_3Cl$] with the ratio of 26.82% and malachite[$Cu_2CO_3(OH)_2.H_2O$] with the ratio of 16.82% were found as main compounds depending upon corrosion.

From their percentages, it is possible to calculate amount of copper corroded per 100 g copper sample. If we have 100 g sample, from this amount of copper present in cuprite can be calculated as follow;

Since molar weight of cuprite ($Cu_2O$) is 142. If 142 g of cuprite includes 126 g copper, then 56.36 g cuprite has 50 g copper.

If we repeat the same calculation for paracatamite;

Molar weight of paratacamite is 212.5 g. If 212.5 g paratacamite includes 126 g copper, then 26.82 g paratacamite will have 15.9 g copper.

For malachite, molar weight is 238 g, If 238 gr malachite includes 126 g copper, then 16.82 g malachite includes 8.9 g copper.

As a result, total corroded copper per hundred gram to be expected according to the corrosion products determined by XRD is 50+15,9+8,9=74.8 g which means approximately 75% of examined surface were exposed to corrosion.

From the XRD traces of sample Kt-36, cuprite ($Cu_2O$) with the amount of 1.39%, paratacamite [$Cu_2(OH)_3Cl$] with the amount of 51.45% and malachite [$Cu_2CO_3(OH)_2.H_2O$] with the amount of 47.15% and nantokite (CuCl) with the amount of $0.69*10^{-3}$% were found as main compounds depending upon corrosion.

The same calculation presented above to find the corroded copper can be repeated for this sample also.

Paratacamite and malachite formation in sample Kt-36 remarkably higher compared to sample Kt-34. However, cuprite formation which was dominant at sample Kt-34 reduces to very small amount in sample Kt-36.

As explained above, the element composition in all layers of sample Kt-36 was carried out in SEM-EDS. The chlorine content in intermediate layers between outer layer and the core region which has not severely corrosion attack, was observed in appreciable quantities. The corrosion product supposed to form here is nantokite (CuCl). However, in XRD analysis nantokite was observed in neglible amount.

The reason that nantokite didn't appear in XRD analysis is the fact that examined powder which was acquired by scratching the outer layer of samples didn't include the nantokite formation layer.

XRD traces of minerals were studied by using their diffraction peaks. The results show that the peaks identified for cuprite, malachite and paratacamite were consistent with the literature values found in Mineral Powder Diffraction File Databook.

From the data book, for cuprite (5-667), for malachite (41-1390) and for paratacamite (825-1427), diffraction file XRD values were used in the identification of XRD traces of the minerals (Figure 5.12, Figure 5.13).
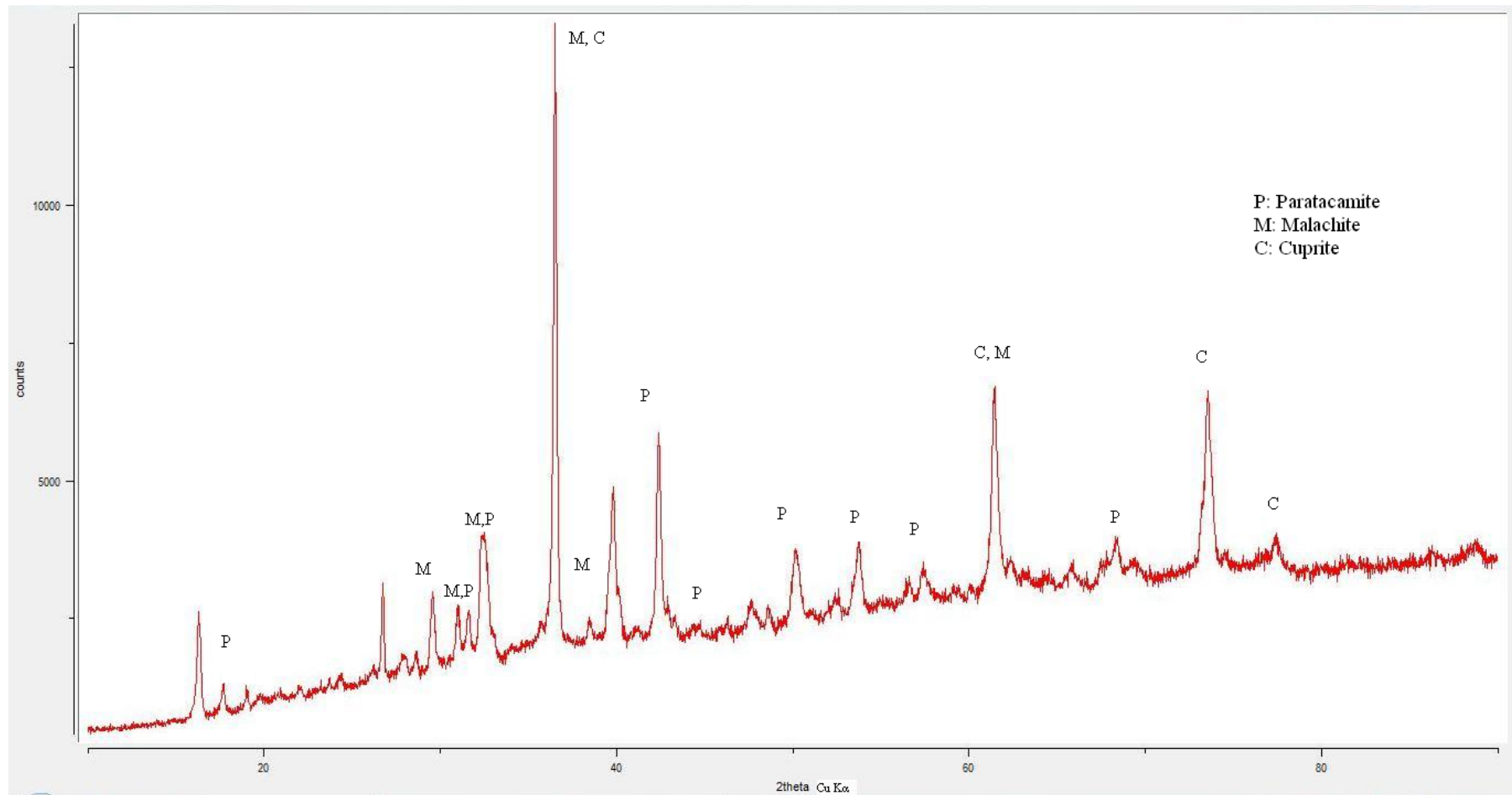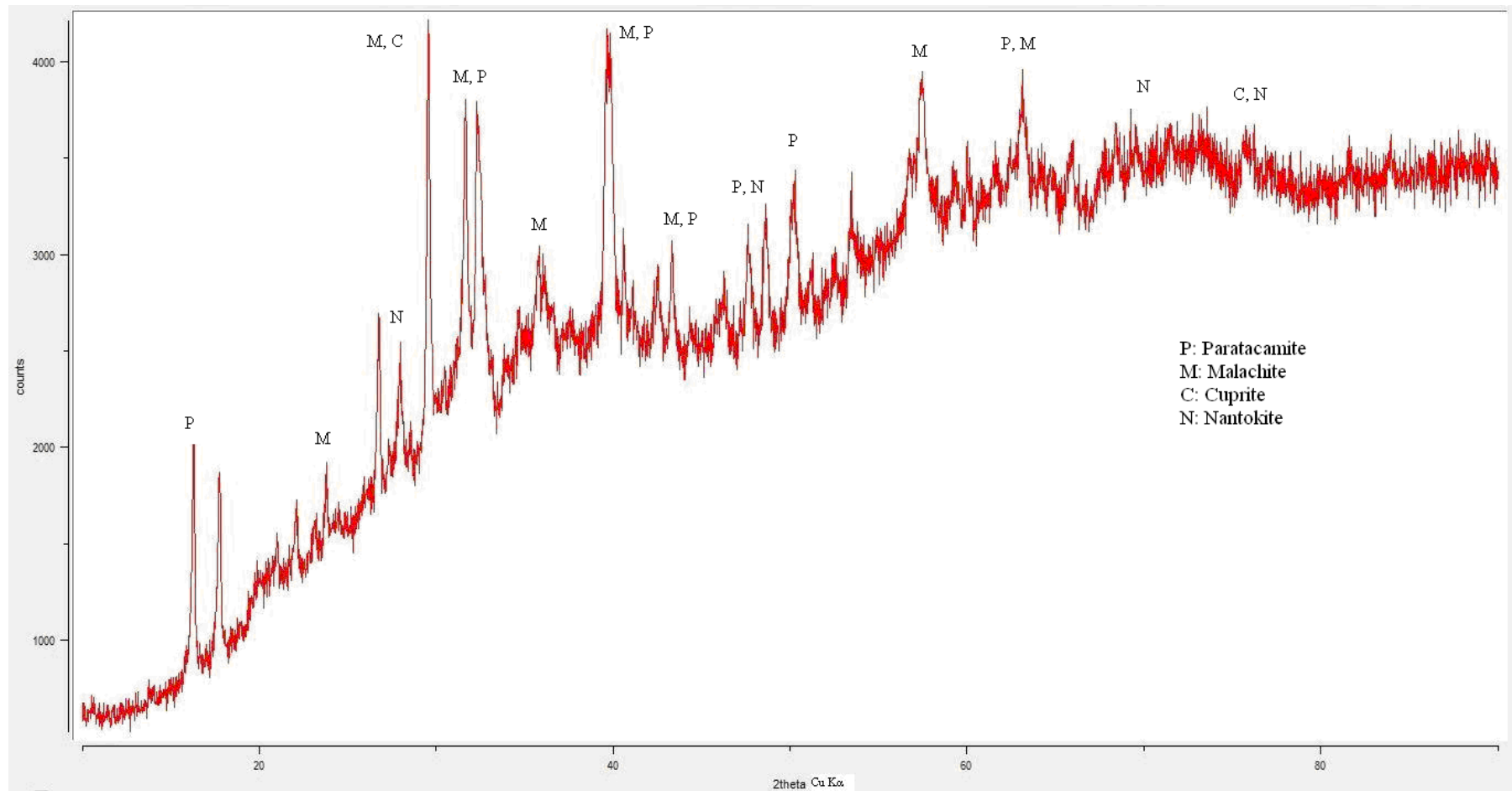
Figure 5.12 X-ray spectrum of sample Kt-34

Figure 5.13 X-ray spectrum of sample Kt-36

### 5.2.3 The Microstructure Analysis by Optical Microscope and SEM

Metallography can be defined as microscopic study of structural characteristics of a metal or an alloy (Avner 1986).

The main objective of metallography is to reveal the microstructure of the sample which will provide us all processes like cold working, hot working, heat tretment etc. applied on it.

The microstructure investigation helps us to make some comments about the ancient metallurgist's skill.

In this frame, all samples which are not suitable for exhibition and separated for studying (Kt-34 – Kt-65) were examined for microstructure revealing by both optic microscope and SEM.

There are two types of processing on metal to give a desired shape; casting and forging.

Casting is smelting metal and pouring it into a mould for which obtaining the desired shape and leaving it for solidifying.

Together with the gaining skill to obtain higher temperatures sufficient for smelting of metal, man started to convert it to the forms which facilitate his life.

All metal products have to be "cast" to give the desired shape. In other words, in order to obtain a tool required from metal, first of all, metal has to be smelted and poured it into the mould that is shaped to get the tool. The result may be a "casting" which is cooled in a specially shaped mold as a finished product to meet the requirements or an "ingot", which is an intermediate shape that will be produced for further processing to obtain finished products.

When smelted metal is poured into mold, it starts to solidify at which crystallization takes place.

The temperature of the liquid metal is dropped below its freezing point, stable aggregates or nuclei appear simultaneously at various points in the liquid, which acts as centers for further crystallization. As cooling continues more atoms start to solidify by attaching to already existing ones or forming new nuclei itself. This

crystal growth propogates in three dimensions resulting in a characteristic treelike structure which is called a dendrite (Avner 1986).

These formations will grow until they meet each other. If the cooling rate is fast, the dendrites will be small or vice versa.

If the metal is free of impurities, in slow cooling of such molten metal the dendritic structure may not be observed.

However, the dendrites are more commonly observed in ancient cast structures, due to the fact that the native copper was depleted and obtaining of relatively pure copper is not possible.

In microscopic analysis of this study, dendritic formation was seen clearly in many samples. The microstructures shown in Figure 5.14 and Figure 5.15 have clear appearance of dendrite formation.
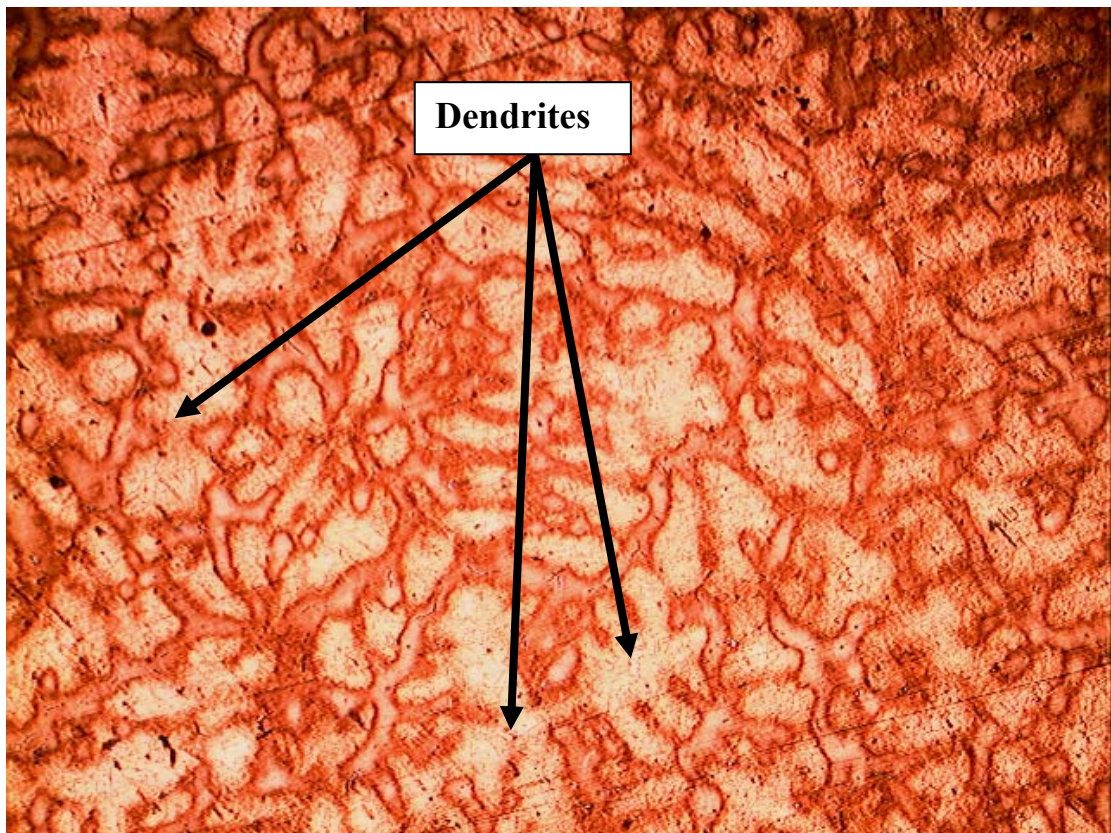


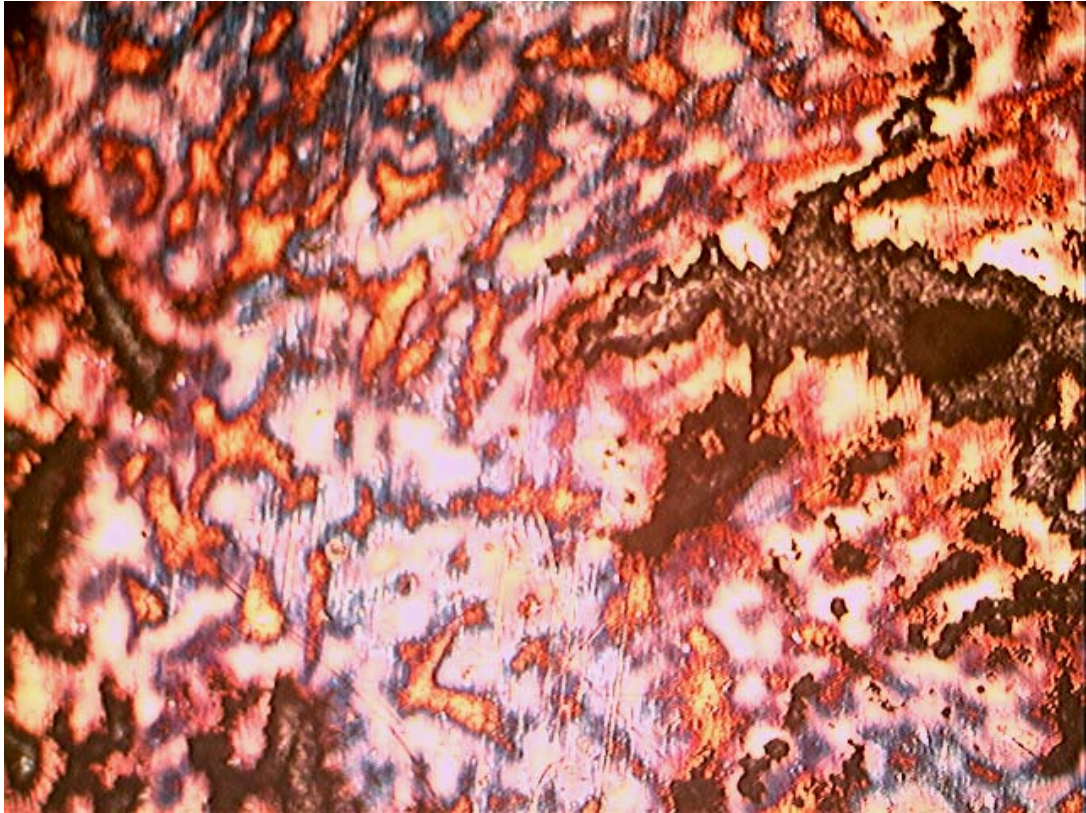Figure 5.14 Dendritic structure observed in sample Kt-48 (X100)

Figure 5.15 Dendritic structure observed in sample Kt-54 (X100)

As mentioned above, while one of the two processing on the metal is casting, the other is hammering or with common used terminology working.

Working comprises all the methods used for changing the shape of the metal. Generally, as cold and hot working, it is involved in human's life throughout history.

Cold working is a deforming process which changes metal plastically (deformation that does or will remain permanent after removal of the load which caused it) by applying force at a temperature lower than the recrystallization temperature.

As a result of cold working, the hardness increases because of increase in the number of dislocations which is a defect in crystal structure of material enabling the plastic deformation.

In other words, by applying cold working on a metal, the internal structure of it is changed. Grains become flattened while the hardness and britleness of the

structure increase. Elongated i.e. flattening of grains by hammering can be seen in sample Kt-39 (Figure 5.16).

Further working beyond fully work hardened may result in crack in structure.



Figure 5.16 Elongated grains revealing the effects of hammering in Kt-39 (X200)

When hammering is applied on a metal form, the inclusions present in the structure will be affected. They will also elongate throughout the force applied on it. The structure micrograph of sample Kt-62 shows the elongated inclusions which imply the applied force on this object by ancient Kültepe metalsmith (Figure 5.17).

As a result of work hardening, the metal object for further working needs heat treatment which is called annealing to be accomplished by heating of it to a temperature that causes recrystallization accomplished.
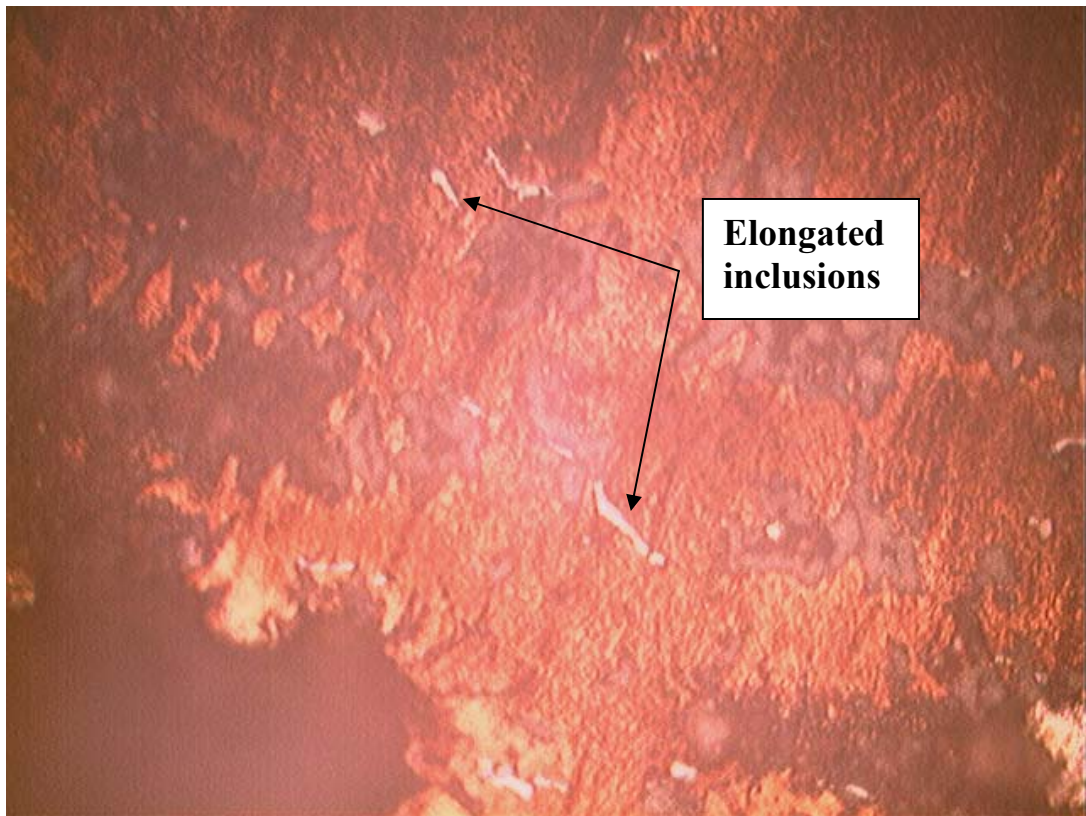
Figure 5.17 Elongated inclusion as a result of working on sample Kt-62 (X300)

Full annealing is the process by which the distorted cold-worked lattice structure is changed back to one which is strain-free through the application of heat. This process is carried out entirely in the solid state and is usually followed by slow cooling in the furnace from the desired temperature. The annealing process may be divided into three stages: recovery, recrystallization, and grain growth (Avner 1986).

Recovery is primarily a low-temperature process which causes a rearrangement of internal defects, known as dislocations, into lower-energy configurations while the grain shape and orientation remain the same. The main purpose of recovery stage in modern metallurgy is to obtain significant reduction in residual stresses, which will result in elimination of stress-corrosion cracking and minimization of distortion. However, during stress-relief operations the strength and ductility are not affected too much.

Recrystallization is the formation of a new strain-free grain structure. As the

upper temperature of the recovery range is reached, minute new crystals appear in the microstructure. These new crystalls have the same composition and lattice structure as the original undeformed grains and are not elongated but are approximately uniform in dimensions (equiaxed). The new crystals generally appear at the most drastically deformed portions of the grain, usually the grain boundaries and slip planes. The cluster of atoms from which the new grains are formed is called a nucleus. Recrystallization takes place by a combination of nucleation of strain-free grains and the growth of these nuclei to absorb the entire cold-worked material. (Avner 1986).
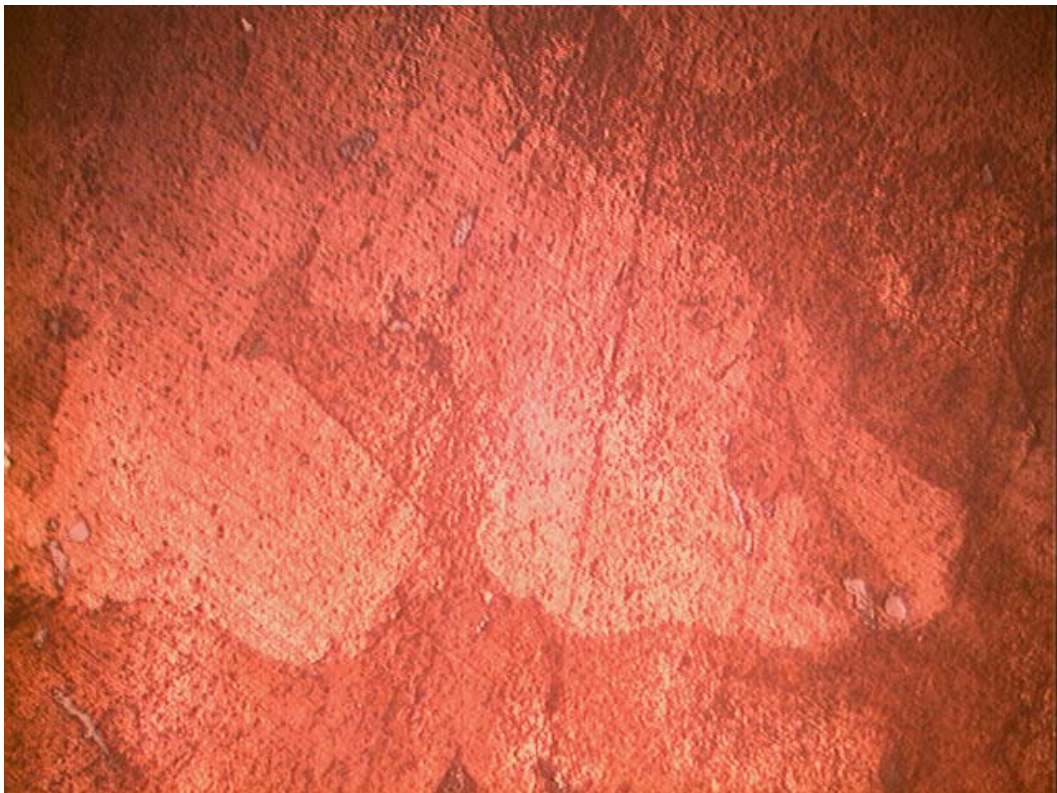


Figure 5.18  Grain boundary formation of sample Kt-62 (X300)

During recrystallization, deformed cold-worked grains which have high internal stress are replaced by new, strain-free grains. New orientations, new grain sizes, and new grain morphologies form during recrystallization. The driving force for recrystallization is the remaining stored energy that was not expended during

recovery. The strength reduces and the ductility increases to levels similar to those of the metal before cold working.

Recrystallization is considered complete when the mechanical properties of the recrystallized metal approach those of the metal before it was cold worked. Recrystallization completely eliminate the effects of cold working applied on the metal in terms of mechanical properties. Mechanical properties, such as hardness, yield strength, tensile strength, percent elongation, and reduction in area, change drastically over a very small temperature range.

Large grains have lower free energy than small grains. This is associated with the reduction of the amount of grain boundary. Therefore, under ideal conditions, the lowest energy state for a metal would be as a single crystal. This is the driving force for grain growth. Opposing this force is the rigidity of the lattice. As the temperature increases, the rigidity of the lattice decreases and the rate of grain growth is more rapid. At any given temperature there is a maximum grain size at which these two effects are in equilibrium (Avner 1986).
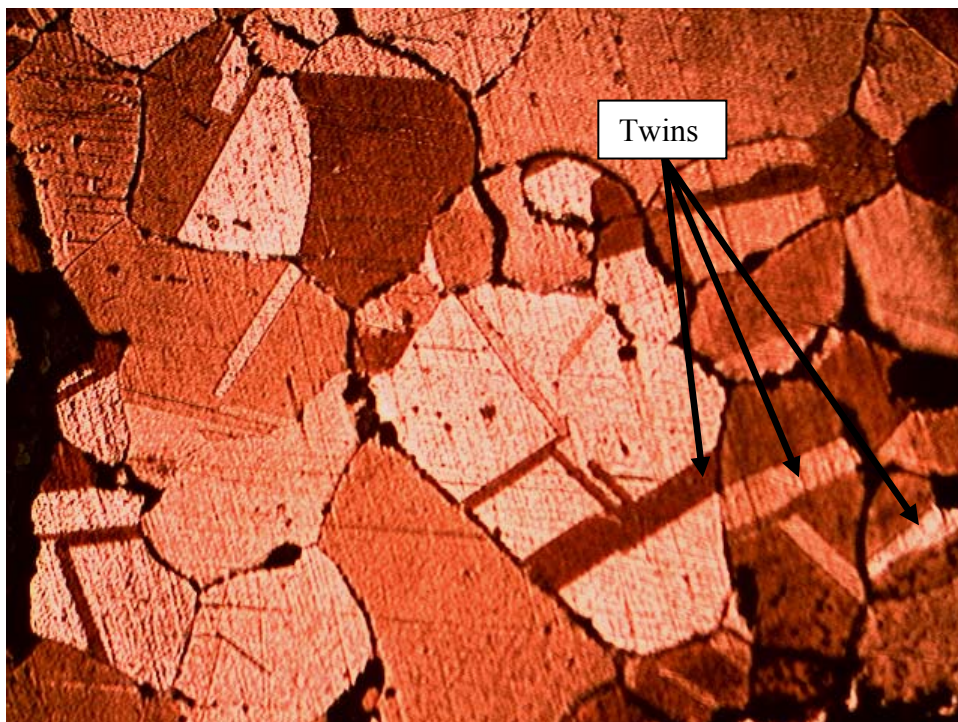


Figure 5.19 Cold worked and annealed microstructure of sample Kt-47 (X100)

When annealing process is applied to the work hardened metal which has face centered cubic lattice structure (f.c.c.) like copper, a strange phenomenon appears in the grain structure called twin bands as shown in Figures (5.19 and 5.20).

The twins which are clear indication of worked and annealed combination are formed because of a change in the normal growth mechanism (Avner 1986).
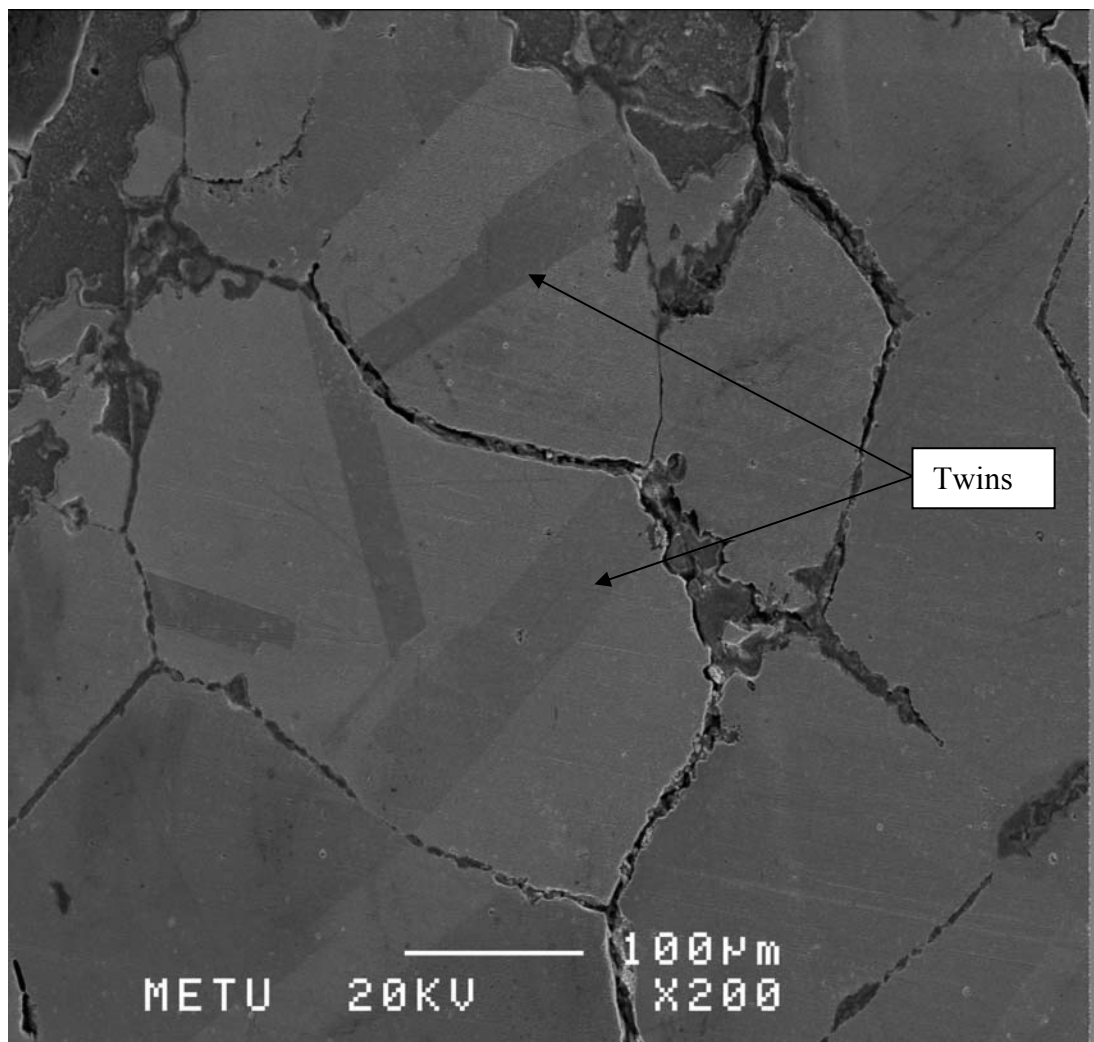


Figure 5.20 Cold worked and annealed microstructure of sample Kt-47 in SEM

The ancient metalsmith also continued to cold working after recrystallization, without repeating the heat treatment which is understood from distorted twin lines and strain lines in the grains as shown in Figure 5.21.

Figure 5.21 Worked again after annealed microstructure of sample Kt-49 (X300)

**5.2.4 Lead Isotope Analysis of Some Samples**

A great deal of controversy has surrounded the technique of lead isotope analysis (LIA) in the 25 years since it was first applied to study the absolute provenance of ancient copper-base artefacts in the eastern Mediterranean by Gale and Stos-Gale in 1982. In the past decade, the standing of the technique has gradually improved in tandem with a better understanding of its correct application in an archaeological context (Weeks et al. 2009).

In this frame, it is thought that realizing of LIA to some samples uncovered from Kültepe in this study may provide a contribution to understand Kültepe metallurgy in terms of metal origin of artifacts..

LIA was applied to ten samples (Kt-37, Kt-41,  Kt-42, Kt-46, Kt-49, Kt-50, Kt-54, Kt-57, Kt-59, Kt-64).

The results are given in Table5.6.

$^{206}Pb/^{204}Pb$ ratio changes between 18.536812 of Kt-46 and 18.895816 of Kt-57, average being 18.613131.

$^{207}Pb/^{204}Pb$ ratio changes between 15.606074 of Kt-50 and 15.801305 of Kt-59, average being 15.707496.

$^{208}Pb/^{204}Pb$ ratio changes between 38.114752 of Kt-50 and 39.361669 of Kt-49, average being 38.861227.

$^{207}Pb/^{206}Pb$ ratio changes between 0,831215 of Kt-57 and 0,848983 of Kt-59 average being 0,843978.

$^{208}Pb/^{206}Pb$ ratio changes between 2.068859 of Kt-57 and 2.130603 of Kt-50, average being 2.087992.

$^{208}Pb/^{207}Pb$ ratio changes between 2.442392 of Kt-50 and 2.489127 of Kt-57 average being 2.474337.

Lead isotope ratios of 10 samples from Kültepe was given in Figure 5.22 and Figure 5.23 as $^{207}Pb/^{206}Pb$ vs $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ vs $^{206}Pb/^{204}Pb$.

So far, isotopic homogeneity was observed in all samples except Kt-50. This might be interpreted as indicative of their origin in the product of one individual smelting or alloying operation.

Table 5.6 Lead isotope analysis results

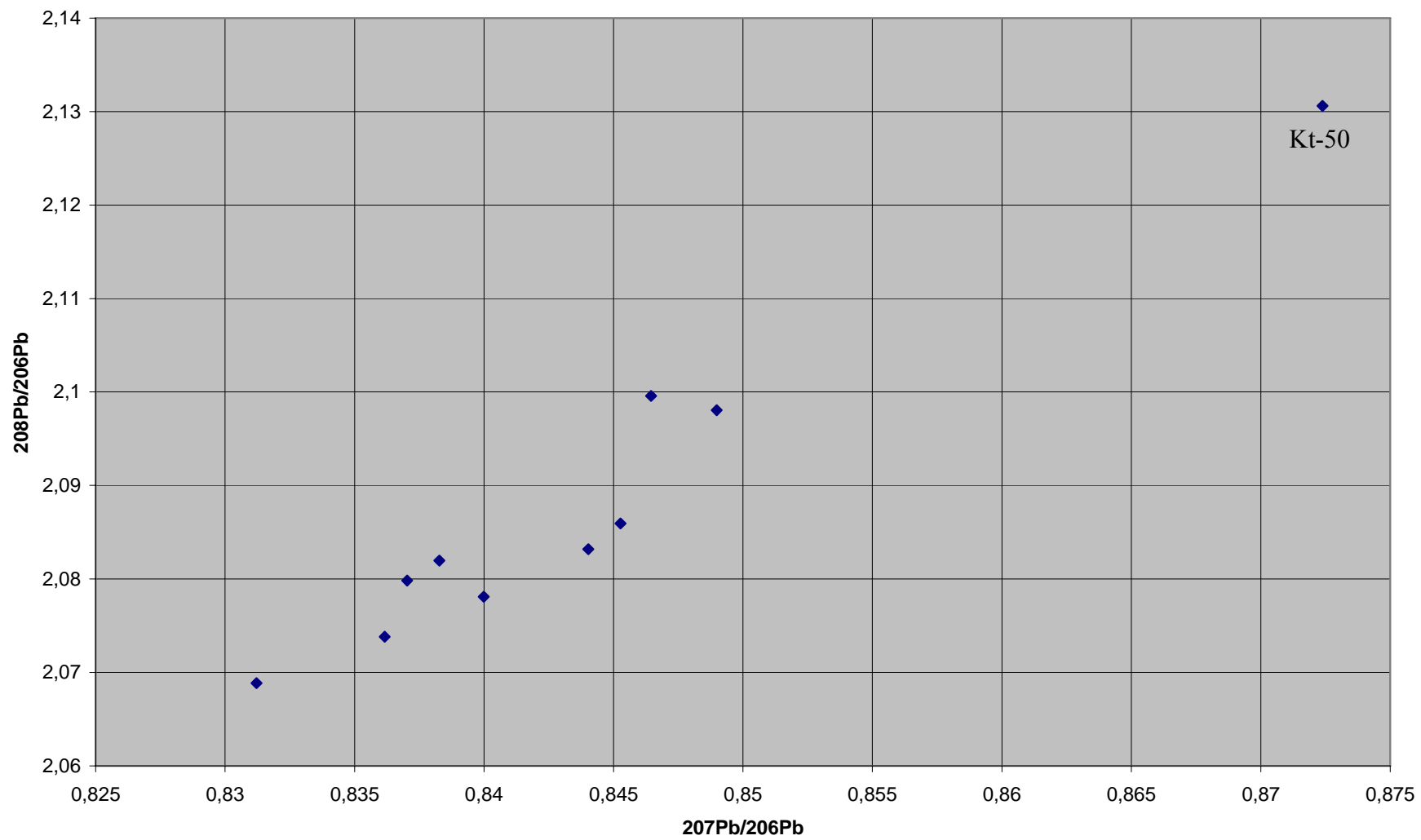| Samples | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ | $^{207}Pb/^{206}Pb$ | $^{208}Pb/^{206}Pb$ | $^{208}Pb/^{207}Pb$ |
|---------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Kt-46 | 18.536812 | 15.669805 | 38.667938 | 0.845271 | 2.085946 | 2.467805 |
| Kt-37 | 18.587191 | 15.687446 | 38.719808 | 0.844022 | 2.083186 | 2.468232 |
| Kt-41 | 18.573122 | 15.618595 | 38.593593 | 0.839991 | 2.078090 | 2.474056 |
| Kt-64 | 18.764223 | 15.706161 | 39.026199 | 0.837033 | 2.079816 | 2.484738 |
| Kt-57 | 18.895816 | 15.707204 | 39.096115 | 0.831215 | 2.068859 | 2.489127 |
| Kt-49 | 18.747097 | 15.867759 | 39.361669 | 0.846454 | 2.099580 | 2.480479 |
| Kt-50 | 17.884826 | 15.606074 | 38.114752 | 0.872380 | 2.130603 | 2.442392 |
| Kt-55 | 18.750942 | 15.718643 | 39.039939 | 0.838272 | 2.081959 | 2.483651 |
| Kt-59 | 18.613377 | 15.801305 | 39.049604 | 0.848983 | 2.098056 | 2.471217 |
| Kt-42 | 18.777908 | 15.691969 | 38.942649 | 0.836161 | 2.073829 | 2.481676 |

Figure 5.22 Lead isotope ratios of 10 samples ($^{207}$Pb/$^{206}$Pb vs $^{208}$Pb/$^{206}$Pb)
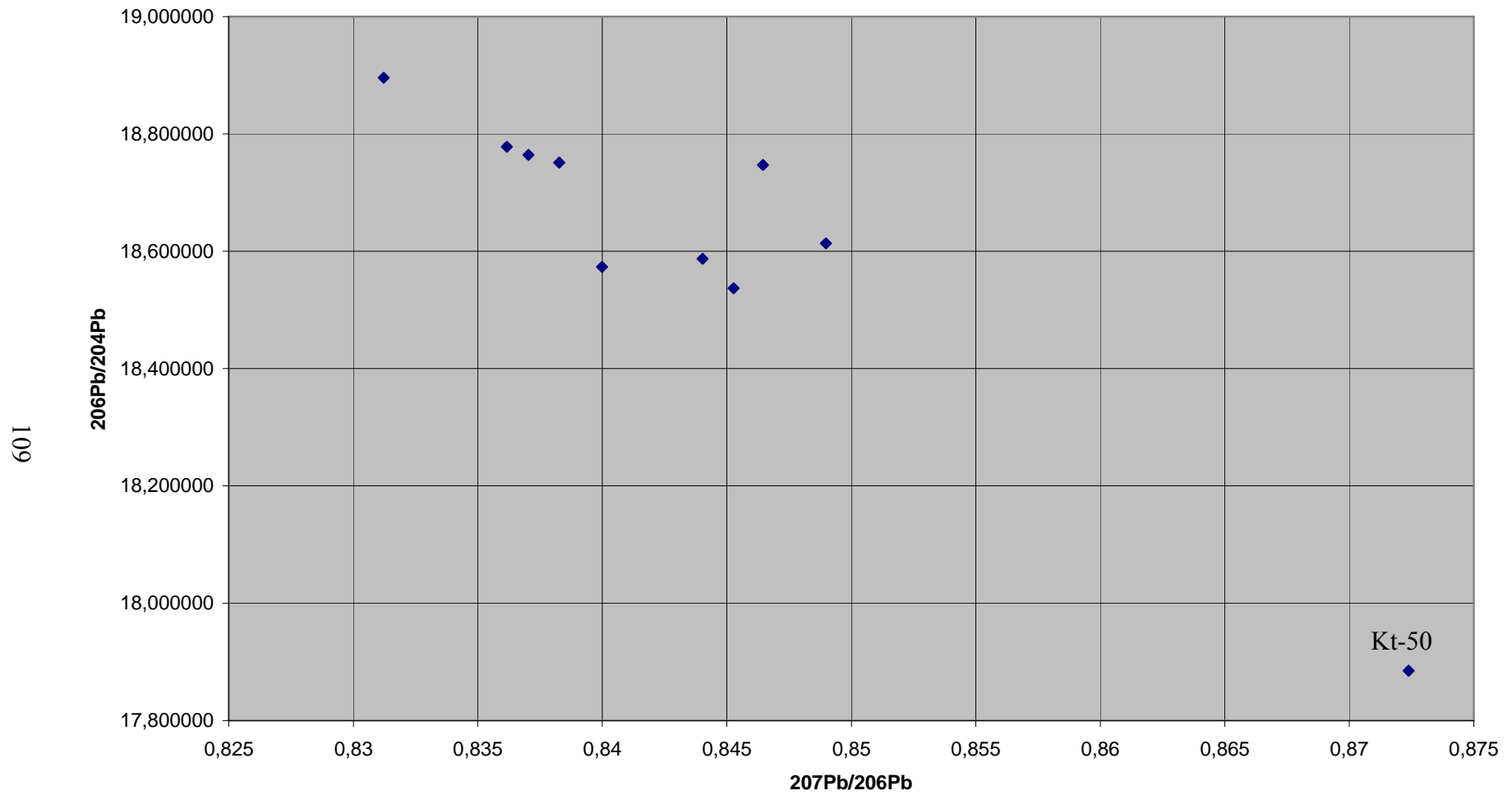
Figure 5.23 Lead isotope ratios of 10 samples ($^{207}$Pb/$^{206}$Pb vs $^{206}$Pb/$^{204}$Pb)

# CHAPTER 6


## CONCLUSION


Metal with a complex industry from mining operations to extracting and from casting to hot, cold working processes behind it, has been one of the major elements that influenced the social and economic development of societies since its discovery.

There have been many scholars who have been endeavoring to show the correlation of the progression of metal industry with the wealth of the societies. The literature on this subject has been growing enormously.

Anatolia which is the fusioning place of many civilizations has created an attraction for many societies with a plenty of mineral resources besides its geographical advantages. Therefore Anatolia with its rich metal deposits became a very important metal supplier and metal working center throughout the ages.

The literature which attempts to reveal the importance of Anatolia in terms of the development of metal industry and the effects on the neighbors has been also growing although it has not reached the level that Anatolia deserved yet.

Kingdom of Kanesh with its modern name, Kültepe has had also very strategic position for metal industry as being the administrative center of ten Karum in Colony Period in Anatolia. Even though Kültepe sheltered very outstanding examples of metallic artifacts of its age, the detailed study about metal processing of this area has not been performed so far.

As stated in many parts of the thesis, with this study it is aimed to make a contribution to understand the metal working technologies and copper trade with its environs in Colony Period of Kültepe.

In order to accomplish this aim, thirtythree metal artifacts which are in the inventory of Anatolian Civilization Museum were examined to reveal their chemical content by portable X-Ray fluorescence spectrometer (PXRF). In addition, thirtytwo samples taken from Kültepe Excavation Site were studied in terms of chemical and microstructural analysis by using optical micvroscope and scanning electron microscope coupled with energy dispersive X-ray analyser (SEM-EDS).

Progression of corrosion in the studied artifacts was examined by SEM from the outest layer towards inside. In order to find out the types of compounds formed upon corrosion, X-ray diffraction analyses (XRD) of corroded samples was carried out.

From the results of all experiments, the following conclusions were obtained.

Thirtythree arrtifacts examined in the museum depots by PXRF can be subdivided into two groups as warfare tools (20 samples) and daily utensils (13 samples). Warfare tools are composed of spearheads, flat axes, shaft-hole axes, daggers, a chisel and a fork weapon while daily utensils include sickle blades, rings, drinking cups, a bracelet, a finger cymbal, a small bowl, a small shovel, a fired pipe piece and a small animal sculpture.

Elemental composition of two groups mainly seem to be similar with the exception of antimony which is only present in the utensils group.

Tin and lead amounts are higher in warfare group with respect to daily utensils group. Especially lead exist in warfare group about three times of daily utensils group's. This difference should be investigated by further study whether lead is deliberately added to the certain group of tool.

In the warfare group, the shaft hole axes show a discernible feature with the existence of tin with amount of 7.60% and over which imply that tin is deliberately added to copper. This difference should be clarified by further study whether all shaft hole axes contain such an amount of tin.

The fork weapon (Kt-20) shows a very interesting situation, when the elemental composition of the sections were examined.

The elemental composition from two different sections (1 and 4) from handle part and the elemental composition from two different sections (2 and 3) from fork part show remarkable difference. Average copper percentage is 81.4% at handle part while it is 93.37% in fork part. In addition to this, average tin content is 14.24% at handle part while it is 5.05% at fork part. At handle part arsenic was present with amount of 0.82 % but at fork part, no arsenic was found.

All these may be expressed that fork and handle parts were manufactured separately from different composition and then joined together later.

Thirtytwo artifacts taken from Kültepe excavation area can be examined under three groups namely; chisel group, pin group and other unclassified 3 samples.

Elemental composition of all groups do not show any difference. However, due to environmental effects, additional elements like silicon, magnesium and chlorine, etc. were observed in the elemental composition of the samples.

The ancient Kültepe metal smiths seem to learn adding tin with an average value of 3.80% to obtain tin bronze which has better mechanical properties compared to copper itself in chisel production, since chisel requires hardness to perform the task expected from it.

One of the interesting points observed in all samples is the presence of remarkable amount of gold while silver is present in all groups with a relatively small amount.

However, a bowl fragment differs with its high tin content of 11.43% representing typical tin bronze. This amount of tin in an alloy is the indicator of deliberately adding of tin to copper. This observation should be clarified by further study whether all bowls contain such an amount of tin.

As stated above, all these fragments stayed beneath the soil approximately 4000 years. Naturally during a span of 4000 years, all metal artifacts are exposed to the oxidation, humidity and soluble salts such as alkaline and alkaline earth chloride, nitrate, carbonate, sulphade, phosphate and etc. in the environment.

From the XRD analysis cuprite ($Cu_2O$), paratacamite [$Cu_2(OH)_3Cl$] and malachite[$Cu_2CO_3(OH)_2.H_2O$] were found to be main compounds produced upon corrosion.

As a result of corrosion analysis, five layers were observed. First layer is the contact layer with soil and especially earth elements like silicon and magnesium which were observed. This layer is the most corroded one which copper content was the lowest with the amount of 56.21%.

The effect of chlorine appears severely in the second layer. In this layer chlorine content inceases to 20.05% while in the third layer it grows up 29.20%. Naturally, when approaching the core, diffusion seems to slow down. In fourth layer chlorine percentage was 18.88% while in the core it reduced to 1.91%.

As a conclusion, corrosion formation in a bronze object which buried under soil a very long time consists of three main layers. The outest layer is composed of soil elements and malachite [$Cu_2CO_3(OH)_2.H_2O$]. Following it, there is a layer that paratacamite ($Cu_2(OH)_3Cl$) and cuprite ($Cu_2O$) are the dominant corrosion products and below this layers nantokite (CuCl) which is in contact with core metal seems to exist.

The another important point to be concluded in corrosion analysis is that arsenic which exists in main structure with the amount of 3.16% disappear in the regions to be attacked by corrosion. The reason of this phenomenon may be the formation of soluble salt of arsenic. And then as soluble salt, arsenic will lead away from the lattice of the structure.

The microstructure examinations of samples constituted the backbone of the study. In the examination of thirtytwo samples in both SEM and optical microscope, it was concluded that ancient Kültepe metalsmiths of Colonial Period were skilled in manufacturing many types of tools from copper based metal.

They had the knowledge to pour molten metal into a mold to produce an object of desired shape. They were aware of shaping the casted object by hammering and forming fracture in case of excess working. They had the knowledge of heat treatment that allows them forging the object many times till giving the desired shape

without breaking the piece.

In addition, They discovered that the addition of some elements to copper hardens the structure. In this frame the bronze to be obtained by deliberately adding of tin to copper was attained. Shortly, they found out to make alloy which is the mixing of two or more molten metals.

Moreover, 13 out of the examined 65 samples (20% of all samples) contain high amount of tin in the range of 6.24% and 11.9% which indicates the deliberately adding of it to copper. This result is interesting in terms of these artifacts production period which coincides with Middle Bronze Age of Anatolia. Instead it is expected that bronze which gives its name to that age, was included in many of artifacts in higher quantity. However, since Anatolia imported tin from Assur at that period, it may be concluded that tin was so valuable material that it was used in just some specific tools which requires hardening.

Whether the attained skill of ancient Kültepe metalsmiths was the result of the trade to be carried out between Assyrian and Anatolia or they were the inheritor of their metalsmith ancestors, should be investigated by further study which will comprise the examination of uncovered metal object dated before colonial period.

Lead isotope analysis was carried out to provide a contribution to understand Kültepe metallurgy in terms of metal origin of artifacts.

Lead isotope ratios of 10 samples belonging to Colony Period of Kültepe shows a cluster in both ($^{207}Pb/^{206}Pb$ vs $^{208}Pb/^{206}Pb$) plot and ($^{207}Pb/^{206}Pb$ vs $^{206}Pb/^{204}Pb$) plot except one sample (Kt-50). This may be interpreted as the fact that the original materials of the samples are the same while ring shaped sample (Kt-50) is out of this cluster.

The LIA of the other metal artifacts uncovered from the other ancient center of Anatolia of the same period should be carried out by further studies to reach detailed conclusion that may give the relations between these centers.

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