KIRKLARELİ, DEMİRKÖY OTTOMAN IRONWORKS:
A Technological Investigation

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ABSTRACT

KIRKLARELİ, DEMİRKÖY OTTOMAN IRONWORKS:

A Technological Investigation

This study was part of a multidisciplinary industrial archaeology project. The objective of the project was to investigate social, economic and technical aspects of Ottoman iron production technologies during the eighteenth and nineteenth centuries. To reach this goal regional surveys, archaeological excavations and archive studies were carried out at Demirköy (ancient Samakovcuk), Kırklareli, the only remaining iron production and foundry left in Turkey from the Late Ottoman Period.

Both the regional surveys and archaeological excavations yielded extensive remains from the Ottoman ironworks including mining activities, smelting furnaces and slags. Preliminary analysis indicates that local hematite and magnetite sand were used as the main iron ore source. High furnaces (Stückofen) and bloomery furnaces were discovered during the regional surveys and archaeological excavations. This indicates that both cast iron and wrought iron were produced in appropriate furnaces in Demirköy. Cast iron was mainly used to produce ordinance for the Ottoman artillery. Wrought iron was consumed mainly for domestic needs in the form of nails, horseshoes, farm tools and other implements.

Slag samples collected from the peripheral small workshops were mainly fayalitic in nature left from the bloomery furnaces. Glassy slag was collected mainly around the main foundry where the actual casting of iron objects was carried out.

Nails were the most abundant metallic objects recovered at archaeological excavations together with few other highly corroded cast and wrought iron implements. Cast iron objects displayed a typical gray cast iron microstructure whereas wrought iron objects can be classified as mild steel. There was no conclusive evidence for the production of wrought iron by a finery process.

ÖZET

KIRKLARELİ, DEMİRKÖY OSMANLI DEMİR İŞÇİLİĞİ:

Teknolojik inceleme

Bu çalışma disiplinlerarası bir endüstriyel arkeoloji projesinin parçasıdır. Projenin amacı 18. ve 19. yüzyıl Osmanlı demir üretim teknolojilerinin sosyal, ekonomik ve teknik yönünü araştırmaktı. Bu amaç doğrultusunda, Türkiye'de Geç Osmanlı Dönemi'ne ait tek demir üretim merkezinin bulunduğu Kırklareli, Demirköy'de (eski adıyla Samokovcuk) yüzey araştırmaları, arkeolojik kazılar ve arşiv çalışmaları yapıldı.

Hem yüzey araştırmaları hem de arkeolojik kazılar sonucu bölgede cevher, ergitme fırınları ve cüruf gibi Osmanlı demirciliğinin önemli kalıntıları ortaya çıkarıldı. Ön çalışmalar bölgede demir cevheri kaynağı olarak yerel hematit ve magnetitli kum kullanıldığını gösterdi. Saha araştırmaları ve arkeolojik kazılar sırasında yüksek fırınlar (Stückofen) ve vigne tipi fırınlar ortaya çıkarıldı. Bu da Demirköy'de, uygun fırınlarda hem dökme hem de dövme demir üretildiğini göstermektedir. Dökme demir genellikle Osmanlı topçuları için top üretmek amacı ile kullanılmıştır. Yumuşak demir ise çivi, nal, tarım araçları ve diğer günlük araç-gereçlerin üretiminde kullanılıyordu.

Çevredeki çalışma işliklerinden toplanan cüruf örnekleri genellikle fayalitik yapıdaydı ve bunlar vigne tipi fırın yanürünüdür. Camsı cürufa ise esas demir döküm objelerin üretildiği ana dökümhane çevresinde rastlandı.

Arkeolojik kazılarda en çok bulunan metal objeler, oldukça paslanmış dökme ve dövme demir parçaların yanı sıra çivilerdi. Dökme demir objelerde tipik gri dökme demir mikroyapısı gözlemlenirken dövme demir objeleri yumuşak çelik olarak sınıflandırmak mümkündü. Yumuşak demir üretiminin arıtma işlemi kullanılarak dökme demirden gerçekleştirildiğini gösteren bir kanıta rastlanmadı.

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LIST OF SYMBOLS / ABBREVIATIONS

ΔG	Change in Gibbs free energy
c	Concentration of the analyte (mole/L)
T	Temperature
T_E	Equilibrium temperature
α	Ferrite solid solution phase of iron and carbon with bcc structure
γ	Austenite solid solution phase of iron and carbon with fcc structure
ε	Molar absorptivity (Constant)
bcc	Body centered cubic structure
fcc	Face centered cubic structure
AA	Atomic Absorption
AAS	Atomic Absorption Spectroscopy
EDAX	Energy Dispersive Analysis by X-ray
EDX	Energy Dispersive Analysis by X-ray (alternative usage)
FAAS	Flame Atomic Absorption Spectroscopy
SEM	Scanning Electron Micrograph
XRD	X-ray Diffractometer

1. INTRODUCTION

Metallurgy started and developed in areas that have both natural resources and developed communities with surplus of food so that they could employ part of their labor force for mining and metal-working. First, people shaped native metals like copper and maybe gold and silver into simple ornaments and tools by hammering. Second stage was smelting of copper from its secondary ores such as malachite and azurite. Third stage was making alloys of copper with arsenic, antimony, tin and zinc. Experience in copper metallurgy soon paved the road to iron technology. Like native copper, the earliest examples of iron were meteoric in origin. It was very rare and precious and for many centuries it was considered mystical, as *metal from the heavens.* (Fagan, 2004)

The main difficulty of iron production from its ore was its high melting point (1530^{o}C) since it was not possible to reach such high temperatures in early smelting furnaces. Thus, it could not be obtained in liquid form as was the case with previous metals. Initially iron was produced as a solid mixture of spongy iron, slag and charcoal, and was called a “bloom”. The important step in this technology was to obtain a liquid slag during smelting so that minimum amount of slag would remain in the solid mass of bloom. The final stage in this technology was to forge the bloom at white heat to squeeze out slag inclusions and consolidate the spongy mass into wrought iron. Archaeometallurgical investigations of prehistoric Anatolian cultures showed that as in the case of copper and copper alloys, most of the major achievements in iron metallurgy were also accomplished by Anatolian cultures. Metallurgists and metal smiths of central Anatolia during the second millennium BC were credited as the earliest innovators of iron metallurgy. Many cuneiform tablets were recovered from the royal archives of the Hittites at Boğazköy related to production and exchange of iron. It is possible that iron was invented independently in China. In the New World iron was not smelted until Europeans arrived.

For many centuries basic technology of bloom iron production did not change. During this time bigger iron furnaces were constructed and water power was utilized for the operation of bellows and forging hammers. During the Roman period bloom iron production was standardized and perfected. Until 14th -15th centuries AD bloomery process was the only known technology to produce iron. Eventually furnaces became higher and with the addition of more and better quality charcoal higher temperatures and reducing conditions were reached which made possible the production of liquid iron. Under such reducing conditions, dissolution of carbon in iron decreased the melting point of iron. Iron that contains about 5% C melts at about 1200^{o}C. Cast iron that was produced in high furnaces was extremely hard and brittle and could not be shaped by hammering. It was, however, possible to shape objects by casting.

Iron technology was an important Turkish cultural heritage even before they migrated to Anatolia. This strategically important metal was also extensively used by the Ottomans for utilitarian needs as well as in warfare. Ottomans were casting their small cannons from iron. In addition to casting cannons every year hundreds of thousands of iron cannon balls were cast. Iron was used for different tools and chains at artillery battalion, it was used for shovel, pick and axe at entrenchment, and also for nail, horseshoes and alike at fortresses and bridges. Ottoman Empire produced massive amount of wrought and cast iron at many different locations such as Bilecik, Keban and Samokov. Demirköy, near Kırklareli was another important iron producing center mainly because of its close location to Istanbul. Produced goods were easily delivered to Istanbul by boats sailing from Iğneada located about 25 km east of Demirköy.

The aim of this study is to investigate the technology used to produce both wrought and cast iron at Demirköy during the 18th and 19th centuries. The archaeometallurgical materials studied in this work were recovered from Demirköy during regional surveys and archaeological excavations that were carried out at a workshop near the main foundry.

2. HISTORICAL BACKGROUND

2.1. Ancient Iron Technology in Anatolia before 1200 B.C.

The earliest source of iron is believed to be meteoric in origin. Iron meteorite may contain between 6-20% nickel. On the other hand, terrestrial smelted iron contains very low amounts of nickel (Table 2.1). Therefore, nickel content of early iron objects can be the initial criteria for determining its possible source. It is most likely that our ancestors came across meteoric iron and made simple implements by hammering.

Table 2.1. Average composition of iron meteorites. (Yalçın, 1999)

Meteorite Type	Fe	Ni	Co	P	# of samples analyzed
Heksaedrit	92.6	6.07	0.61	0.25	78
Oktaedrit	86.8-92.3	6.54-11.65	0.50-0.61	0.16-0.24	202
Ataksit	79.6	18.85	1.01	0.12	38

The beginning of the Iron Age is generally dated to about 1200 BC in Anatolia and the Near East. However, earliest iron finds in Anatolia date back to the third millennium BC. Considering that pure iron occurs rarely in nature, the most important question was the origin of these objects. Table 2.2 lists the iron objects that were recovered from various sites in Anatolia predating 1200 BC.

Table 2.2. Pre-Iron Age iron finds from Anatolia. The table includes all finds hitherto published as "iron" (Yalçın, 1999)

Site	Object	Date	Comments
Tilmen Höyük	Bracelet	Early Third Millennium	No analysis
Alaca Höyük	Gold-handled dagger	Early Bronze Age II (2800-2500 BC)	Low Ni
	Two gold-headed pins		Single analysis 2.7% Ni
	Necklace terminal		No analysis
	Semi-lunar disc		2.4% Ni
	Knife fragment		No analysis
Troia	Mace head	Troy II (2800-2500 BC)	Ore/bloom ?
Tarsus (Gözlükule)	Iron lump	Early Bronze Age III (2400-2100 BC)	No analysis
Alişar	Pin fragment	1900-1700 BC	No analysis
Kusura	Metal fragment	1800-1600 BC	No analysis
Alaca Höyük	Assorted Fragments (jewellery, tools, weapons)	1800-1200 BC	No analysis, two metallographic studies
Boğazköy	Assorted pieces (tools, weapons)	1450-1200 BC	No analysis, two metallographic studies
Korucutepe	Iron pieces?	1400-1200 BC	No analysis
Tell Açana	Iron pieces	1450-1200 BC	No analysis

The oldest iron object known so far in Anatolia is a twisted bracelet that was a grave offering at Tilmen Höyük, Gaziantep, dating to the third millennium BC. Since it is not scientifically analyzed it is not known if it is made from meteoric or smelted iron. Most of the iron finds from the third millennium BC, however, come from Alaca Höyük. Six iron objects were found in the royal tombs: a gold-handled dagger; two ornamental pins with gold heads; a necklace terminal; a semi-lunar disc and a fragment of a knife.

Gold-handled dagger (A1.K.14) is the best known example from Alacahöyük. (Koşay, 1951; Wertime, 1973) (Figure 2.1). It was found in grave K with three bronze solar discs. The blade is made out of iron that is highly corroded now. The blade contained low levels of nickel which is a strong indication that it is made from smelted iron rather than meteoric origin. However, analysis was done on highly corroded sample therefore further investigation should be carried out.

Figure 2.1. Gold handled iron dagger (ACM, Ankara)

Analysis of two other iron items, a pin and a semi-lunar disc, from the third millennium BC context yielded 2.7% and 2.4% nickel respectively (Table 2.2). These two items were also considered to be not originating from meteoric iron due to their low nickel content. They could have been produced from terrestrial native iron, whose source is not known, or they could be smelted from iron ore.

A mace-head from Troy II, found during the Schliemann's excavations, was identified as iron by Schliemann himself. It was described as "two pieces containing iron oxide" and according to Schmidt (1902) the find was not metallic iron. Chemical composition is shown in Table 2.3.

Table 2.3. Chemical composition of mace-head found at Troy II (Wt.%) (Pernicka, 1995)

SiO_2	**Al_2O_3**	**Fe_2O_3**	**FeO**	**CuO**	**MgO**	**NiO**	**CaO**	**CO_2**	**H_2O**	**Sum**
2.24	0.22	72.94	6.34	1.12	0.11	2.44	1.08	1.54	12.15	100.18

It can be seen that the mace-head is made out of various oxides of iron. Pernicka (1995) suggests that the find might be a piece of slag from a completely corroded iron bloom, or iron ore taken from the oxidation zone. Taking account of the chemical composition and macroscopic structure, the Troy II mace-head may be made out of oxidized iron ore.

Another iron find described as an iron lump from Tarsus is dated to Early Bronze Age III, but there isn't any description or analysis of it. The finds from Alişar, Kusura Alacahöyük, Boğazköy, Korucutepe and Tell Atchana are all dated to second millennium BC and none of them have been analyzed. Among the Alaca Höyük objects two nails, a pin, a panel, a dagger, an arrow head, a bracelet and a knife fragment make the biggest group. Among these, five objects were studied by Muhly (1980). Muhly states that they are definitely iron, while three were highly corroded and were not attracted by a magnet. Among these finds, polished section of a highly corroded knife fragment shows a possible pearlite structure. Microstructure of the polished section of another sample showed both ferritic and pearlitic components with slag inclusions (Muhly et al, 1985). Maddin mentions the possibility that these inclusions may appear during hammering and stay in the iron, but it is also possible that these objects were produced from bloom iron. Generally, iron produced from bloomery furnaces contains this kind of inclusion. According to this hypothesis, there are some archaeological finds dating to the second millennium BC indicating that smelting was practiced during this period. (Yalçın, 1999)

Another interesting object is a steel sword with bronze handle (Figure 2.2). This Hittite sword dates to about 1400-1200 BC. Its microstructure revealed that it was constructed by forging several layers of iron that contained different amounts of carbon (Yalçın *et al,* 2006)

Figure 2.2. Hittite steel sword with bronze handle (Ruhrlandmuseum, Essen)

2.2. Iron Age

Early iron technology became widespread for the first time in Anatolia during the first millennium BC. Iron was produced in bloomery furnaces in solid state. During reduction and later while hot forging, some amount of carbon may diffuse into iron. The end product would be a mild steel. The latest work at Toprakkale, Anzaf and Miletus shows that steel was used deliberately in Anatolia in the first millennium BC (Yalçın, 1993; Yalçın *et al,* 1995). The Urartian (9^{th}-7^{th} century) and the Milesian (7^{th}-6^{th} century) weapons and daily tools were made out of mild steel. It is no coincidence to find in Greek texts of the first millennium BC the words khalibs for steel and sideros for iron both used together. According to Greek texts the Khalibs were the inventors of steel. They lived in the area southeast of the Black Sea during the first millennium BC and therefore may have been communicating with the Urartian cultures.

Intentional steel production was probably not completely understood by the Hittite, Urartian, Lydian, Greek and Khalib cultures, who were the important metal producing communities. Whether they smelted the ductile steel or carburized the metal is not yet clear. According to written texts, both methods were certainly in use in the middle of the first millennium BC at the latest. The steel and iron samples from Archaic Miletus indicate that they used both methods to produce steel. The objects from Anzaf castle show clearly that the process of iron technology was well-advanced in the first millennium BC. For example, some of the spearheads were made by laminating several pieces of iron that have different carbon content, a technique still used today. (Yalçın, 1999)

2.3. Roman Period

There were no new innovations in iron technology during the Roman Period, however, there was an enormous increase in the scale of iron production. Iron technology spread throughout the Empire. The amount of iron slag found prior to the Roman period was measured in kilograms or hundreds of kilograms. The slag heaps from the Roman period, however, was described in hundreds of tons. It is probable that this increase in scale stemmed from improved techniques such as the use of bellows-blown shaft furnaces instead of the draft induced small furnaces.

There was both domestic and military demand for iron. There was evidence that from the time of Diocletian (AD 245-313) all weapons of the imperial army were made in Roman iron workshops. According to *Notitia Dignitatum*, during the 4th and 5th centuries AD, there were 32 such factories. Some of these factories were specialized to produce certain items such as swords, spearheads and shields. Evidence of the efficiency of Roman iron production and distribution became evident at the legionary fort of Inchtutil in Scotland where 5 tons of iron nails (900,000 nails of various sizes) were discovered. This fort was built in AD 83 and was evacuated soon after in AD 87. They were all made out of forged bloomery iron. (Tylecote, 1976)

2.4. Ottoman Period

Ottomans had access to very rich ore deposits which were extensively exploited by Byzantines and Seljuks before them. They continued to operate these mines. In addition, local governors both in Balkans and Anatolia provinces were obliged to find out old mines and search for new ones.

Like their European opponents Ottomans protected ore deposits in their territory. Saltpeter, sulfur as well as copper, iron, and lead were strategically important minerals. The palace declared these minerals as prohibited goods or “memnu eshya” and prohibited their export to other countries.

Ottoman iron and iron products were also in great demand in the east. For example, about 1570, Iran Shah had at least three representatives who were Ottoman citizens living at Divriğ. Their duty was to supply horseshoe and other iron products to the Shah. It is written that one of them could buy more than 100.000 horseshoes annually for Safevis. Istanbul forbid the exportation of strategically important prohibited goods, and gave order to its local authority to assassinate Shah’s representative.

Two methods were used for the operation of the mines. The first one was to commission an “emin” for the operation, namely direct control of the mine by the government. The second one was to delegate the right to operate to an entrepreneur or investor for a short period of time, mostly for three to six years, namely “iltizam”. Mining was mostly done during summer, namely between May and November. Due to difficult working conditions, miners worked in two hours shifts and five days a week. These mines could be worked 24 hours a day by rotating shifts.

2.4.1. Iron Production Sites during Ottoman Period

Anatolian iron production centers are well mentioned in Ottoman archives. From the 16th to the end of 18th centuries it is not known how all North Africa, Syria, Lebanon, Iraq and Palestine met their needs of iron. According to archives, from the 16th century the most important iron production centers were Kiğı, near Erzincan, and Bilecik in the Marmara Region. It is also known that during the 16th century Gerecgan, near Van was an important iron center operated by the government. (Agoston, 2006)

Kiğı was the most important iron production center in Anatolia for a long time. Kiğı mainly produced cannon balls but also non-military service was given. East Anatolian iron needs were supplied mostly from the Kiğı iron workshops. Also, sometimes when Istanbul was in need of iron products, Kiğı workshops delivered needed goods. For instance, a document dated 29 September 1577 mentions that most of the Samokov's iron workshops were ruined and those that operate were used for cannon ball production and that was why Kiğı should once again deliver nails to Istanbul. (Agoston, 2006)

The second most important iron production center in Anatolia was Bilecik. In 1566 there were 67 iron furnaces and nearly all of them were producing cannon balls. A document dated to 1551 mentions that three wrought iron experts from Samokov were sent to work at Bilecik. That means Bilecik was also producing wrought iron for domestic and farming tools as well as military equipment. (Agoston, 2006)

The Balkans were generally more important than Anatolia with respect to iron production. The main reason is the constant availability of the three components of iron production; namely ore, charcoal and all season stable water sources. Anatolia does not possess such suitable geographical and climate conditions. Also, transportation of finished iron product was easier from the Balkan iron producing centers. (Agoston, 2006)

Southwest Bulgaria and Bosnia were the important iron production centers. The most important Ottoman iron production centers were Eğri Palanga (Kriva Palanka) and the region between Kratova (Kratovo) and Filibe (Plovdiv) (Agoston, 2006). Important iron deposits in the Balkan region were at Samokov, south of Sofia, at Çiprovic and Etropole. Iron ore was also found at Rudnick north of Kosovo, Eridere northwest of Macedonia, Rodopi Mountains and Samokovcuk, at Trace, also known as “Demirköy”. (Agoston, 2006)

In the 15th century “campi Samacoui” was a small iron production camp which later became one of the biggest Ottoman iron production centers, according to Petantius, in 1502 (Tanyeli, 1994). Half a century later, all of the iron needs of Süleymaniye Mosque were supplied from Samokov. Samokov, means wrought iron workshop; "samo" and "kov", respectively meaning "self" and "forge, hammer", and “samokov” comes from the mechanical forge powered by water. (Tanyeli, 1994)

For about 330 years, Samokov was the most important iron production center in the Balkans. Not only the city but also the surrounding villages were smelting and smiting iron. Samokov’s production was mainly used for military and naval needs. Specified amounts of iron were delivered to shipyard in Istanbul, annually. Also when the Ottoman navy was destroyed at Inebahtı all of the workshops at Samokov were forced to produce extra iron for shipyards. Their products were different types of nails used for ship building; ship anchors; and shafts for cannons. (Agoston, 2006)

During the 17th century Samokov continued its massive iron production. For example, Evliya Çelebi writes that at Samokov there were 100 iron workshops (Tanyeli, 1994). Also, Jirecek writes that during old Turkish period there were 72 smelting workshops, “vidna” or “vigna”, and 18 refining workshops, “madan” (Tanyeli, 1994).

Samokov iron industry continued its production without change until 19th century. At the begining of 1800's the Ottoman Government was not pleased with the quality of Samokov iron and tried to import European technology. One archive dating 1830 mentions that; to improve the quality of iron, French technicians were commissioned. However, it was not possible to modernize Samokov. In 1837 Ottomans were able to build a high shaft furnace at Samokov, but production was constantly decreasing and quality was substandard. Before 1877-78 Ottoman-Russian war there were 25 smelting workshops and 12 refining workshops. When Bulgarians started to rule in 1878 there were just four workshops (Agoston, 2006).

2.4.2. Ottoman Period Cannon Casting

Cannon production can be taken as an indicator of the metal technology of a given community. Cannons were introduced to Ottomans by Europeans. However, Ottomans were quick to understand the importance of cannons in warfare and pursued constantly to develop their technology.

During the second part of the 15th century Ottoman founders were casting the biggest cannons at that time. These big bombards were awkward, difficult to turn, slow shooting (few shots a day) and their degree of utility was debatable, but they exerted big technological and organizational powers that only very few European countries could afford. These big cannons were pride of Emperors and Kings indicating advances in technology, rather than useful war machines.

Books of accounts of Tophane-i Amire dating to the 1520's, 1680's, 1690's and also the 18th century indicate that massive amount of different size of cannons were produced. Ottomans produced many different types of cannons. There was no standardization. Ottomans mostly preferred to cast bronze cannons even though they were more expensive. They were using typical tin bronze containing 8.6-11.3% Tin and 89.5-

91.4% Copper. This is the best chemical composition for Bronze that gives good casting conditions and produces best physical properties for cannons.

Cannon technologies of Europe and Ottoman Empire were very different from each other. Europeans especially in the 17^{th} century were casting all forms of cannons from iron, whereas the Ottomans were still casting their middle-sized and big cannons out of bronze. Although the Ottomans experimented iron cannons as early as the beginning of the 16^{th} century; in early modern period they only cast small cannons from iron. There may be two possibilities for not using iron for all types of cannons. First, bronze cannons were more reliable and safer to use. Second, copper was abundant in the Ottoman period. (Agoston, 2006)

2.5. Demirköy (Malki Samokov)

The closest iron production center to Istanbul was "Malki Samokov" or "Samokovcuk" (meaning small Samokov) now known as "Demirköy" (meaning iron village). Demirköy is located at the northwestern region of Thrace on the metalliferrous zones of Istranca Mountains (Figure 2.3). It is about 25 Km away from the nearest port giving it the opportunity of naval transport of products to Istanbul. The oldest document about Samokovcuk dates to 4 March 1696. It was a decree from the Sultan stating that a foundry should be constructed to produce "yuvalak", cannon balls.

Starting from the end of the 17^{th} century to the last quarter of the 19^{th} century, iron production continued at Samokovcuk with occasional interruptions. Samokovcuk and nearby Torliye (in old times Turula, and now it is called Hamdi Bey) iron products were send to Istanbul by İğneada port.

Figure 2.3. Demirköy, Samokovcuk region

Iron industry at Samokovcuk was renewed and main foundry complex was enlarged in 1821. An archive document states "…build one new furnace next to the three furnaces inside main workshop and three other new furnaces around main workshop…" (Tanyeli, 1994). To improve the technology of iron production a foundry worker was sent to England. One yearbook of Edirne dating to 1875 states that Samokovcuk foundry was still producing horseshoes and even machinery and tools. Samokovcuk iron production probably stopped during the 1877-1878 Ottoman-Russian war. Around 1912 the region was commissioned to a British company. However in 1916 during the First World War the permission was cancelled. (Agoston, 2006)

3. IRON METALLURGY

3.1. Metallurgy

First known iron to prehistoric people was meteoric iron, *metal from the heavens*. Simple metal objects produced from meteoric iron were very limited. Such implements had no economic value and did not improve their way of life; they were just prestigious objects. Actual iron metallurgy started when metal was produced from its ores known as extractive metallurgy. This is a very complex process and requires high technology. The steps of extractive metallurgy involve the recognition of ores, mining, ore dressing, reduction, possible refining and finally production of desired objects. To carry out these complex series of steps, raw materials should be available as well as developed social structure where work force is available. It is known that the first iron objects produced from smelted iron are found at northeast Anatolia. It is not sure if Hatti or Hittites were first to use it, but Hittites are credited to have developed iron technology.

Iron is produced from its ore either by direct method or indirect method. In direct method iron is produced in solid state in bloomery furnaces. Wrought iron is obtained by forging the bloom. Indirect method, however, has two steps. In the first step cast iron is produced in blast furnaces. Cast iron is then decarburized in finery. The end product of decarburization process is again a bloom which is forged to obtain wrought iron. In either case there are many crucial steps required for iron production (Figure 3.1).

Iron ores are first mined followed by ore dressing where the ore is enriched. The enriched ore together with charcoal and fluxing agents if necessary are charged to a furnace. Depending on the type of furnace used either bloomery iron or cast iron is obtained. Indirect method of wrought iron production first appears in Europe about 14^{th} and 15^{th} centuries.

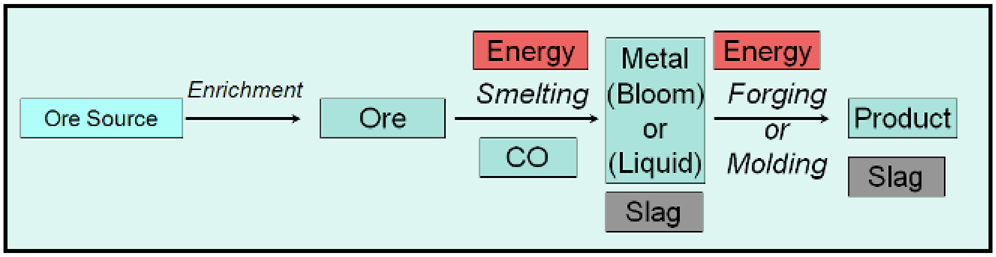


Figure 3.1. Process chart of iron production

3.2. Iron Ores

Minerals are natural inorganic substances, which has a definite chemical composition, physical properties and molecular structure. An ore is a metal-bearing mineral, or aggregate of such minerals, mixed with non-metallic siliceous constituents (Thrush, 1968).

There are more than 1200 iron containing minerals. Some of the most common iron ores are listed in Table3.1. The ores are usually rich in iron oxides and vary in colour from dark grey to rusty red. The three oxides and a carbonate of iron, namely, magnetite (Fe_3O_4), hematite (Fe_2O_3), limonite (a mixture of goethite and lepidocrocite ($FeO(OH){\cdot}nH_2O$)) and siderite ($Fe\ CO_3$) are the most widely used iron ores.

Table 3.1. Iron minerals

Mineral Name	Chemical Formula	%Fe
Magnetite	Fe_3O_4	72.36
Hematite	Fe_2O_3	69.94
Goethite (Limonite)	FeO(OH)	62.85
Lepidocrocite (Limonite)	FeO(OH)	62.85
Siderite	$FeCO_3$	48.20
Pyrite	FeS_2	46.55

3.3. Iron Mining

Early miners with their limited tools could only reach ores that were just below the surface by digging narrow shafts that were about 10-15 meters long. The ores at this level are the highly enriched, colored secondary ore deposits. Simple stone and bone tools were used. They would follow the ore vain and collect these rich ores that probably did not need concentration before smelting.

When the rich deposits of secondary ores were consumed the miners had to penetrate deeper into the ore deposits by opening underground mining galleries. The mining galleries in hard rocks were opened by fire setting technique. When rocks were heated to high temperature they would become softer and could be easily crushed by simple stone tools.

3.4. Ore Dressing

Ore dressing is used to separate the valuable minerals from the worthless gangue minerals and increase the concentration of the ore. This is an enrichment process. Higher ore concentration means more efficient smelting process and higher product (Pryor, l978).

During the early periods, the ores were separated from the gangue minerals by simple crushing and handpicking. Later, metallurgists separated them by using specific gravity differences of minerals by simply washing them in sluice boxes. By the 20th century, flotation process was used to separate ores from the gangue minerals.

3.5. Fluxing Agents and Slags

All ores contain siliceous gangue minerals even after extensive ore dressing processes. The remaining gangue minerals must be separated from the metal during smelting. Fluxes are added to smelting charge to remove the unwanted remaining gangue minerals from the reduced metal by forming a liquid slag. In the bloomery process it is very important to produce liquid slag, so that it will be possible to have a bloom with minimum slag contamination (Table 3.2). Quantities of the three major components of slags determine its melting point (Table 3.2). It can be seen from table 3.2 that a slag with composition of 59% FeO, 29% SiO_2 and 12% CaO will have a melting point of 1115^oC.

Table 3.2. Free running temperatures of slag (Tylecote, 1976)

Composition %			Free running temperatures ^oC
FeO	SiO_2	CaO	
78	22	0	1180
70	30	0	1200
62	38	0	1180
60	40	0	1400
59	29	12	1115
40	40	20	1150
35	35	30	1200
30	30	40	1500
0	50	50	1540

There are two types of fluxing agents, basic oxides and acidic oxides. Basic oxides are the oxides of Ca, Mn, Mg, Fe, Zn, Pb, Na and K and provide oxygen ions when dissolved in a slag (Reaction 3.1).

Main acidic oxide is SiO_2 and absorbs oxygen ions provided by the basic oxides (Reaction 3.2). Al_2O_3 is amphoteric oxide capable of reacting with both acids and bases, therefore it can be used as acid in need.

$$MO \longrightarrow M^{+2} + O^{-2} \qquad (3.1)$$

$$SiO_2 + 2O^{-2} \longrightarrow SiO_4^{-4} \qquad (3.2)$$

Depending on the volume of the gangue minerals that an ore may contain, proper ratio of basic and acidic oxides are added to fuse the gangue minerals to a relatively low melting slag. The most common slag combination is iron silicate known as fayalite (Reaction 3.3)

$$SiO_2 + 2FeO \xrightarrow{>600^oC} 2FeO.SiO_2 \qquad (3.3)$$

3.6. Chemistry of Smelting

There are two main aims in metal smelting: Reduction of the metal oxide to metal and formation and separation of the gangue minerals, as slag.

The tendency for the extraction of metals from their oxides can be explained by thermodynamic principles. The spontaneity of a chemical reaction depends on enthalpy and entropy of the system (Equation 3.4). As Gibbs' free energy decreases, reaction is favored and it is more possible to take place. The Ellingham diagram is essentially a graph representing the thermodynamic driving force for a particular reaction to occur, across a range of temperatures. With the data for several reactions plotted on the same graph, the relative stabilities of different elements with respect to their oxides can be seen. It is also possible to compare the relative driving force for an element for oxidation or sulphidation in an environment containing both oxygen and sulphur as reactants. Ellingham diagram display the free energy variations of metal oxides with respect to temperature (Figure 3.2).

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \tag{3.4}$$

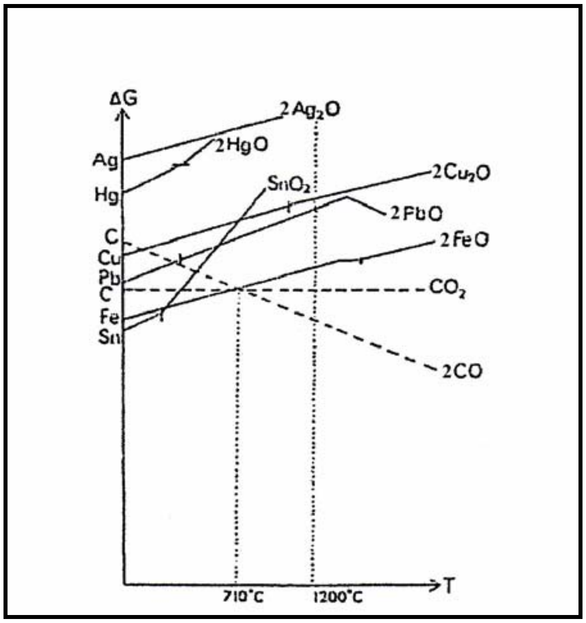


Figure 3.2. Ellingham's diagram

In the Ellingham diagram, the free energy axis represents the relative stability of metal oxides. Elements that have high oxidation potential such as Fe, Al and Mg have lower values for ΔG, which means a greater affinity for oxygen. Elements such as Cu, Hg, Ag have low oxidation potential and their oxide formation is less spontaneous. For metal oxides ΔG becomes more positive with increased temperature. Only ΔG of CO has a negative slope which means that CO formation is favored at high temperatures. When the lines of CO and CO_2 are crossed, a temperature of 710^{o}C will be found (Figure 3.2). At this temperature CO formation is favored instead of CO_2. At temperature above 710^{o}C, carbon – oxygen combustion equilibrium shifts to the right providing high level of CO for the reduction process (Cottrell, 1967) (Reaction 3.6). Metal oxides such as MgO, MnO and Al_2O_3 which are below the CO line, have greater affinity for oxygen and cannot be reduced by CO.

Consider the two oxidation reactions below, whose lines on the Ellingham diagram cross each other:

$$2Fe + O_2 \rightleftharpoons 2FeO \tag{3.5}$$

$$C + O_2 \rightleftharpoons CO_2 \tag{3.6}$$

At the point that the lines cross, the standard free energy changes of two reactions are equal. This means that a closed system containing the metals A and B will be at equilibrium. This can be shown by considering the reaction below, obtained by subtracting Fe oxidation reaction from C oxidation reaction:

$$C + 2FeO \rightleftharpoons 2Fe + CO_2 \tag{3.7}$$

At $T = T_E$, ΔG for this reaction is zero, and no reaction occurs. However above this temperature Fe is reduced by C, and below it C is reduced by Fe.

Smelting is carried out by reduction of ore by carbon monoxide at high temperatures (generally 1000^o – 1200^oC). The reductant, carbon monoxide, forms above 710^oC when charcoal is burned (Reaction 3.8, 3.9, 3.10). Since CO has greater affinity for oxygen than most metal oxides it will be oxidized to CO_2 while the metal is reduced (Reaction 3.11).

$$2C + O_2 \rightleftharpoons 2CO \qquad (3.8)$$

$$CO_2 \rightleftharpoons C + O_2 \qquad (3.9)$$

$$CO_2 + C \rightleftharpoons 2CO \qquad (3.10)$$

Smelting of iron occurs in steps. If it is started with hematite, hematite reacts with CO over 710°C to produce magnetite (Reaction 3.12). Magnetite is reduced with CO to produce wüstite (Reaction 3.13). And finally wüstite is reduced with CO to produce elemental iron (Reaction 3.14).

$$MO + CO \longrightarrow M + CO_2 \qquad (3.11)$$

M = Metal

MO = The oxide of the metal

$$Fe_2O_3 + CO \rightleftharpoons Fe_3O_4 + CO_2 \qquad (3.12)$$

$$Fe_3O_4 + CO \rightleftharpoons FeO + CO_2 \qquad (3.13)$$

$$FeO + CO \rightleftharpoons Fe + CO_2 \qquad (3.14)$$

3.7. Furnace Types and Their By-Products, Slags

3.7.1. Bloomery Furnace, the Bloom and Fayalitic Slag

Bloomery furnace is used in direct production of iron. It may be in various shapes as shown in Figures 3.3 and 3.4. It is possible to reduce iron and obtain a liquid slag at about 1200^{o}C (Table 3.2). Product of the bloomery furnace is a bloom and must be forged to obtain wrought iron. (Tylecote, 1976)

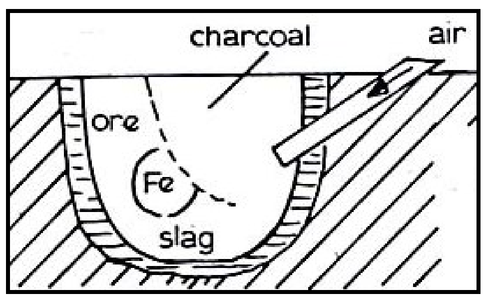


Figure 3.3. Catalan furnace

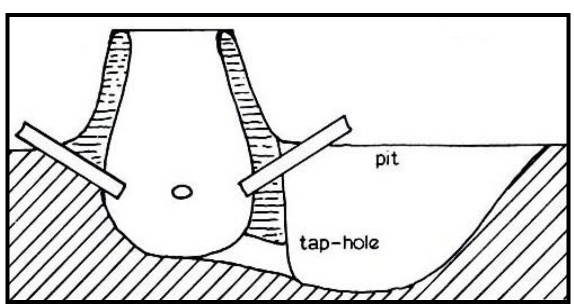


Figure 3.4. Slag-tapping bowl furnace

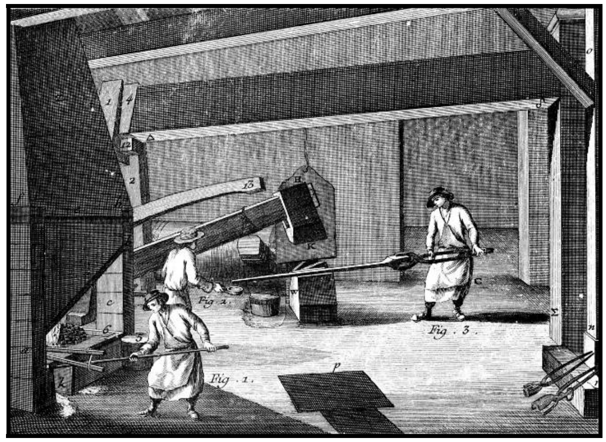


Figure 3.5. Forging hammer powered with water (Agricola, 1556)

The operation of bloomery furnace is rather complex. It is important to create a reducing atmosphere of carbon monoxide in the furnace, by partial oxidation of charcoal (Equation 3.10). The flame at the top of the furnace will appear blue, indicative of carbon monoxide. The carbon monoxide penetrates into the ore particles and reacts with the iron oxide to form carbon dioxide, reducing the iron oxide sequentially to metal (Equation 3.11). In a bloomery furnace some of the iron oxide reacts with the other oxides present such as silica and alumina, to form slag, the waste product of iron smelting. This slag may be tapped or left to cool at the base of the furnace (Figures 3.3 and 3.4). It is very important to be able to produce liquid slag. The temperature is increased by blowing more air (oxygen) into the furnace, although this can stop the formation of the reducing gas carbon monoxide. The thickness of the walls of the furnace helps to stop heat loss, and using charcoal as the fuel helps to keep the temperature high. Another problem with iron smelting is that pure iron melts at 1536^{o}C. Such temperatures cannot be reached in a bloomery furnace. In the bloomery furnace the metal particles coalesced to form a pasty lump called the “bloom” which is produced as a solid mixture of spongy iron, slag and charcoal. The smelting process takes about 8 hours (Godfrey, 2002).

Fayalitic slag is formed in the bloomery furnaces which is simply iron silicate ($2FeO.SiO_2$). Fayalitic slag from bloomery furnace generally contains three main phases: wüstite, fayalite and glassy anorthite. In figure 3.6 microstructure of a fayalitic slag is shown. On this microstructure, the leaf-like, light grey phase is wüstite (FeO), medium gray phase is fayalite ($2FeO.SiO_2$) and the darkest phase is anorthite ($CaO.Al_2O_3.2SiO_2$). Sometimes there are iron inclusions. Iron prills are seen as white irregular shapes in Figure 3.7.

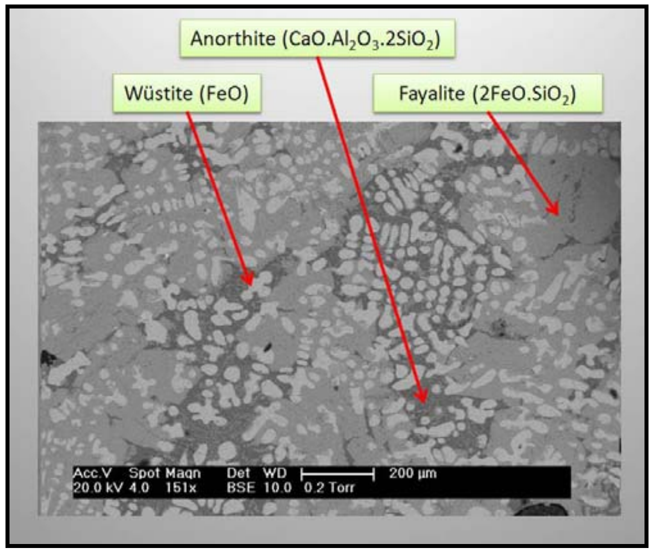


Figure 3.6. Fayalitic slag microstructure

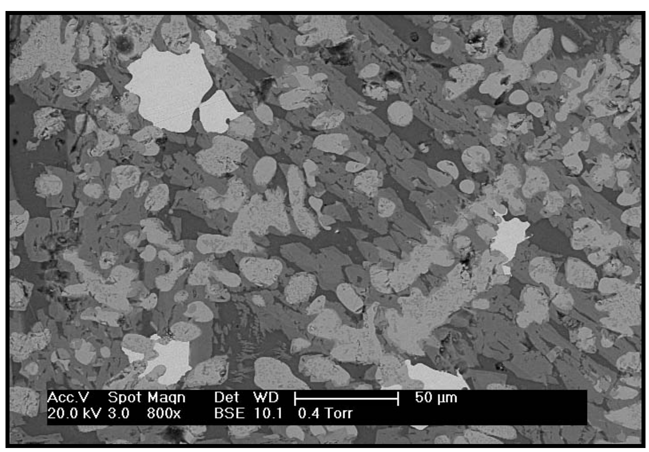


Figure 3.7. Fayalitic slag with iron inclusions (white phase)

3.7.2. Blast Furnace, Cast Iron and Glassy Slag

Blast furnaces (stückofen) began to appear during the 14^{th} – 15^{th} century BC in Europe. They were taller than bloomery furnaces and the air blast was provided by water-power driven bellows. This combination allowed the furnace temperatures to reach close to 1500°C. Dissolution of carbon in iron to about 5% C lowered its melting point and iron metal could be obtained in liquid form.

At these high temperatures much less iron is needed to liquefy the slag. Addition of calcium oxide replaces the iron in the slag and almost 80% of the iron in ore can be recovered.

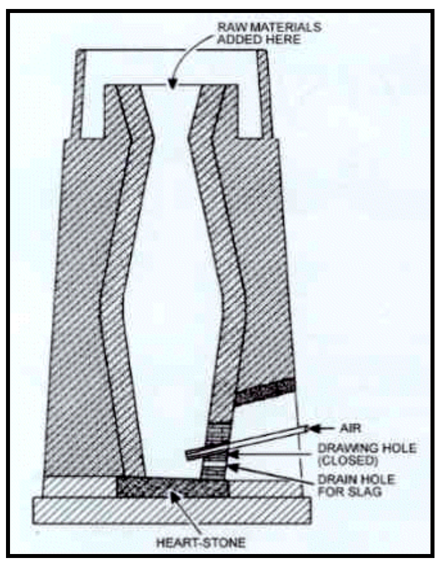


Figure 3.8. Blast furnace

Glassy slag with high amounts of silicate do not show any crystalline structure (Figure 3.9). According to the fluxing agents used, anortite ($CaO.Al_2O_3.2SiO_2$) and other minerals can form. Iron content of glassy slags is generally less than 10%. Sometimes cast iron prills can be seen. These inclusions are round because furnace temperature is higher than the melting point of iron.

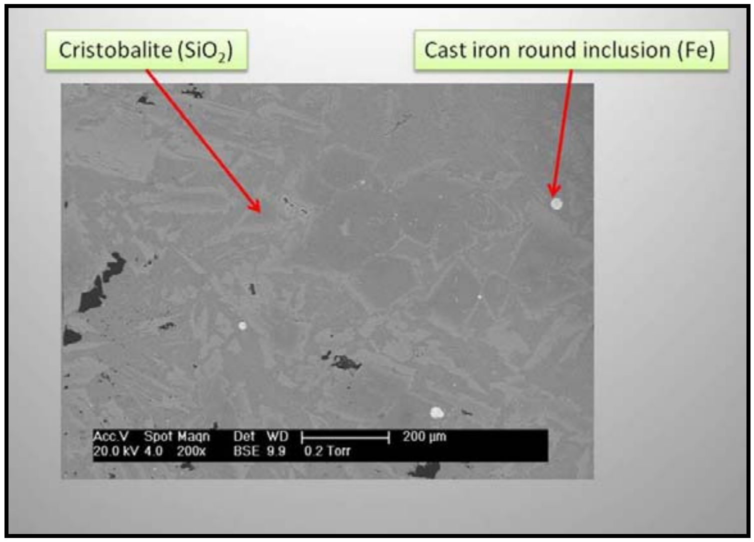


Figure 3.9. Glassy slag

Cast iron produced in the blast furnace by the indirect process can be converted to wrought iron in a finery.

3.7.3. Finery Hearth and Its By-Product, Finery Slag

Finery furnace (Figure 3.10) operates above 1200°C allowing cast iron to melt and react with the oxygen blown from the bellow. Under the high oxidizing conditions, carbon in the cast iron is oxidized (Equation 3.6). The spongy iron, also called bloom has to be consolidated by forging.

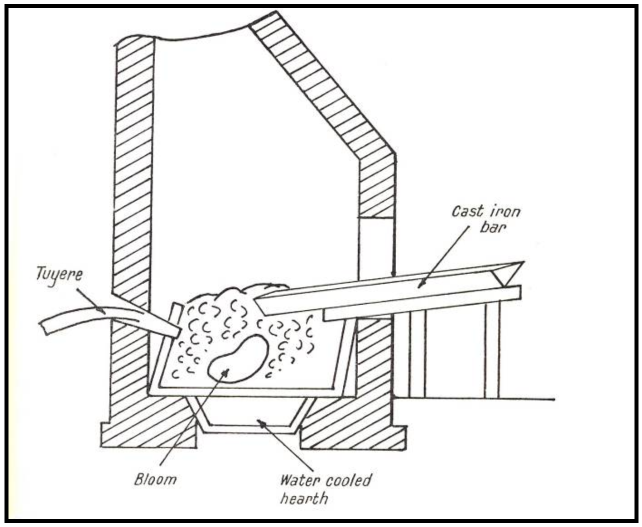


Figure 3.10. Walloon finery hearth (Tylecote, 1987)

During the oxidation, together with carbon considerable amount of iron is also oxidized. The slag that is produced in a finery hearth is known as finery slag. It has a spongy structure and may have iron oxide content as high as 85%. Microstructure of a finery slag is shown in Figure 3.11.

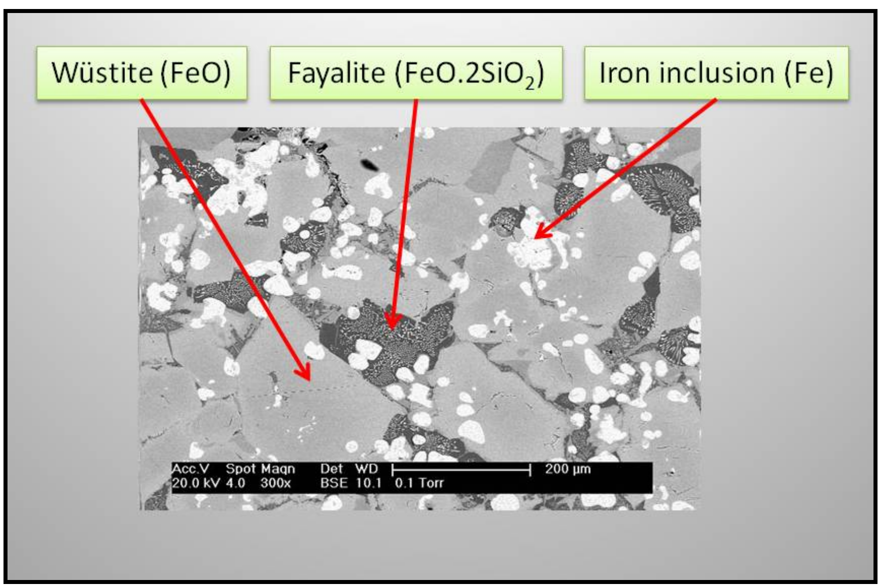


Figure 3.11. Finery slag

3.8. Iron-Carbon Alloys and Types of Iron

Alloys are metallic substances that contain at least two elements. The base element must be a metal whereas the minor component, also known as the alloying element, may be a metal or a non-metal. When the alloying element is added to the base metal, it may fill in the gaps between the atoms of base metal or substitute for the base metal. Alloying element may be insoluble, partially soluble or totally soluble in the base metal. Depending on its solubility, a solid solution or a solid mixture may form. If there are only two components the alloys are called "binary alloys" (Callister *et al* 2003). Addition of an alloying element generally changes the properties of the base metal. The most characteristic change is an improvement in the mechanical properties where hardness is increased as well as the melting point of the base metal is lowered.

Carbon is the most important alloying element for iron. Iron-carbon alloys possess many different properties depending on the amount of the carbon present. To study these effects one must study the phase diagram of Fe and Fe_3C. (Figure 3.12)

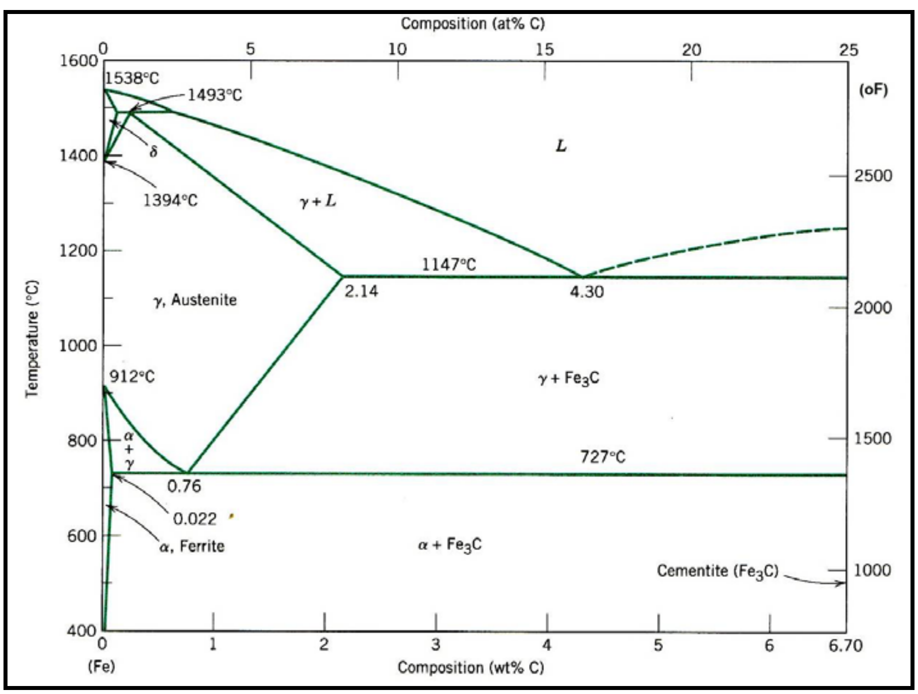


Figure 3.12. Fe-Fe_3C phase diagram (Callister *et al* 2003)

Pure iron also known as α-iron or ferrite has a body centered cubic (bcc) structure at room temperature. In this structure the solubility of carbon is about 0.022%. when pure iron is heated over 900^{o}C, bcc structure turns into face centered cubic (fcc) structure. The fcc structure is known as γ-iron or austenite and the solubility of carbon is increased to about 2.14% at around 1100^{o}C.

Eutectic composition of carbon in steel is 0.76%. When austenite that contains 0.76% carbon is cooled below 727^{o}C, the structure transforms into bcc structure and the excess carbon reacts with iron to form cementite (iron carbide, Fe_3C) (Equation 3.15). The structure that forms is pearlite which is a lamellar mixture of ferrite and cementite (Figure 3.13).

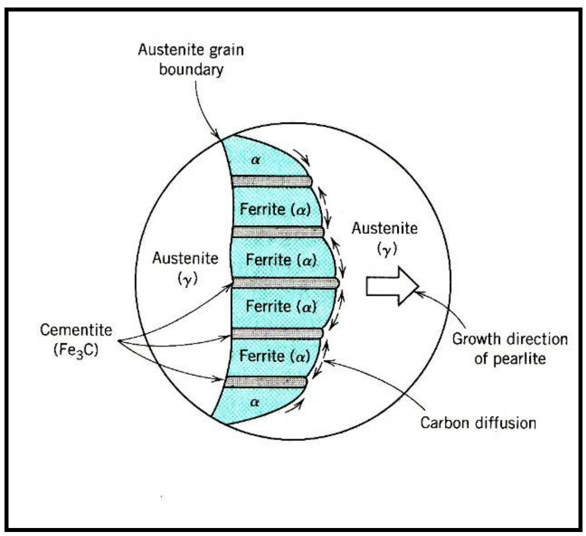


Figure 3.13. Schematic representation of the formation of pearlite from austenite (Callister *et al* 2003)

Two very important phase changes take place at 0.76% C and at 4.3% C. At 0.76% C, the transformation is eutectoid, called pearlite (Reaction 3.15; Figure 3.14). And at 4.3% C, the transformation is eutectic, called ledeburite (Reaction 3.16). Pearlite is a lamellar mixture of ferrite and carbide (cementite) formed by decomposing austenite of eutectoid composition. This structure is formed because ferrite cannot dissolve excess carbon that austenite contains and precipitation occurs (Callister *et al* 2003).

$$\gamma\text{-Fe (austenite)} \longrightarrow \alpha\text{-Fe (ferrite)} + Fe_3C \text{ (cementite)} \quad (3.15)$$

$$\text{L (liquid)} \longrightarrow \gamma\text{-Fe (austenite)} + Fe_3C \text{ (cementite)} \quad (3.16)$$

3.8.1. Wrought iron

Wrought iron is a pure iron without any carbon also known as α-iron or ferrite. It melts at 1536^{o}C. It is ductile, softens when heated and can be easily shaped by hammering when hot. It is used to make a variety of tools and weapons like knife, spear heads, arrow heads, axe, reaping hook, hoe, nail, horse shoe, scissors and plow. The microstructure of α-iron (ferrite) grains is shown in Figure 3.14. The polished surface is etched by 2% nital.

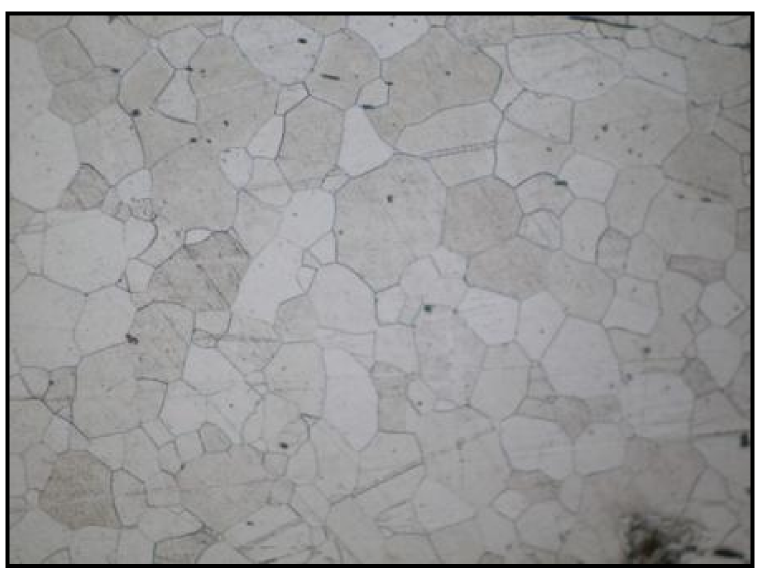


Figure 3.14. Microstructure of α-iron (ferrite)

3.8.2. Steel

Steel is an iron-carbon alloy that contains up to 1.5% carbon (Figure 3.12). Steel can be produced by decarburization of cast iron or by carburization of wrought iron. However, it is important to note that in bloomery furnaces steel that contains up to 0.8% carbon may form.

Microstructure of steel consists of alternating layers or lamellae of the two phases, called pearlite (Figure 3.13 and 3.15). Cementite forms when the fcc crystal of austenite structure turns into bcc structure at 910^{o}C. Its structure may also contain ferrite or cementite depending on carbon content. Microstructure of 0.8% carbon containing iron will form 100% pearlite. Microstructures of steel containing less than 0.8% carbon can be seen in Figure 3.16.

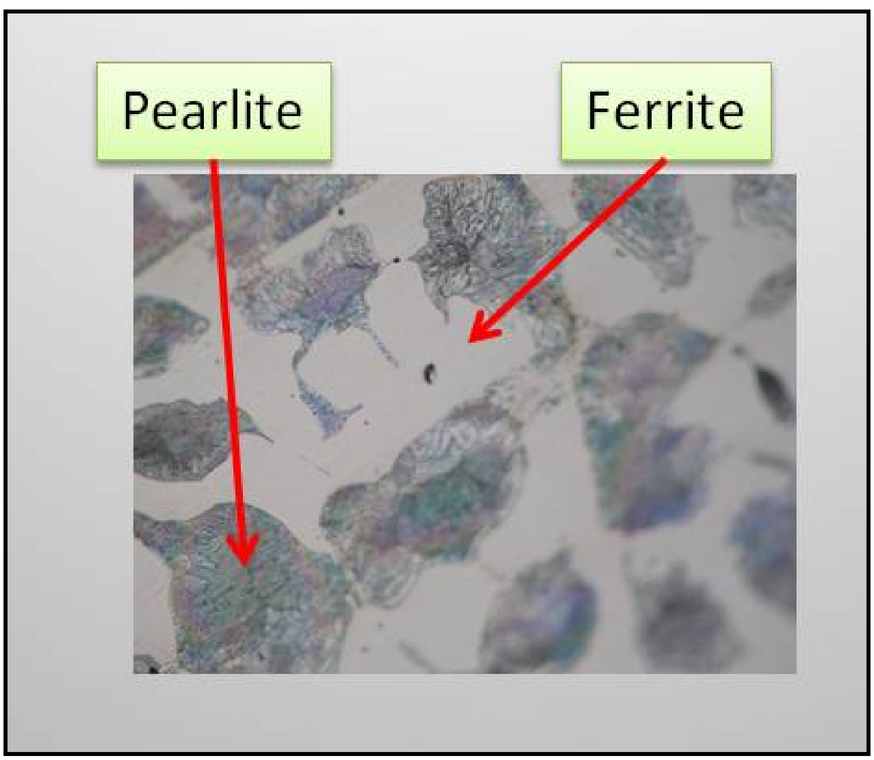


Figure 3.15. Microstructure of steel

3.8.3. Cast iron

Cast iron contains more than 2% up to 6.5% carbon. It melts at about 1300^{o}C allowing it to be cast in moulds. It is produced in blast furnaces. Cast iron is very brittle and melts without softening when heated. Production of cannons, cannon balls, stoves, fountains, fence and piano framings are some applications of cast iron. Microstructure of cast iron contains white pearlitic iron and black graphite flakes (Figure 3.16). Depending on the cooling rate there are two types of cast iron. Quickly cooled cast iron forms white cast iron which is very brittle so applications are limited. Graphite flakes are very small in white cast iron. Slowly cooled cast iron forms gray cast iron which has wider applications. Nital etched microstructure of cast iron is shown in Figure 3.17.

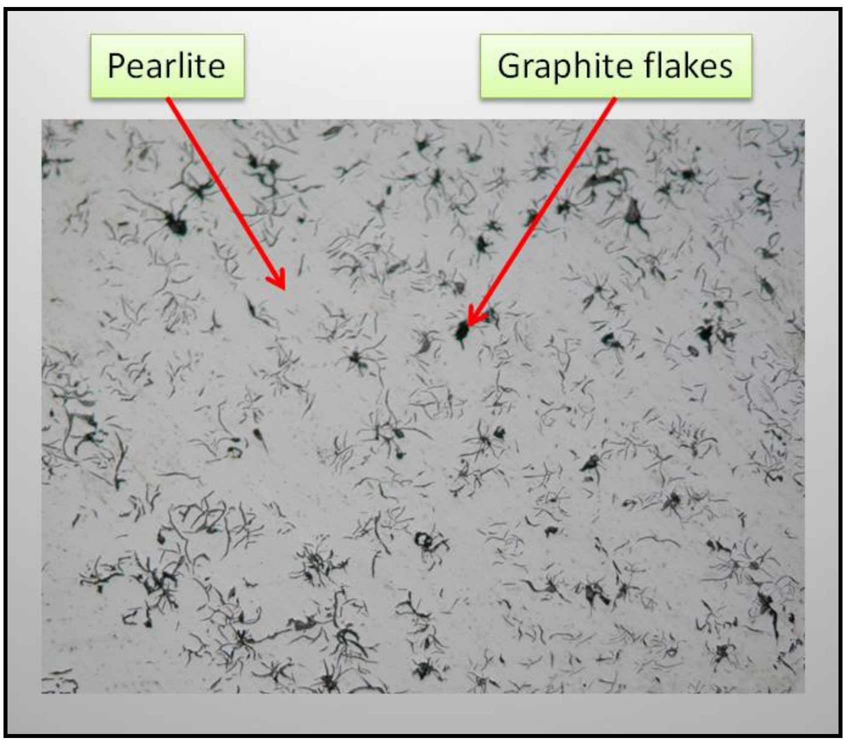


Figure 3.16. Microstructure of cast iron without etching

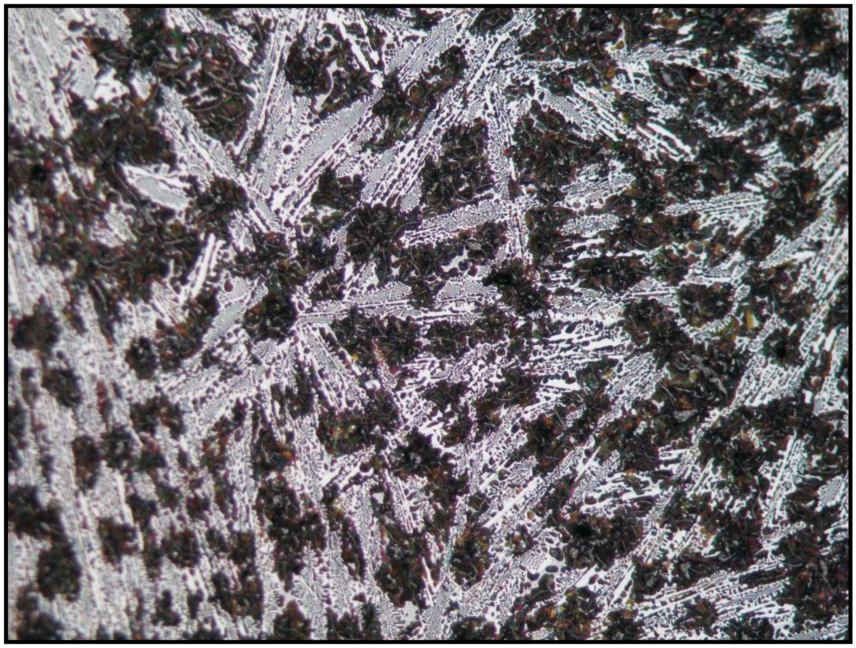


Figure 3.17. Microstructure of cast iron after etching

3.8.4. Heat treatment of steel

Ferrite, at room temperature does not dissolve carbon but with increased temperature ferrite structure transforms into austenite. Austenite can dissolve up to 2% carbon. This process is called "cementation" or "case hardening". When wrought iron is heated at 950^{o}C under a pile of charcoal for a long time, carbon can diffuse into the iron matrix as much as 1.5 mm increasing the carbon content to about 0.5% (Callister *et al* 2003)

The rate of cooling a piece of steel from the austenite structure to room temperature is very critical. The rate determines the nature of pearlite formation. If 0.8% carbon containing iron is cooled to room temperature slowly, a very coarse pearlite forms. If the cooling rate is about 5-10 seconds a very fine pearlite forms. However, if the steel is quenched in water quickly, a very brittle martensite structure forms. Since large pieces may not cool at the same rate it may cause severe deformations.

Martensite is very hard, brittle and has the highest tensile and yield strength. Steel with martensite structure is not very applicable. That is why heat treatment or "tempering" is applied on martensite. Tempering is reheating slowly the quenched steel to produce a very fine pearlite. Temperature must be higher than 575^{o}C for about 1 day and must be re-quenched (Callister *et al* 2003). The hardness of various materials are compared in Figure 3.18.

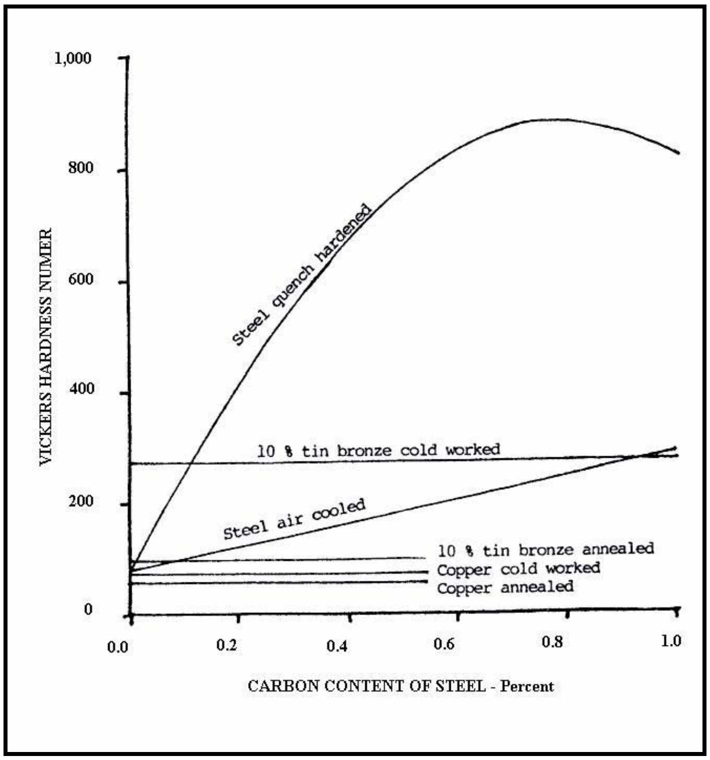


Figure 3.18. Comparison of hardness of steels with those of copper and bronze

4. ANALYTICAL METHODS

In this study, many ore, bloom, slag and metal samples were investigated in order to understand iron production technologies at Demirköy. Carbon analyses of the metal samples are done by pyrolysis instrument. Microstructural investigation is done by scanning electron micrograph (SEM) and optical microscope. The mineral composition of ores and slag samples are done by x-ray diffraction (XRD). Semi-quantitative analyses of slag and metal samples are done by energy dispersive x-ray (EDAX). Atomic absorption spectroscopy (AAS) is also used to determine chemical composition.

4.1. Instruments Used

- Varian SpectrAA 250-Plus Atomic Absorption Spectrometer
- Philips XL 30 ESEM-FEG
- Rigaku D/max-Ultima+/PC X-ray Diffractometry
- LECO CHN – 600
- Olympus BX51 Research Microscope

4.2. Sample Preparation

4.2.1. Preparation of metal samples

About 20 mg of sample is drilled out from the metal object. The metal flakes are dissolved in 10ml of con. HCl in a 50 ml beaker; Covered with watch glass dissolution is completed by heating the solution on a hot plate without boiling for about 30 min. or until the sample is completely dissolved. The solution is then diluted into a 25 ml volumetric flask with 10% HCl. The original solution is further diluted as needed for analysis.

4.2.2. Preparation of ore and slags

A representative ore or slag sample is prepared by mixing sections from different parts of the sample. The mixture is ground to 100 mesh in a ceramic and/or agate mortar. About 50 mg of a sample is weighed in a Teflon beaker. It is wetted with 2-3 drops of deionized water followed by the addition of 3 ml cons. HF and 1 ml cons. $HClO_4$. The beaker is then heated in a hood on a hot plate until it is dry and evolution of fumes stop. The residue in the Teflon beaker is dissolved in 5 ml of aqua-regia by gentle boiling for about 20 minutes. The solution is then diluted to 50 ml with 6 N HNO_3. It is important to add 1 ml, 500 ppm lanthanum solution before dilution (about 10 ppm in the sample). Lanthanum is used to suppress the ionization of Ca and Mg during atomization step in AAS analysis.

4.2.3. Preparation of samples for microstructural analysis

Samples were cut with a steel saw with water cooling. Initial polishing is done by emery paper. Then specimens are dried and embedded into epoxy resin under vacuum. After a day the hard, cylindrical samples are polished with abrasives starting from 400 µm to 1µm in size. (Buehler, 2007). Both polished and 2% nital etched surfaces are examined.

X-ray diffraction (XRD) of the samples are determined on 100 mesh powder.

4.3. Flame Atomic Absorption Spectroscopy

The FAAS is optimized with specific wavelength and gases for each analyte element. Standard calibration solutions are prepared for each analyte elements. Reference materials are prepared to check the calibration and instruments' reliability.

4.4. Elemental Analyses by Pyrolysis

Analyses were done on about 250 mg powdered samples. Samples were prepared by powdering the sample in a steel mortar. Samples were weighed in a single-use crucible before pyrolysis.

4.5. X-Ray Diffraction Spectroscopy (XRD)

Mineral composition of some ores and slags are analyzed by X-ray diffraction spectroscopy (XRD).

4.6. Scanning Electron Micrograph (SEM)

Environmental scanning electron micrograph (SEM) is used to determine the microstructure of both metal and slag samples. Energy dispersive x-ray analyses (EDAX) are used to determine the average chemical composition as well as the chemical composition of unknown phase.

4.7. Optical Microscopy

Optical microscopy is also used to determine the microstructure of both slag and metal samples.

5. RESULTS OF DEMİRKÖY FOUNDRY-WORKSHOPS AND ARCHAEOMETALLURGICAL MATERIALS

5.1. Demirköy Ottoman Foundry

Main foundry at Demirköy has two parts: administrative and workshop (Figure 5.1). The workshop is located below the administrative part having elevation difference of about 7 m. This level difference allows the building of water powered waterwheels. Partially destroyed remains of two high-furnaces (blast furnace) still exist in the work area (Figure 5.2).

Figure 5.1. Main foundry complex: administrative part

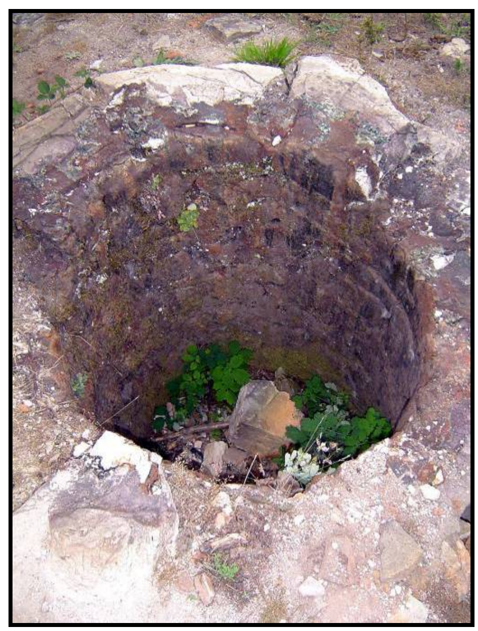


Figure 5.2. One of the destroyed high-furnaces

There are seven iron-smelting sites around the main foundry (Figure 5.3). These workshops were located near ore sources and near riverbeds. About 20 bloomery furnaces were discovered during the surveys. These furnaces were constructed using stones without mortar (Tanyeli, 1994). They are cylindrical in shape and walls of furnaces narrow towards the top of the furnace to an opening. At these smelting sites there is no evidence about possible water wheel construction to power the bellow. Probably human powered bellows were used to blow air into the furnaces in these small installations.

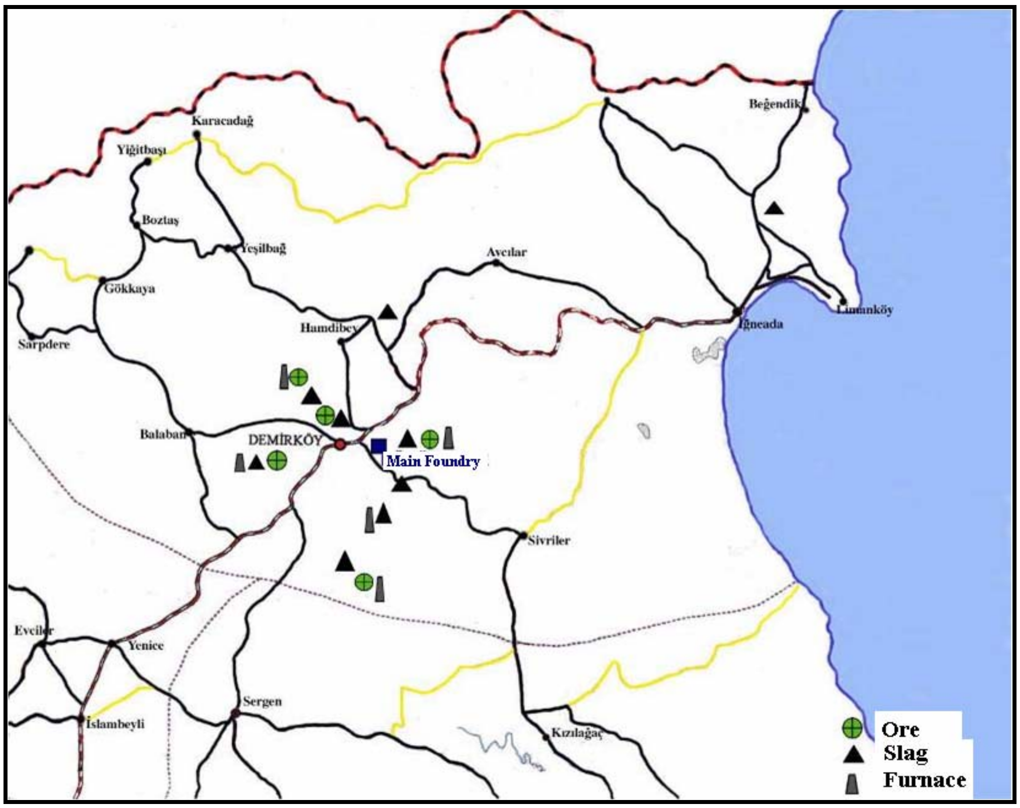


Figure 5.3. Iron-smelting sites around the main foundry

In 2005 and 2006, archaeological excavations were carried out in the “smaller workshop” located about 250 meters west of the main foundry. This workshop was about 50 meters by 20 meters and had several sections (Figure 5.4) (Özbal-Gerritsen, Gerritsen, 2007). The workshop on the west (Area 1) had two furnaces. Excavations during the 2005 season showed that one of the furnaces was used for smelting copper. Slag and furnace remains from the totally destroyed second furnace indicates that it probably was an iron blast furnace.

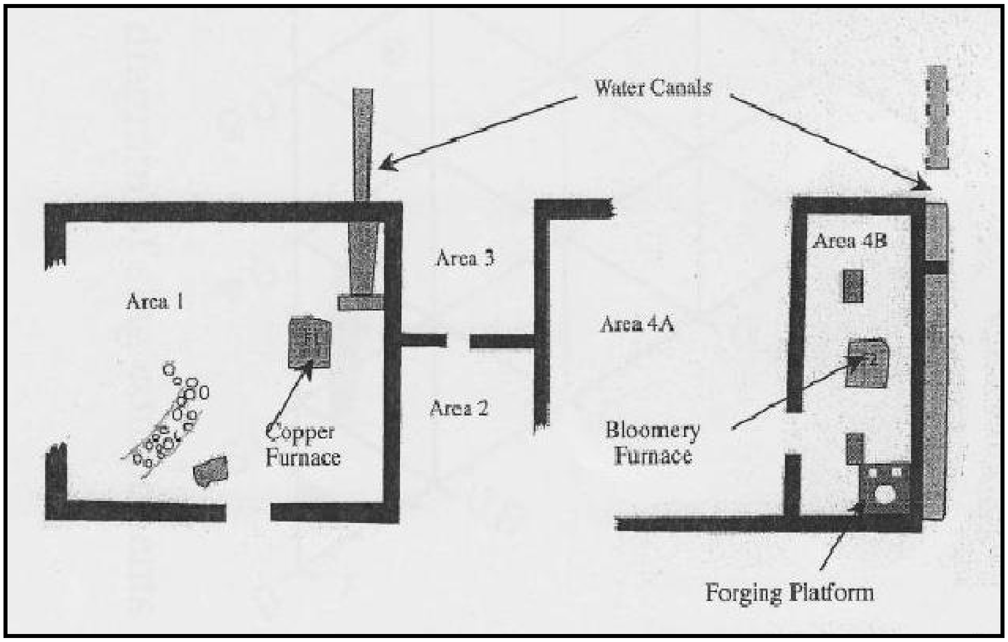


Figure 5.4. Smaller workshop excavated in 2005 and 2006

At the section on the east end of the workshop (Area 4B) there was another furnace which was very well preserved (Figure 5.5). The rectangular stone furnace was constructed almost at the center of the workshop (Figure 5.6). The dimension of the furnace was 2.68 x 3.10 meters. The stone structure was built without mortar up to the height of about 75-85 cm. The furnace has not been excavated so the inner features are not known. A water canal at the east wall of the workshop provided water power for both the bellows and the forging hammer that was located in front of the furnace to the south (Figure 5.5; Figure 5.6). Samokov furnaces in Bulgaria may be good representatives of the same technology (Figure 5.7, 5.8).

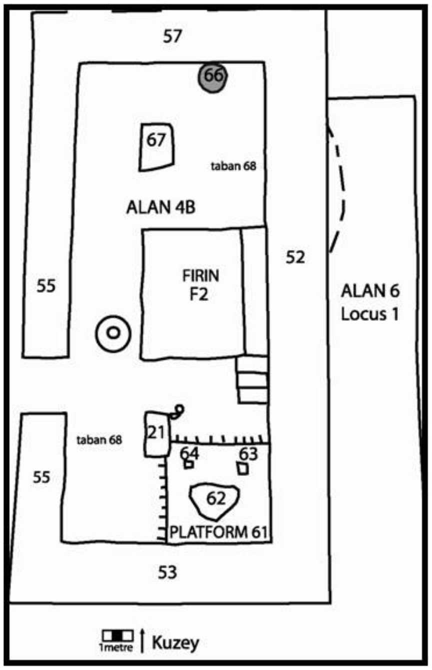


Figure 5.5. Area 4B after 2006 excavations

Figure 5.6. Bloomery furnace (F2) at Area 4B

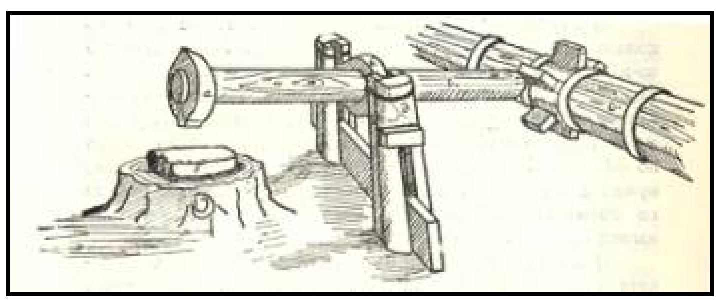


Figure 5.7. Forging hammer powered with water, from Samokov

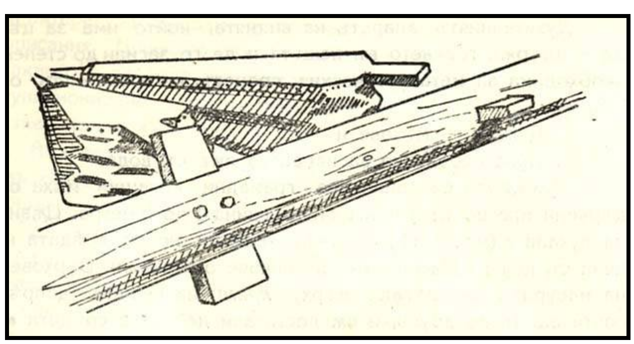


Figure 5.8. Water powered bellows from Samokov

5.2. Analysis Methods and Results of Archaeometallurgic Materials

The chemical analysis and microstructure determinations of the samples were done at the Boğaziçi University Archaeometry and AR-GE laboratories. Chemical analysis was done by atomic absorption spectrometry. The microstructure of the samples is determined both by scanning electron microscope and by optical microscopy on the polished surfaces. Semiquantitive EDX is used to determine the overall composition as well as the composition of different phases. X-ray diffraction is used to determine the mineral composition of the ore and slag samples.

5.2.1. Ore:

Major iron ore deposits around Demirköy are hematite and magnetite sand. Archaeological excavations showed that magnetite sand was the main iron ore used in Demirköy. Several magnetite sand storage areas were exposed during the excavations. Magnetite sand is still visibly recognized along the river sediments. In Hamdibey, along the Bulanık Dere one liter of river sediment yielded 350 grams of magnetite sand. Magnetite sand can be enriched to almost pure magnetite by washing several times in a sluice. During washing low density sand is washed away by running water leaving the heavy magnetite behind. Different ore samples collected from various locations in Demirköy is enriched by washing in the sluice shown in Figure 5.9.

Figure 5.9. Sluice used for magnetite enrichment

Analyses of different sand were done by FAAS and iron content is converted to magnetite (Fe_3O_4). Magnetite rich sand collected from the riverbed (Figure 5.10) containing 32% Fe_3O_4 can be enriched to 49% Fe_3O_4 by single washing in a sluice table (Table 5.1). Even sand that does not show any visible evidence of magnetite (Figure 5.10) can be enriched to 32% by single washing. Fe_3O_4 content of the ore samples at the main foundry storage was 63% (Figure 5.11). Almost 100% magnetite sand can be obtained after several washings.

Table 5.1. Sluice enriched sands and ore from foundry deposit (Wt.%)

Sand Type	**Magnetite %**
"Black sand"	32
Sluice enriched "Black sand"	49
Sluice enriched "White sand"	32
Ore from foundry storage (Fig. 5.11)	63

Where,

"Black sand" = Magnetite rich sand from riverbed

"White sand" = Sand with visually no magnetite from riverbed

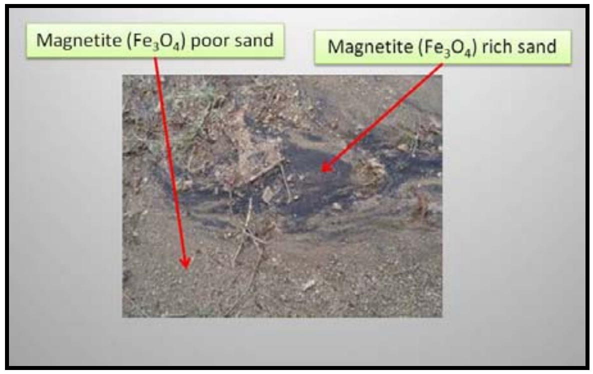


Figure 5.10. Magnetite sand at riverbed in Demirköy

Figure 5.11. Magnetite sand storage pit at the main foundry complex

5.2.2. Slags

A large collection of slag samples are acquired from the peripheral workshops, from the main foundry as well as from the archaeological excavations at the small workshop. The locations of the slag types from various workshops are shown in Figure 5.12. Microstructure and phases of 25 slag samples were investigated by scanning electron microscope (SEM). SEM-EDX was also used to determine the overall composition as well as the composition of different phases (Table 5.2). Among the 25 slag samples that were studied, 15 were classified as fayalithic, 8 glassy and 2 could be either smiting or finery slag (Butchwald and Wivel 1998, Bachmann 1982). Most of the fayalithic slag samples were recovered during the surveys from the peripheral smelting workshop around the main foundry. Five of them, however, were from the excavated bloomery furnace at the small workshop. The glassy slag samples were recovered around the main foundry and at sites where possible blast furnace could be constructed. Two ternary diagrams (figures 5.13 and 5.14) are constructed to show the relative percentages of the main components of slag samples, namely FeO, $SiO_{2,}$ CaO and FeO, SiO_2, MnO. On the ternary diagrams the square points represent the fayalithic slags where as the circles represent the compositions of the glassy slags. The slags represented by triangle points can be either from a smithing or a finery operation. The fayalithic slags having high wüstite content are clearly grouped all together in the fayalithic regions of slag compositions (Bachmann 1982). The glassy slags from the blast furnaces high in silicate are grouped in the region where cristobalite formation is favored. Almost all of the slags samples listed in Table 5.2 contain noticeable amounts of titanium and phosphorus that must be originating from the ore. Some slag samples also had significant amounts of vanadium and tungsten. Sulfur is seen in minor quantities only in six slag samples. Similarly the mineral compositions of 24 slag samples were determined by X-ray diffraction, (XRD) (Table 5.3).

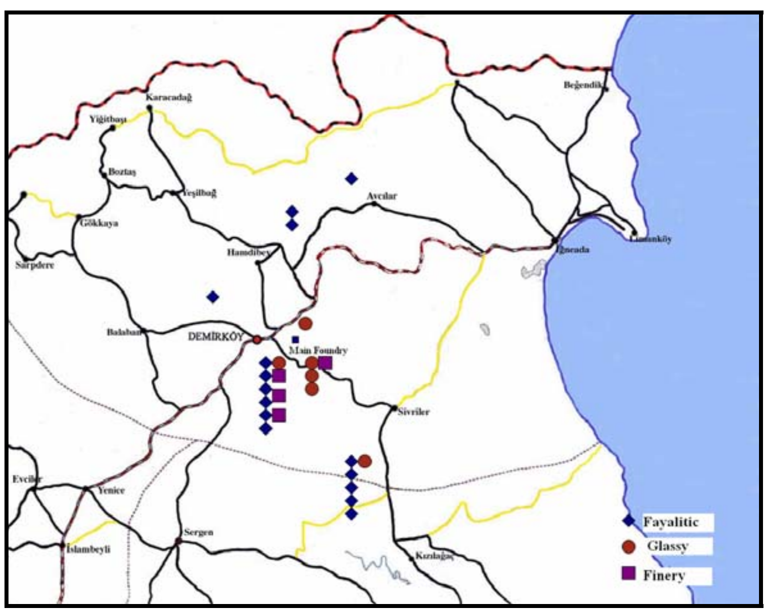


Figure 5.12. Seven iron-smelting sites around the main foundry

Table 5.2. Semi-quantitative analyses of Demirköy slags by SEM (EDAX) (Wt.%)

Sample	**Sample Place**	**Slag Type**	**FeO**	**SiO_2**	**CaO**	**MnO**	**Al_2O_3**	**MgO**	**P_2O_3**	**K_2O**	**Na_2O**	**V_2O_5**	**W_2O_3**	**TiO**	**Cr_2O_3**	**CO**	**SO_3**
04/700	Dolapdere	Fayalitic	60.22	19.59	4.56	0.40	4.91	1.08	1.18	1.22	0.43		3.52	1.50	0.20	0.96	0.23
04/703-A	Bıçkıdere	Fayalitic	42.79	23.21	8.69	1.62	7.20	2.04	1.89	3.45	0.64		0.31	4.31	0.29	3.03	0.39
04/703-B	Bıçkıdere	Fayalitic	50.60	20.31	5.91	0.85	4.99	3.09	0.78	1.31	0.63	0.72	0.71	4.37	0.10	4.70	0.75
04/706	Hamdibey	Fayalitic	54.43	28.09	2.77	0.87	7.38	2.20	0.72	2.16	0.58			0.82			
04/712	Hamdibey	Fayalitic	59.98	19.10	4.80	1.35	5.51	2.72	1.30	1.12	1.16	1.08		1.87			
04/713	Hamdibey	Fayalitic	63.79	18.30	4.70	0.90	5.21	2.44	1.08	1.03	0.56			2.03			
04/715	Bıçkıdere	Fayalitic	49.44	14.88	4.70	1.02	4.07	2.35	1.77	1.36	1.09	1.20		2.77	0.63	12.83	1.10
04/717	Bıçkıdere	Fayalitic	58.91	22.83	3.76	0.80	6.25	1.56	0.92	1.34			1.05	1.64	0.30		
04/718	Bıçkıdere	Fayalitic	52.22	23.60	5.20	1.17	6.99	1.75	1.12	1.78	1.01	1.10					
04/719	Bıçkıdere	Fayalitic	57.46	22.97	3.34	0.84	7.46	1.86	0.70			1.05		4.10			0.28
05/709-2	Small Workshop	Fayalitic	38.11	27.47	12.47	1.44	7.03	3.68	2.72	1.51	1.40			3.02			
05/710-A	Small Workshop	Fayalitic	42.71	23.46	5.31	1.37	9.12	6.34	3.29	1.53	3.69			1.59			
05/710-B	Small Workshop	Fayalitic	60.49	19.76	4.19	1.20	5.45	3.01	1.13	0.92	1.33			2.51			
05/711	Bıçkıdere	Fayalitic	62.31	15.99	5.70	1.06	5.54	2.81	1.36	1.30	1.69			2.24			

Table 5.2. (continued)

Sample	Sample Place	Slag Type	FeO	SiO_2	CaO	MnO	Al_2O_3	MgO	P_2O_3	K_2O	Na_2O	V_2O_5	W_2O_3	TiO	Cr_2O_3	CO	SO_3
05/717	Small Workshop	Fayalitic	51.38	24.20	7.40	0.87	6.26	2.24	2.10	1.60	1.13	0.52		1.64			
04/704	Bıçkıdere	Glassy	1.58	42.80	20.60	2.20	10.00	7.92	1.52	6.74	2.42			4.17			
04/716	Small Workshop	Glassy	14.09	25.66	9.97	1.27	6.71	5.17	0.79	1.76	0.88	0.51		11.33	0.53	20.15	0.53
05/701	Main Foundy	Glassy	14.55	46.10	11.70	0.36	13.10	4.62	1.49	2.83	1.86			3.56			
05/702	Main Foundy	Glassy	0.84	55.60	16.90	0.98	12.10	5.32		3.19	1.41			3.59			
05/703	Main Foundy	Glassy	7.96	50.00	10.10	1.03	13.70	4.16	1.16	3.84	2.72			4.33			
05//705	Üç Dereler	Glassy	0.82	47.60	17.40	1.34	11.30	7.07	0.84	3.72	1.73	0.30		7.35			
05//716	Small Workshop	Glassy	2.94	45.98	15.80	1.17	11.40	9.41		2.69	0.79			9.78			
05//720	Main Foundy	Glassy	0.72	52.90	15.70	1.25	12.30	6.09	0.89	3.77	2.71			4.20			
05//726	Small Workshop	Glassy	1.90	68.10			19.90			5.71	4.36						
05//708	Small Workshop	Finery	81.67	7.20	2.63	1.37	1.83	3.35	0.61					0.22			
05/719	Small Workshop	Finery	68.17	14.30	2.13	1.22	5.76	1.10	1.17	3.20	0.60			2.39			

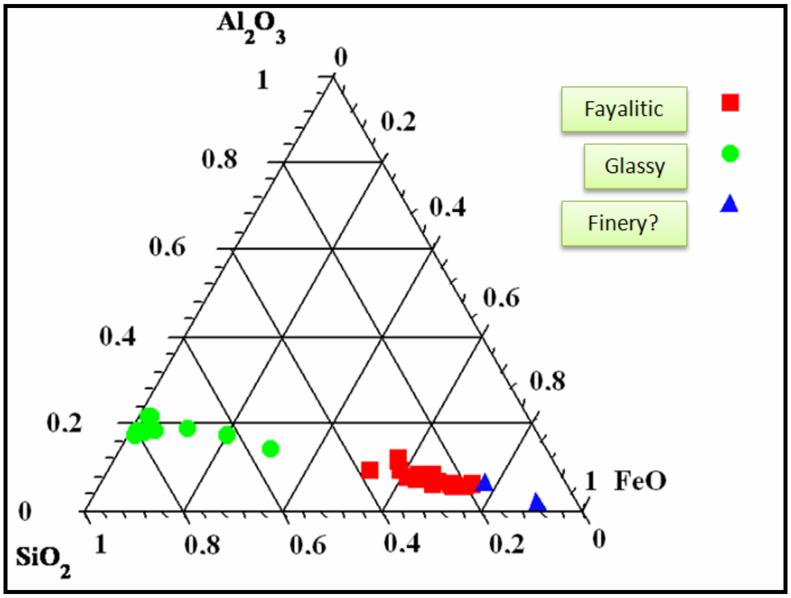


Figure 5.13. SEM (EDAX) data of slags plotted on ternary diagram (mass fraction)

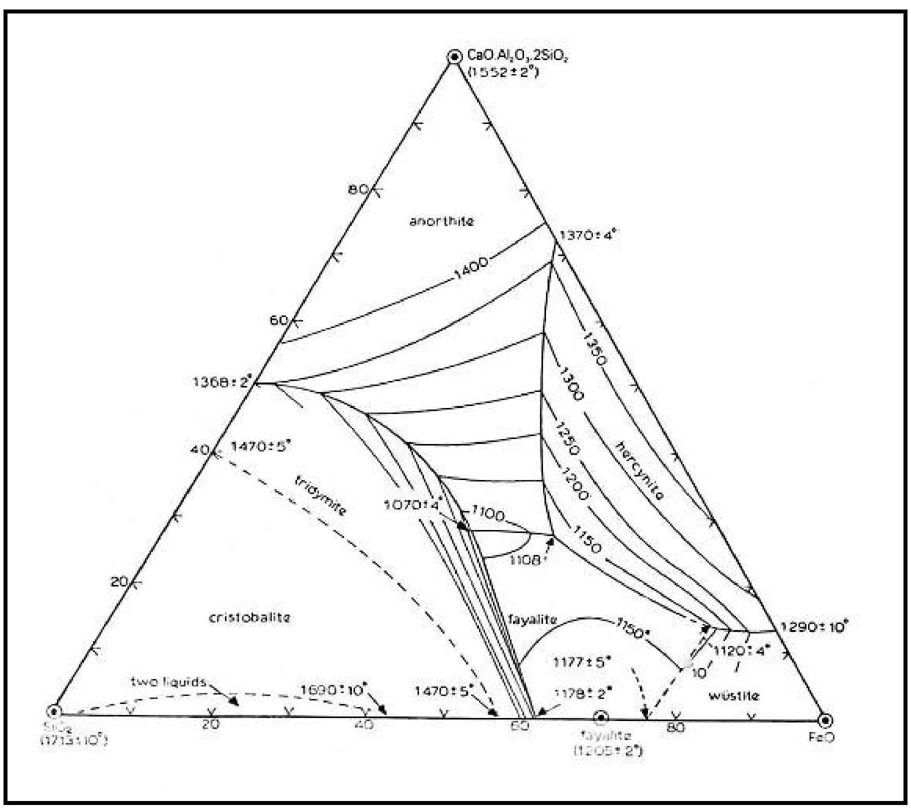


Figure 5.14. Ternary diagram of FeO-Anothite-SiO_2 (mass percent)

Table 5.3. XRD data of Demirköy slags

Sample #	Sample Place	Slag Type	Main Minerals
05/703	Main Foundry	Finery	Fassite, Maghemite, Rutile
05/708	Small Workshop	Finery	Diopsite, Magnesioferrite, Wollastonite
05/725	Small Workshop	Finery	Magnesium Chromium iron oxide, Diopside, hematite
05/719	Small Workshop	Finery	Magnesioferrite, Hematite, Rutile
04/704	Bıçkıdere	Glassy	Leucite, Perovskite, Augite, Akermanite
05/701	Main Foundry	Glassy	Dipside, Maghemit, Albite
05/702	Main Foundry	Glassy	Quartz, Faujasite, Marcasite
05/720	Main Foundry	Glassy	Quartz, Ferroglancophane, Diposite
05/726	Small Workshop	Glassy	Silicate, Cristobalite, Ahromferite, Anorthide
04/700	Dolapdere	Fayalitic	Wustite, Fayalite, Chromite,
04/703-A	Bıçkıdere	Fayalitic	Titanomagnetite, Leucite, Monticellite, Quartz
04/703-B	Bıçkıdere	Fayalitic	Wustite, Diopsite, Fayalite
04/715	Bıçkıdere	Fayalitic	Fayalite, Coper iron oxide, Argentopyrite, Wustite
04/717	Bıçkıdere	Fayalitic	Magnesium iron Oxide, Wuestite, Fayaliye, corundum
04/718	Bıçkıdere	Fayalitic	Wustite, Magnesuiferrite, Fayalite, Sodiumcalcium phosphate
04/719	Bıçkıdere	Fayalitic	Magnetite, Fayalite, Wustite, Albite
04/706	Hamdibey	Fayalitic	Fayalite, Quartz, Sanidine
04/712	Hamdibey	Fayalitic	Magnetite, Quartz, Fayalite, Albite, Leucite
04/707	Small Workshop	Fayalitic	Wustite, Diopsite, Leicite
05/709	Small Workshop	Fayalitic	Magnetite, Tephroite, Fayalite, Hongquiite
05/710-A	Small Workshop	Fayalitic	Fayalite, Magnesioferrite, Hongquiite, Quartz
05/710-B	Small Workshop	Fayalitic	Magnetite, Fayalite, Goethite, Quartz
05/713	Small Workshop	Fayalitic	Iron oxide, Magnetite, Fayalite, Monticellite
05/717	Small Workshop	Fayalitic	Wustite, Maghemite, Fayalite

Glassy Slags: The 8 glassy slag samples that are examined are most likely byproduct of blast furnaces where cast iron is produced. In order to reach the high temperatures that are required in blast furnaces, it is necessary to use bellows that are operated by waterpower. Four glassy samples analyzed are from the main foundry where there are elaborate architectural features for water wheel and elaborate canal systems for water. The furnaces at this workshop are also high furnace type where cast iron was produced. The other four glassy slag samples are all from workshops where topological setup is suitable for the construction of water wheels with associated water canals. It can be concluded that for the production of cast iron in tall furnaces, bellows operating with waterpower is necessary to reach the required high temperatures.

The results of the overall compositions of the glassy slags are given in Table 5.2. As expected, the slags that were classified as glassy have low iron oxide (FeO) values (0.82 – 14.6%), however quite high in silicate (SiO_2) (25.7 – 68.1%), in aluminum oxide (Al_2O_3) (6.71-19.9% and lime (CaO) (9.97 – 20.6%) values. Since the furnace temperature was high, there was no need for the high concentration of iron oxides in order to produce liquid slag. Almost all of the glassy slags samples contained small round cast iron prills. Figure 5.15 displays the back scattered electron image of a glassy slag (05/720) with an iron prill of about 1 mm in diameter embedded in the glassy matrix of a slag sample collected from the main Foundry. The prill is round since it was in the molten state. The leaf-like black figures in the prill are graphite, i.e., carbon. Carbon that is soluble in iron at high temperatures precipitates when the temperature is lowered slowly. The prill is an excellent example of a gray cast iron.

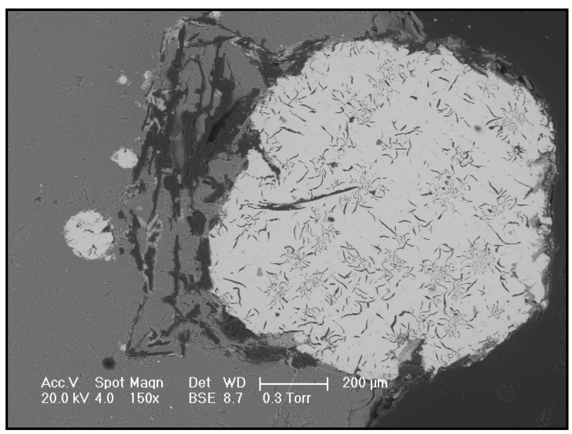


Figure 5.15. Microstructure of glassy slag

Fayalithic Slags: Fayalithic slag samples were collected from all iron working workshops except the main foundry and the slag deposit associated with. These types of slags are the byproducts of bloomery furnaces and can have melting point as low as about 1000^{o}C. They are associated with workshops in the periphery of the main foundry that have relatively small furnaces that are partly buried in the ground and are called ‘Vigne” in the Ottoman archives. The excavated bloomery furnace near the main foundry also yielded only fayalithic slag. In these workshops, neither water canals nor topographic features for a water wheel could be seen except the one in the excavated furnace. The main components of fayalithic slags are fayalite (FeO_2SiO_4), wüstite (FeO) and a glassy matrix of anorthite ($CaO.Al_2O_3.2SiO_2$). From time to time, small angular pieces of iron prills can be seen. The average FeO content of the 15 fayalithic slag samples is about 53.7%. As with all direct smelting of iron in bloomery furnaces, the efficiency Demirköy bloomery furnaces are very low. Average silicate content was 21.4% Lime 5.57 and aluminum oxide was 6.22. In addition to the above-mentioned components, these slags may also contain spinels minerals that are high in titanium and aluminum, leucite, montecellite and mellelite. Figure 5.16 shows the back-scattered electron image of a slag sample (04/713) collected from a workshop in Hamdi Bey. In this image, the light gray dendritic regions that appear like leaves on a branch are wüstite. The darker grey regions that appear as bands are the fayalite crystals. Both wüstite and fayalite are imbedded in the dark glassy anorthite phase. The matrix also contains angular iron prills that shows no melting characteristics.

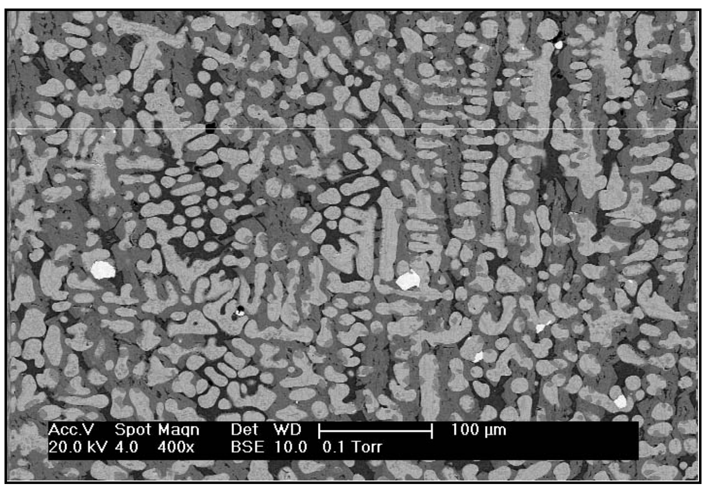


Figure 5.16. Microstructure of fayalitic slag

The four fayalithic slag samples (05/709-2, 05/710-A, 05/7010-B and 05/717) listed in Table 5.2 were collected around the tap hole and the slag canal of the excavated bloomery furnace, located at the east side of the small workshop. In figure 5.17, the back-scattered electron image of slag sample 05/709-2 found in the slag canal is shown. As in the case of other fayalithic slags, the light gray region in the form of leaves on a branch are the wüstite and the darker bands are the fayalite crystals. The crystalline phases are imbedded in a glassy phase. There are also angular iron prills, which are very rich (16.0%) in tungsten. The results are a clear indication that bloomery iron production was the last smelting operation at this furnace.

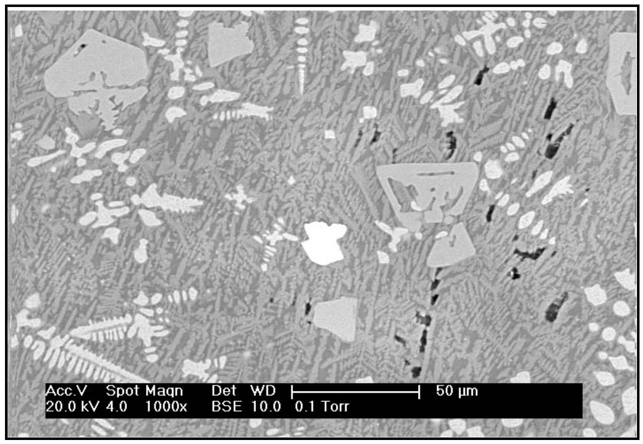


Figure 5.17. SEM of 05/709-2

Refining slags: Two slag samples classified as refining slags were obtained from the slag heaps located at the south of the main Foundry (05/708, 05/719). These types of slags may form during operations where the cast iron is converted into wrought iron. There are several different methods by which the carbon in the cast iron can be oxidized during the conversion to wrought iron; thus, slags from the refining processes can show large variations. During the oxidation of carbon from the molten cast iron in an open hearth, considerable amounts of iron metal are also oxidized. As the carbon is removed the remaining iron turns into a wrought iron bloom that must be forged to produce consolidated wrought iron. The refining slags may contain more iron oxide than the fayalithic slags from the bloomery furnaces. Refining slags generally have a spongy structure without any flow marks since they are not melted. The main components of refining slags are wüstite with some fayalite and a glassy matrix. Since refining slags form from cast iron, they should not contain impurities such as Al_2O_3, MnO, MgO, Na_2O, K_2O, P_2O_5 and TiO_2 that originate from the ore or from fluxing agents. In table 5.2, the slags samples (05/703) that was classified as refining slags still contains considerable amounts of impurities that are probably originate from the ores and the fluxing agents and cannot originate during the decarburization of cast iron. These slags were formed either during the forging of bloom or during some other operation. Only in slag sample (05/708) has components expected to originate from the refining operation. Work on refining slags is still in progress.

5.2.3. Metal samples

During the 2005 and 2006 archaeological excavations at the small workshop various iron objects are discovered. It was very fortunate that it was possible the recover both a cast iron ingot (merchant bar) as well as blooms from the bloomery furnace. Since the blooms and ingots represent the unrefined metal direct from the furnace they can yield technical information about the furnace conditions and help us understand the smelting processes. In this respect microstructure of nine metal samples are investigated using both SEM and optical microscope. Among these metals that were studied three were blooms, three were wrought iron objects, two were cast iron ingots and one was a cast iron object.

5.2.3.1. Analysis of blooms and wrought iron objects:

Samples are taken for micro structural analysis from three different bloom iron ingots that were discovered in the small workshop. A small section was cut from one of the oval blooms (06/105) (Figure 5.18) that had a mass of 62 Kg. The bloom iron contained 0.23% carbon and thus can be considered as mild steel. The back-scattered image of the polished section of the bloom is shown in figure 5.19. The light grey colored region is the wrought iron with considerable cavities and slag inclusions. Closer examination of the slag inclusion showed all the characteristics of fayalithic slag. In figure 5.19, wüstite and fayalite crystals are imbedded a glassy anorthite matrix. Nital etched optical microscope image (Figure 5.20) shows polygonal ferrite crystals with considerable slag inclusions.

Figure 5.18. Cut piece from the bloom 06/105

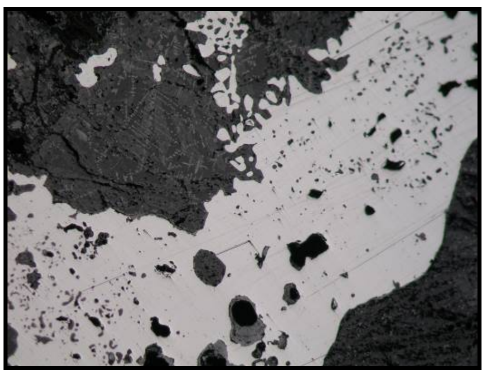


Figure 5.19. Microstructure of the polished bloom 06/105

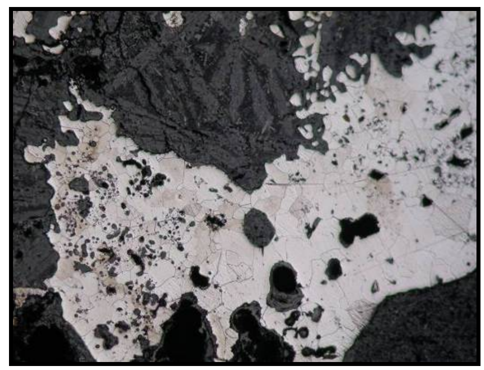


Figure 5.20. Microstructure of the etched bloom 06/105

A section of bloom sample 06/105 is forged at a local black smith shop. Forging eliminates most of the slag inclusions and consolidates the porous bloom iron is to be consolidated into a solid wrought iron. The microstructure of the consolidated wrought iron from the Demirköy bloom is shown in figure 5.21. Polished and nital etched cross section of consolidated iron still contains considerable fibrous slag inclusions. Center part of the fragment is mostly polygonal ferrite. Towards the edges, however, due to carburization pearlite structure can be seen (Figures 5.21 and 5.22).

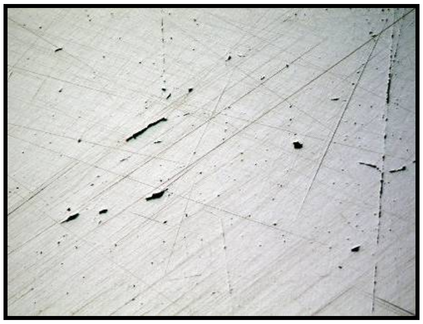


Figure 5.21. Microstructure of consolidated iron from bloom 06/105

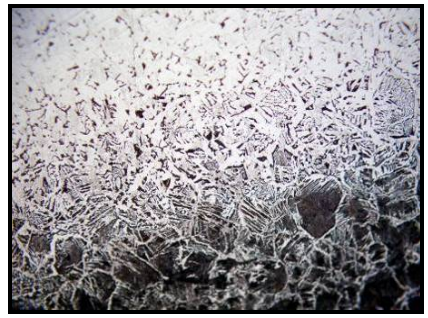


Figure 5.22. Microstructure of etched consolidated iron

The microstructure of a section from a second bloom (06/104) from the same workshop is also investigated. Polished surface was again showed extensive porosity with slag inclusions of fayalitic in nature. The carbon content of this bloom was determined to be about 0.3% somewhat like low carbon steel. Nital etching revealed a hypouetectoid steel structure with irregular ferrite crystals imbedded into a massive pearlite matrix. (Figures 5.23 and 5.24)

Figure 5.23. Microstructure of polished sample 06/104

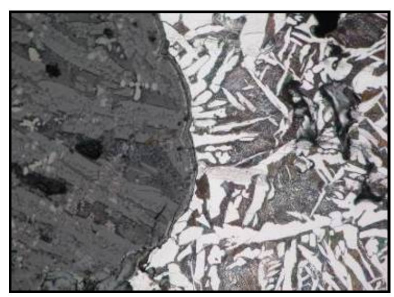


Figure 5.24. Microstructure of etched sample 06/104

The microstructure of the third bloom (06/115) is shown in figures 5.25 and 5.26. Just like the previous two blooms, porous structure with extensive corrosion together with considerable slag fragments was also clearly evident. Etched surface yielded irregularly shaped ferrite crystals in course pearlite matrix.

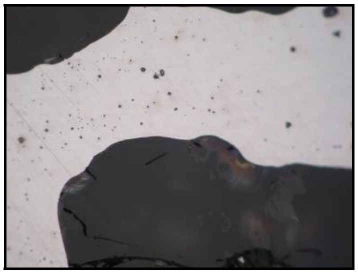


Figure 5.25. Microstructure of polished sample 06/115

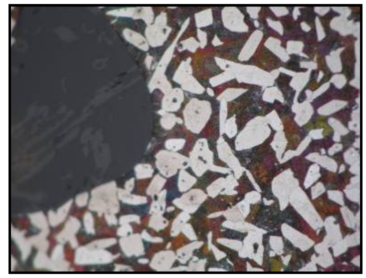


Figure 5.26. Microstructure of etched sample 06/115

Nails were the most abundant metal artifacts that were recovered from the excavation sites. They came in many different size and shape. The microstructure of an iron nail (06/110) from the excavation site was studied. The polished cross-section of the nail also revealed fibrous slag inclusions whose composition resembles fayalitic slag (Figure 5.27). When etched with nital polygonal crystal structure with considerable pearlite structure due an extensive carburization was observed similar to those observed in the consolidated bloom (Figure 5.28). Thus it can be concluded that wrought iron consolidated from the bloom is used in the manufacture of domestic objects.

Figure 5.27. Microstructure of polished sample 06/110

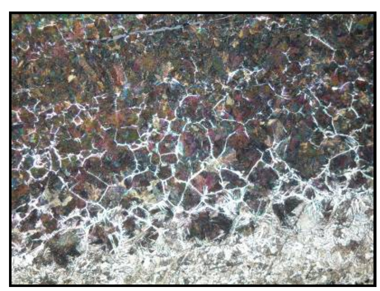


Figure 5.28. Microstructure of etched sample 06/110

Micro structural analysis of a highly corroded U shaped wrought iron fragment (06/119A) is shown in figures 5.28 and 5.29. The carbon content of the object was 0.063%.

The Elongated fayalitic slag inclusions with considerable wüstite crystals in dendrite form are due to extensive hammering. Yet the etched optical microscope image of the sample shows polygonal equaaxial ferrite structure indicating that the sample was annealed after final shape is reached. There is a slight pearlite formation.

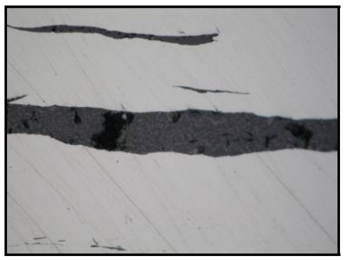


Figure 5.29. Microstructure of polished sample 06/119A

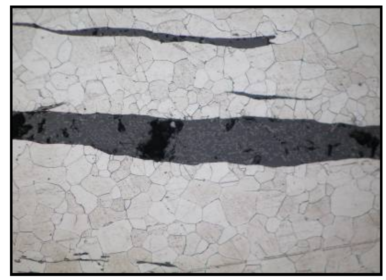


Figure 5.30. Microstructure of etched sample 06/119A

The microstructure of a similar highly corroded flat wrought iron fragment (06/119B) was also investigated. The slags were extensively elongated like the previous sample due to extensive hammering (Figure 5.31). The optical microscope image of this sample (Figure 5.32) yielded a structure of tempered martensite. There are extensive fine pearlite formations with ferrite at the grain boundaries. White needles are the cementite. The structure indicates considerable carburization must have during the extended periods of heating in charcoal fide when the object was being shaped.

Figure 5.31. Microstructure of polished sample 06/119B

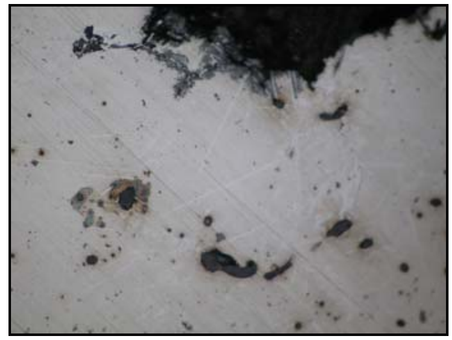


Figure 5.32. Microstructure of etched sample 06/119B

5.2.3.2. Analysis of cast iron ingots and object made out of cast iron:

Excavations at Demirköy also yielded several cast iron ingots as well as objects made out of cast iron. One of the ingots (06/103) discovered near the destroyed high furnace in the small workshop was a rectangular block of metal with two holes at each end and weighed about 38 kg (Figure 5.33). It is formed by two different stages of casting since two distinct layers are visible along the long side. The back-scattered electron image of the sample is a classical example of cast grey iron with large graphite flakes (Figure 5.34). When etched with nital, the pearlite becomes visible and carbon in the form of flakes appear as dark lines. There are also considerable cementite laths (Figure 5.35).

Figure 5.33. Cast iron ingot

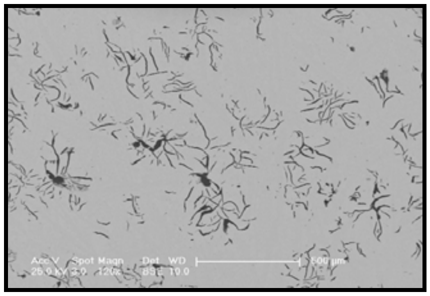


Figure 5.34. Microstructure of the cast iron ingot

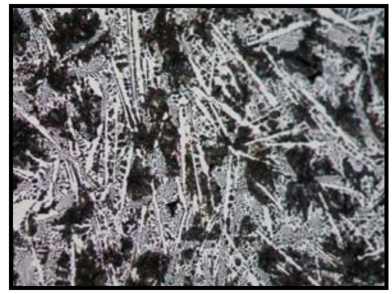


Figure 5.35. Microstructure of the etched cast iron ingot

A second cast iron ingot (06/102) weighing about 40 kg was discovered along the west wall of the water canal. The ingot had a rather flat top with somewhat rounded sides and bottom. The flat top surface could be efficiently used as an anvil. The ingot contains 2.27% carbon. The microstructure of the highly corroded section of this ingot is shown in figure 5.36 where graphite flakes as well as corrosion products are embedded into the metal matrix. Nital etched optical microscope image of the sample (Figure 5.37) appears to have a proeutectoid cementite network surrounding the pearlite colonies.

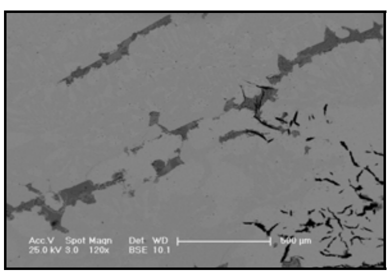


Figure 5.36. Microstructure of polished section of the cast iron ingot 06/102

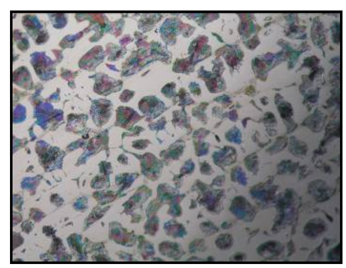


Figure 5.37. Microstructure of etched section of the cast iron ingot 06/102

The only cast iron object (06/117) that is investigated was a 2.5 cm thick rectangular piece of metal with two angular extensions at the short ends (Figure 5.38). The metal was precision cast with highly smooth surface. It is found on the platform next to one of the buried beam support of the forging hammer system. The function of the object is not yet known. The back-scattered electron image of a polished section of this object and its etched optical microscope image are shown in Figures 5.39 and 5.40. Extensive graphite flakes confirms that the object is made out of grey cast iron. Nital etched image shows considerable cementite laths yielding a similar structure to that of the cast iron ingot (06/103).

Figure 5.38. Photograph of sample 06/117

Figure 5.39. Microstructure of polished sample 06/117

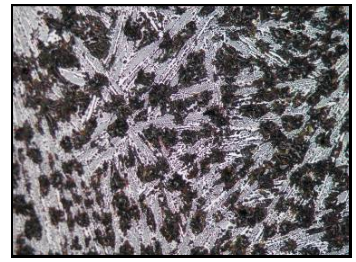


Figure 5.40. Microstructure of etched sample 06/117

5.2.4. Experimental Archaeometallurgy: Nail Production from Demirköy Bloom

A small section is cut from one of the blooms recovered at area 4B. The bloom fragment (Figure 5.41) is forged at a blacksmith shop in Ömerli to obtain consolidated wrought iron (Figures 5.45 and 5.46). A nail, similar to the one recovered at Demirköy, was made by the Ömerli blacksmith from the consolidated iron (Figures 5.42, 5.43 and 5.44). The polished and nital etched optical images of the nail produced at Ömerli and a nail sample (06/110) recovered at Demirköy are shown in Figures 5.53, 5.54, 5.55 and 5.56. Both nails have very similar microstructure with extensive pearlite content and they can both be considered as mild steel.

Nail production steps can be followed from Figure 5.45 through 5.51. And summary of the production of a nail can be seen in figure 5.52. Hot consolidated iron can be seen in figure 5.47. This iron was cut into smaller pieces by hammering on two steel segments acting as scissor (Figure 5.48). Cut piece was heated and put into nail iron which is a specific tool used for making iron (Figure 5.49). By hammering on the iron piece the body and the head of the nail were formed (Figure 5.50).

Polished microstructure of both Demirköy and Ömerli nails show elongated slag inclusions which indicate forging. Pearlite grains can easily be seen as dark, colored grains on etched images where white grains are ferrite.

Figure 5.41. Fragment of bloom (06/105)

Figure 5.42. A nail from Demirköy (06/110)

Figure 5.43. Consolidated iron

Figure 5.44. Reproduced nails at Ömerli

Figure 5.45. Heating of the bloom

Figure 5.46. Forging the bloom

Figure 5.47. Red-hot plate

Figure 5.48. Cutting a piece

Figure 5.49. Fitting the iron piece into the “nail iron”

Figure 5.50. Formation of nail head

Figure 5.51. Final product

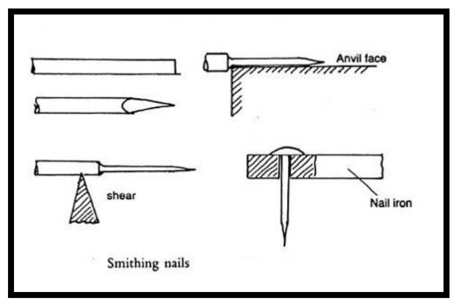


Figure 5.52. Summary of the procedure

Figure 5.53. Microstructure of the nail from Demirköy (06/110)

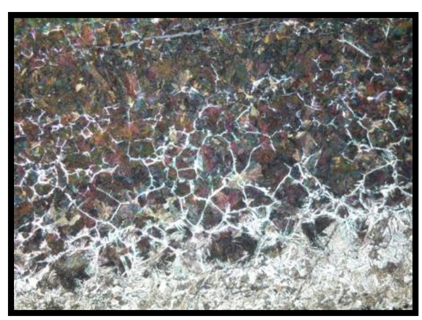


Figure 5.54. Microstructure of the etched nail from Demirköy (06/110)

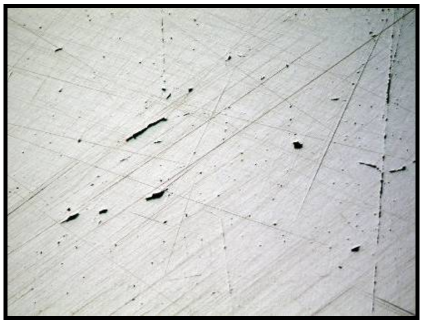


Figure 5.55. Microstructure of nails at Ömerli from bloom iron (06/105)

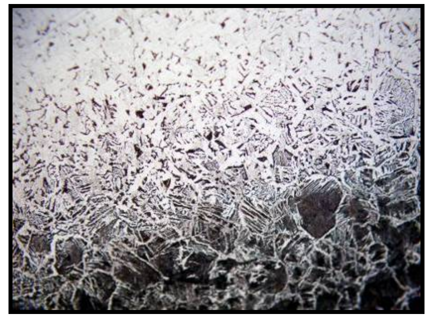


Figure 5.56. Microstructure of etched reproduced nails at Ömerli

6. CONCLUSION

Archaeometallurgical excavations, archival documents and regional surveys shoved that Demirköy was an important iron production site during the last 300 years of the Ottoman period. There are indications that both iron and copper deposits were also exploited during the Roman and Byzantine periods. Copper mining and production may extend to prehistoric periods.

Geological and mineralogical data showed that the local magnetite and hematite deposits were the main ores utilized. Magnetite sand is still visible in the river sediments. Several magnetite storage pits were found at the main foundry complex. Experiment with magnetite showed that it can be enriched easily by simple washing in a sluice box.

Most clear evidence for smelting activity in Demirköy were the remains of massive slag deposits as well as many partially destroyed smelting furnaces. So far none of the smelting furnaces have been scientifically examined. However, the relatively small "vigne" type furnaces in the peripheral workshops were producing bloom iron. Technologically more advanced blast furnaces (stückofen) were found at the main foundry.

Numerous slag samples were collected from the archeological excavations and regional surveys. The slags collected from the peripheral workshops were all fayalitic in nature confirming the production of wrought iron in these furnaces. It is clear that wrought iron production was very important in Demirköy, for the manufacture of items such as nails, horse shoes, and other domestic agricultural tools.

The main purpose for the establishment of Demirköy iron works however, was to produce cannon balls (yuvalak) for the Ottoman army and navy. Such objects which require high precision to cast were produced in the main foundry. Both the furnaces and the massive slag deposits around the foundry were glassy in nature indicating the production of cast iron.

Determination of chemical composition as well as the main structural analysis of several iron objects found at Demirköy confirmed the production of both cast and wrought iron. Cast iron ingot yielded a grey cast iron microstructure. Microstructure of several wrought iron objects showed oriented slag inclusion due to hammering of bloom iron. These wrought iron objects yielded pearlitic microstructure indicating that heterogeneous mild steel was formed in the bloomery furnaces.

A section from a 62 kg. bloom iron ingot was consolidated at a local blacksmith shop and nails similar to that found at Demirköy were produced. Microstructure of the reproduced nails were almost same as the original Demirköy nails.

So far there was no definite evidence in Demirköy for casting cannons or for the production of wrought iron by indirect process. Further archeological excavations have to be carried out to understand the exact nature of the processes applied in the iron workshops.

Further work is needed to determine the actual smelting conditions applied at Demirköy. These will require in depth investigation of both the blast furnace (stückofen) at the main foundry as well as the "vigne" type furnace at the peripheral workshops.

APPENDIX A: MICROSTRUCTURAL IMAGES OF METAL SAMPLES

Table A.1. Classified metals

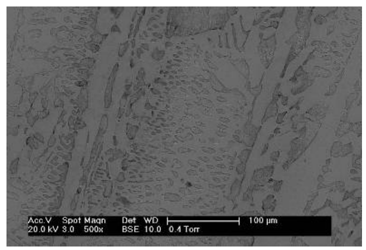
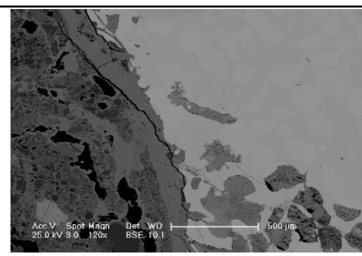
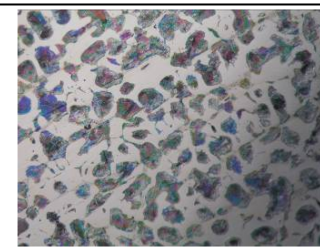
Sample #	Actual Photograph	SEM microstructure	Polished microstructure	Etched microstructure	C% (Wt.%)	Type of Iron
04/101			No image	No image	No analysis	Mild steel
06/102					2.27	Steel

Table A.1. (continued)

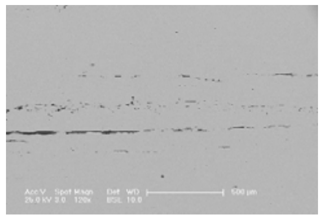
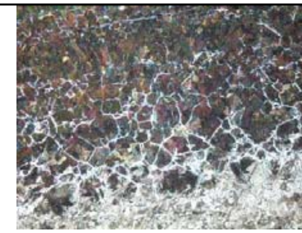
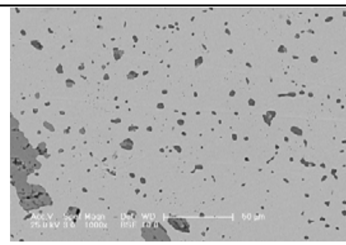
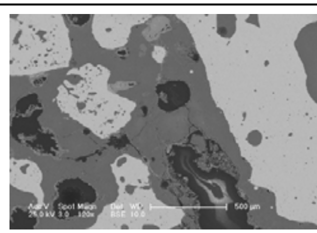
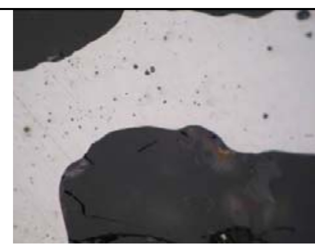
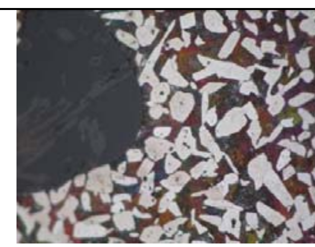
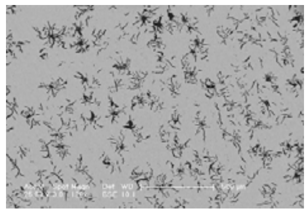
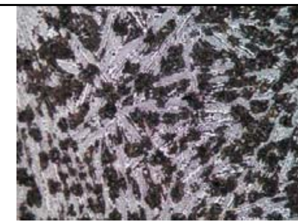
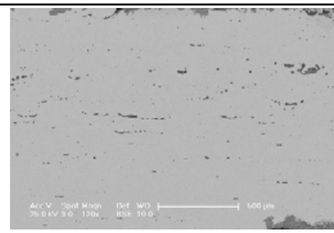
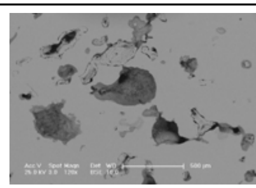
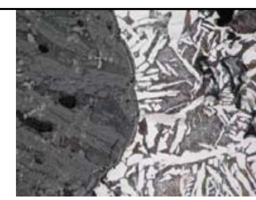
Sample #	**Actual Photograph**	**SEM microstructure**	**Polished microstructure**	**Etched microstructure**	**C% (Wt.%)**	**Type of Iron**
06/110					0.400	Mild steel
06/113					0.200	Wrought iron
06/115					No analysis	Mild steel

Table A.1. (continued)

Sample #	Actual Photograph	SEM microstructure	Polished microstructure	Etched microstructure	C% (Wt.%)	Type of Iron
06/117					No analysis	Cast iron
06/119					0.0623	Wrought iron
06/104					0.304	Mild steel

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