Chapter – II

UNDERSTANDING IRON TECHNOLOGY

2.1 Importance of Iron to Human Evolution

Minerals have been the primary requisite of the human subject. From times immemorial, human being has used minerals and mineral substances in the form of mica flakes, hematite nodules and so on. The earliest activity of human is reflected in his/her efforts to make tools using hard rocks for hunting and foraging purposes. Evidences of exploitation of rocks for tool making have been identified at a number of prehistoric sites where quartzite, quartz, flint and chert were knapped. However with the increase in cranial capacity and cognitive abilities also took a leap leading to the advancement of technologies. Although stone tools provided the necessary pointed and cutting edges for hunting and foraging activities, they required retouching at regular intervals for sharpening the edges and procurement of hard rock depending on its availability.

Metallurgical knowledge in the Indian sub-continent dates back to around 6000 BCE with the finding of a few copper artefacts from the Neolithic level of Mehargarh. We do have evidences of complex metallurgical practices like alloying copper with minor metals such as lead, tin and arsenic from the Chalcolithic level of Daimabad. The Copper hoard at Daimabad and the copper hoards from the OCP levels indicate the transformation of usage of metal from utilitarian purposes to decorative purposes (Sali, 1986).

The next stage of development was the introduction of iron as a technology and not just a mere by-product of Copper technology. The introduction of iron technology in the Indian sub-continent has been ascribed various reasons. Kosambi (1963) ascribes the beginning of the second urbanization in the Ganga-Yamuna Doab region as the main reason behind the flourishing of the iron tool industry. Similar ideas have been propounded by Sharma (2007) who ascribes the clearance of forested tracts in the Ganga alluvium plain to the introduction of iron technology. However iron technology in its nascent form has been traced to the Deccan region and the finding of an iron smelting furnace from the Megalithic level at Naikund has provided some insight to the probable indigenous origin of iron technology in India.

2.2 Iron Ore Formations

Iron ore formations are found in certain regions of the Indian sub-continent with specific geological formation characteristics. However, the larger concentration of economically exploitable deposits is found in sedimentary iron formations of Pre-cambrian age. In the peninsular region, the crystalline and schistose rocks of the Dharwar and Cuddapah systems have ferruginous deposits associated with them (Krishnan, 1982).In the eastern zone, the hematite ore deposits in the Singhbhum region, along with Mayurbhanj region, are associated with post-Cuddapah formation. The Bengal region have deposits of bedded or precipitated iron ore in the iron stone shales in the Damuda series which fall within the Lower Gondwana formation and also in the form of laterite formation. In the Himalayan region, iron ore deposits have been found in association with the Purana formation and Eocene coal deposits (DID, 2006).

The iron ore deposits of the Maharashtra region have been known from 3 areas namely, Bhandara and Chandrapur district in Vidarbha and Ratnagiri in the Konkan region. Here the lenticular bodies of hematite ore occur in association with monodinally folded banded hematite quartzites and phylittes within the pre-Cambrian formation (DID, 2006).

The Banded Iron Formations (BIF) in India are commonly known as Banded Haematite Quartzite (BHQ) and Banded Magnetite Quartzite (BMQ) falling within the Archaean Schist belt. The other type is the Weakly Banded Magnetite-Quartzite formation confined to granulite terrains, specifically the formation in Southern India (Tamil Nadu, parts of Andhra Pradesh, Karnataka and Kerala). The formations in the Archaean Schist belt are the richest iron ore deposits (DID, 2006). As the economic feasibility of the exploitation of the deposits are determined by the final amount of smelted iron it is important to note not all iron ore deposits are mined for industrial purpose as the iron content in the deposits is far less than the amount of charge and flux used for the smelting purpose. Table: 2.1 gives a description of the economical iron ore deposits and it is noted that Haematite and Magnetite are the most commonly utilized ore deposits.

Table 2.1: Description and Chemical Composition of Economical Iron Ore Deposits

State	Deposits	Geological Formation	Chemical Composition (Haematite) %	Chemical Composition (Magnetite) %
Jharkhand & Bihar	Haematite Magnetite		Fe: 62.37 Al_2O_3: 2.10 SiO_2: 1.47 P: 0.06	Fe_2O_3: 42.88 FeO: 24.22 TiO_2: 16.84 SiO_2: 9.76 MnO: 0.53 CoO: Trace MgO: 0.94 P_2O_5: 0.34 V_2O_5: 2.20
Orissa	Haematite Magnetite	Pre-Cambrian	Fe: 64.51	-
Chattisgarh	Haematite	Pre-Cambrian	Fe: 65.80 SiO_2: 1.52 P: 0.047	-
Madhya Pradesh	Haematite	Pre-Cambrian	Fe: 46.43 Mn: 12.26 SiO_2: 12.09 Al_2O_3: 15.00 P_2O_5: 1.69	-
Karnataka	Haematite Magnetite	Dharwarian Age	-	Fe: 50.25- 53.62 TiO_2: 6.86-7.07 V: 0.33- 0.42
Goa	Haematite With minor occurrences of magnetite, limonite and goethite	Pre-Cambrian	Fe: 56-64 SiO_2: 1 – 5 Al_2O_3: 2.8- 8.4 Mn: 0.06- 0.76 TiO_2: 0.20- 0.23 S: 0.020- 0.028	-
Maharashtra	Haematite Titaneferous Magnetite (Bhandara District)	Associated with the Archaean Schist	Fe: 63.75- 66.59 Al_2O_3: 0.84-2.83 SiO_2: 1.82- 6.10 P: 0.017- 0.076 S: 0.010- 0.032	Fe: 54.66 TiO_2: 18.46 V_2O_5: 1.16
Andhra Pradesh	Haematite Magnetite and Low-grade iron	Dharwar and Purana Formation and low grade iron associated with	Fe_2O_3 : 69.20 – 92.27 SiO_2:3.68- 28.84 S: 0.081- 1.79	Fe_2O_3:47.10-53.13 SiO_2:46.08-55.64

		Laterite formation	P: Trace	Al_2O_3:0.20– 2.47 MnO: 0.09- 0.21
Tamil Nadu	Magnetite Quartzite Bands	Pre-Cambrian Dharwarian Sequence		Fe: 35-37
Kerala	Magnetite Quartzite Bands	Pre-Cambrian meta-sedimentary origin		Fe: 35.58
Rajasthan	Haematite	Alwar series of rocks of Delhi Super group	Fe_2O_3: 94.55 Al_2O_3: 2.38 SiO_2: 2.15 P: 0.018	Fe: 28.23- 60.56 SiO_2: 0.6 – 3.2 S: 0.02 – 0.05 P_2O_5 : 0.2 1.61
	Haematite & Magnetite	Ajabgarh Series		

The discussion in Section 2.2 is an integral part of this thesis as the final product which is the smelted iron is derived from the mother rock which is the ore. The history of the metal technology is primarily the study of the first and foremost attempts carried by ancient smelters, often in isolation, which included purification of the metal in the mineral form followed by the conversion of the smelted metal to diverse products for multiple uses. As metals like iron are rarely found in a native state, they are found in ores in the combined state. Ore is a combination of minerals and gangue material. The mined ores vary in mineral constituents and it is necessary to optimize the smelting operation in order to completely remove, or reduce to the minimal level, the undesired constituents in the mineral. The process of extracting the metal from the mineral is called smelting.

2.3 Why is Iron an important metal?

2.3.1 Properties of Iron

Pure iron is silver white in colour with a density of 7.86 gm per cc. At 1520°c it reaches red-hot condition and fuses, and is devoid of its ferromagnetic property which is present otherwise. Iron seldom occurs in its native form other than meteoric iron; however, it can be easily reduced from its oxide form. Iron reacts with chlorine to form chlorides of iron, $2Fe + 3Cl_2 \rightarrow 2Fe\ Cl_3$, and also with oxygen to form oxides, the three common oxides being FeO (Ferrous Oxide), Fe_2O_3 (Ferric Oxide, commonly known as Haematite), Fe_3O_4 (Ferroso-Ferric Oxide, commonly known as Magnetite). Iron in its pure form has very low hardness; hence, the metal in its pure form cannot be forged into objects or tools (Prakash,et.al, 1958). Therefore the term Early Iron Age does not suggest artefacts made out of pure iron as the objects found in the archaeological context are alloyed forms of iron. Alloyed form had better durability than pure iron. The alloyed forms are ductile in nature and are suitable for deep drawing operations.

2.3.2 Methods of Testing

With the advancement in metallurgy and material sciences, a wide range of alloys of varying strengths, properties and resistance to fatigue, corrosion have been made. However, to acquire a full and comprehensive knowledge of the materials and the specific methods of forging or heat-treatment, it is necessary to carry out microscopic examination of the structures. It is important to undertake mechanical testing of materials before working on them. This is because they provide us data on the resistance power of the materials, and their conformity to the specifications standardized by two institutes, British Standard Institution (BSI) in United Kingdom and The American Society for Testing Materials (ASTM) in United States of America. In India we have our own standards framed by the Bureau of Indian Standards (BIS) (Rollason, 1973).

2.3.2. 1 Hardness Test

This test is usually done to determine the resistance power of the material to external forces such as scratching, wear, penetration and the degree to which it can be rolled and cut by machines. The hardness of the materials is measured using any of the methods described below:

a. **Brinell Test** is the method where the surface of the metal is indented using a hardened steel ball and the average diameter of the indention is measured. The Brinell number ‘H’ is calculated using the formulae:-

$$H = \text{load/ area } \frac{2P}{\pi D\,[D-\sqrt{D^2-d^2}]}$$

Where P = load (kilogram)
D = diameter of ball (millimeter)
d = diameter of impression (millimeter)

The visual image of the indention can be also interpreted. The piling up of the metal round the edge of the indention indicates a low rate of hardening due to deformation, and sinking denotes the ability for work-hardening. However the results of Brinell test can be erroneous due to the spherical shape of the indentor and the flattening of the ball (Rollason, 1973).

b. **Vickers Test**: To eliminate the flaws of the Brinell test, this method uses a diamond square – based pyramid which does not deform while indenting the material. The indention is measured in terms of Vickers Pyramid Number (VPN). Vickers tests suits materials with hardness about 600, and fails when the hardness is above 600 (Rollason, 1973).

The other two methods, Rockwell Test and Shore scleroscope are suitable for materials such as gears, testing rolls etc. that have been developed post-industrial revolution, and conventionally not used for testing archaeological metal artefacts.

2.3.2.2 Tensile Test

This test is done to calculate the strength and ductility of a metal (Rollason, 1973). A metal is considered a workable material only if it is ductile and malleable. This test is done on metals before converting them into finished products and therefore has no use in the study of archaeological metal artefacts. However it is important to know that commercial steel is tested on the basis of the stress-strain curve, elongation curve and degrees of fracture, and are accordingly graded for commercial use.

2.3.2.3 Fatigue Test

'Fatigue' implies the failure of a material under repeated applied stress of cyclic nature. This test is required for machinery parts as fatigue is the reason for operation failures due to the break-down of machine parts (Rollason, 1973). Fatigue test is done using Wöhler – type machine and a fatigue limit is calculated which is unique to every material.

2.3.3 Understanding of Iron–Carbon Equilibrium Diagram

Before venturing into the Iron–Carbon Equilibrium Diagram, it is important to understand that a single substance can exist in two or more crystalline forms. Allotropy is typified by a change in atomic structure which occurs at a definite temperature.

Allotropic Changes in Iron

Iron undergoes primarily two allotropic modifications. However, there are 4 changes in iron which gives rise to alpha (α), beta (β), gamma (γ) and delta (δ) structures. α, β and δ have the body centered cubic (B.C.C) structure (Fig: 2.3.3.1), while γ has face centered cubic (F.C.C) structure (Fig: 2.3.3.2) (Rollason, 1973).

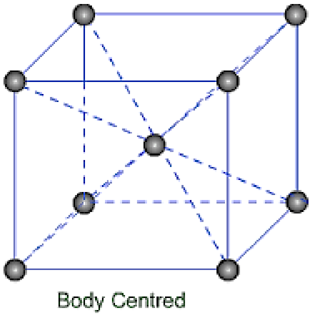


Fig. 2.3.3.1: Body Centered Cubic Structure

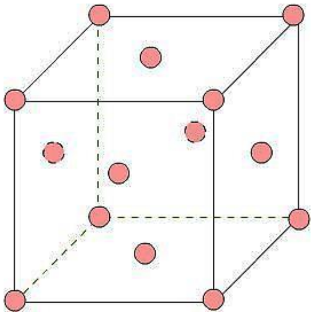
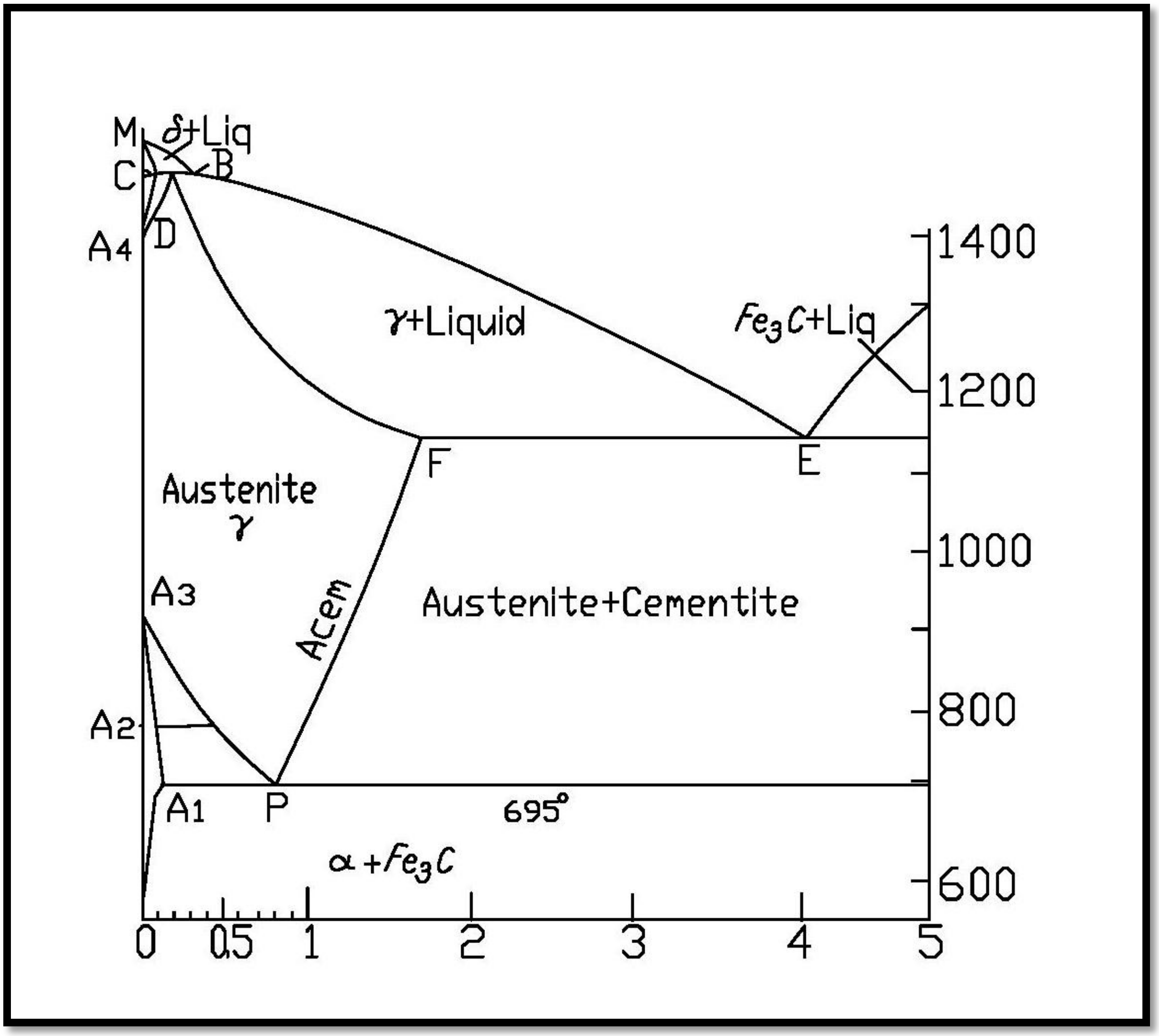


Fig. 2.3.3.2: Face Centered Cubic Structure

The changes in the forms of the iron are distinct at definite temperatures; α transforms to β at 769°C and it has a body centered cubic structure; at 937°C, β transforms to γ and the atomic structure changes to face centered cubic structure (F.C.C). At 1400°C gamma (γ) changes to (δ) and the atomic structure is transformed to B. C. C. However the additionof carbon leads to the formation of pearlite. The changes during the addition of carbon are projected in the Iron (Fe)-Cementite (Fe_3C) equilibrium diagram (Fig: 2.3.3.3).

Carbon is used to modify the property of iron. The critical points are achieved by adding carbon where there is a drastic change in the molecular structure of the material. Carbon changes the colligative properties of pure iron by manipulating the critical points in order to achieve a particular modification. The critical points A_1, A_2, A_3 and A_4 are achieved by adding C. First A_4 point is raised and A_3 is lowered until it coincides with A_1. At this conjecture (P) the element precipitated has the modification of α, β and γ at 695°C and is known as ferrite. A_3P is the ferrite solubility line. Again the temperature is increased to A_4, if there are no precipitates then the entire solution is Austenite. However if the critical point A_4 is lowered to point F by increasing the carbon content and decreasing the temperature then the precipitate formed would be austenite (γ) + cementite (Fe_3C) which is denoted by the cementite solubility line. Again if 1/5 th of the solution at critical point A_1 is heated constantly at 695°C, then the precipitate formed would be a eutectoid composition which would have a pearlite microstructure. A_1PG indicates the pearlite line (Rollason, 1973).



(After Rollason, 1973)

Fig. 2.3.3.3: Iron (Fe)-Cementite (Fe_3C) Equilibrium Diagram

2.3.4 Microstructures and their Properties

Microstructure of a metal can be defined as a microscopic view of the phases in the material. A single phase is a homogeneous structure of a material that has uniformity in its physical and chemical characteristic. However microstructures are not visible to the naked eye and can be viewed only under a microscope, such as Optical Microscope, Scanning Electron Microscope (SEM) or Transmission Electron Microscope (TEM). While studying microstructures certain elements such as grain boundaries, interphase interface and point defects need to be defined.

2.3.4.1 Cast Iron

Cast iron is identified by the presence of a high percentage of carbon (2-4%) and high percentage of silicon. Carbon presence in cast iron is found in two forms, as stable form (graphite) and unstable form (cementite Fe_3C) (Rollason, 1973). Most cast irons have phosphorous content varying between 0.03% and 1.5%. There are two types of cast iron, Grey cast iron is basically cast iron with grey fractures, which is indicative of free carbon as graphite, and White cast iron having white fractures which indicate carbon content in the form of cementite (Fe_3C). Grey cast irons have a microstructure similar to steel, but with an addition of graphite flakes (Scott, 1991). Therefore it is necessary to interpret the microstructures with the carbon content and chemical composition taken into account.

2.3.4.2 Pure Iron

Pure iron is termed so because of nil carbon content and has a small percentage of impurities such as phosphorous, silicon, manganese, oxygen and nitrogen. The microstructure is that of a pure metal, built up of crystals of the same composition. The microstructure formed is known as ferrite (Rollason, 1973).

2.3.4.3 Steel

The addition of carbon to pure iron renders a change in the pure ferrite structure (Fig: 2.3.4.3.a). The addition of carbon forms the compound cementite (Fe_3C) which is formed when it chemically combines with iron. The amount of carbon in combined form is the index for judging the grade of steel. This type of microstructure on examination reveals two phases, ferrite and cementite forming a eutectoid mixture (C: 0.87%) and such microstructure is known as pearlite (Rollason, 1973) (Fig: 2.3.4.3.b).

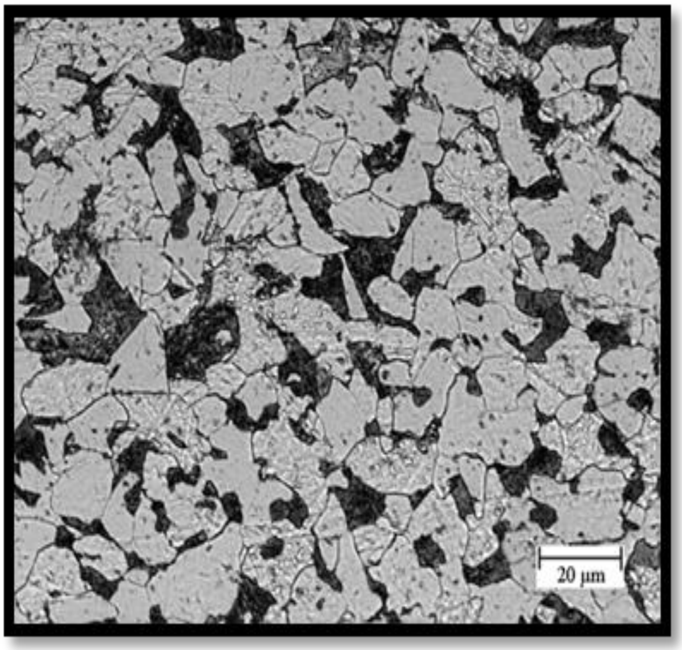


Fig. 2.3.4.3.a: Microstructure Showing Both Ferrite and Pearlite

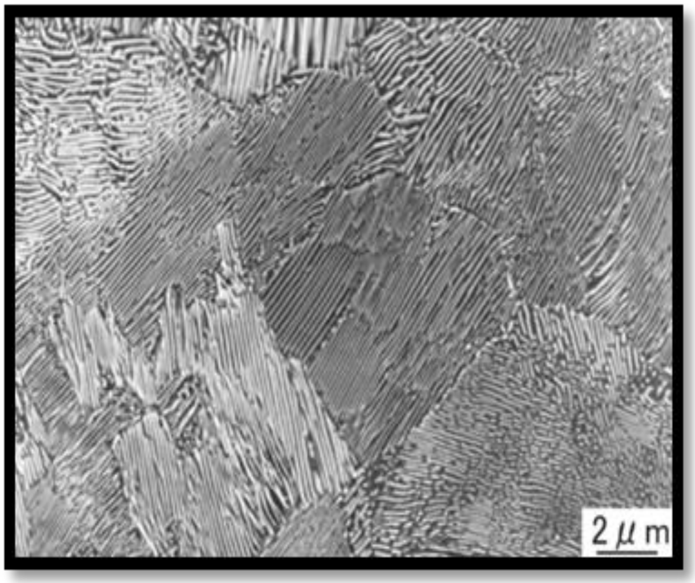


Fig 2.3.4.3.b: Microstructure Showing Only Pearlite

2.4 Methods of Manufacturing Iron

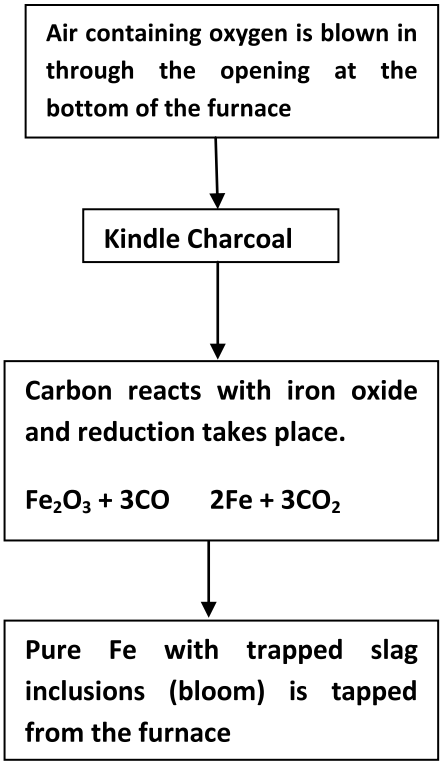
Generally, iron ores are found in form of bedded deposits or in the form of pockets within the rocky terrain, or as deposits in cracks or fissures. However it is important to note that the ores do contain gangue or non-metallic inclusions such as quartz, calcite, silica compounds and other minerals like feldspar and mica flakes. Therefore, prior to the smelting procedure, the gangue and non-metallic inclusions have to be removed. This removal process is known as ore-dressing (Prakash, 1958).

2.4.1 Ore dressing

This process aims at separating the metallic components from the undesirable gangue and non-metallic inclusions in the ore. The most common method is hand-picking, which is done by breaking the ore using hammers and manually separating the non-metallic inclusions from the matrix. A similar method was used by the *Agaria* iron-smelters. However, this is a time-consuming process and it results in the loss of metallic inclusions. Hand picking can be termed as the pre-industrial method. With the dawning of the industrial revolution, other methods have been developed, such as dry centrifugal separators using the theory of specific gravity. Even electromagnets have been used for separation, especially for ferro-magnetic ores. Processes like froth-flotation and electro-static concentration are also used for separating copper, zinc and lead sulphide from their impurities. After separation of the non-metallic inclusion the metallic content is then processed for smelting. It is to be noted that in the pre-historic days only hand-picking must have been practiced (Prakash, 1958).

2.4.2 Smelting

We do get written records of smelting techniques practiced during the pre-industrial era. The wootz steel makers of Salem district in Tamil Nadu used magnetite ore and their smelting procedure is recorded by Heath (1839). Before the ore was smelted, ore dressing was performed which was by stamping on the lumps of ore so as to crush the particles for manual separation of the non-metallic inclusions, such as quartz. It was followed by washing the crushed particles in running water. The separated material was left in the sunlight to dry. After the ore dressing procedure, the final smelting procedure was initiated. First a pear shaped furnace was built using refractory clay and it had two goat-skin bellows. The furnace was constructed one day prior to the smelting procedure. First the furnace was filled with charcoal and then the fuel was lighted. Then the crushed ore particles were placed on the fuel. However, we have no information about the flux added. More charcoal was periodically introduced into the furnace. After a period of four hours, the temporary wall built in front of the opening at the bottom of the furnace was broken down, and then the smelted iron (bloom) was brought out using a tong.



The first stage of refining was done at the smelter's workshop itself, where they used a wooden mallet to forge the bloom so as to remove the slag remains and other impurities. This was done by multiple stages of forging. Then this partly refined bloom was sold to the blacksmiths who fashioned the finished tools out of the bloom.

2.4.3 Smithery Techniques

The smithers produced solid mass of metal in bulk. For fabrication of artefacts the commonly used method was casting using moulds of a fixed shape, or sheets, which were later used for fashioning other artefacts. So the first stage for smithery technique was casting.

2.4.3.1 Casting

Iron used for commercial purpose is hardly ever 'pure' and have impurities which do affect the solidification process. During the solidification process, of the molten metal that is poured into the sand moulds, the heat evolution raises the temperature at the solid-liquid interface, however finger like longitudinal structures grow into the cooler or under cooled region. The microstructure formed during this process show radial fingers with secondary arms at right angles. Multiple formations like this give the appearance of fern tree (Rollason, 1973). This type of microstructure is known as dendritic microstructure (Fig: 2.4.3.1).

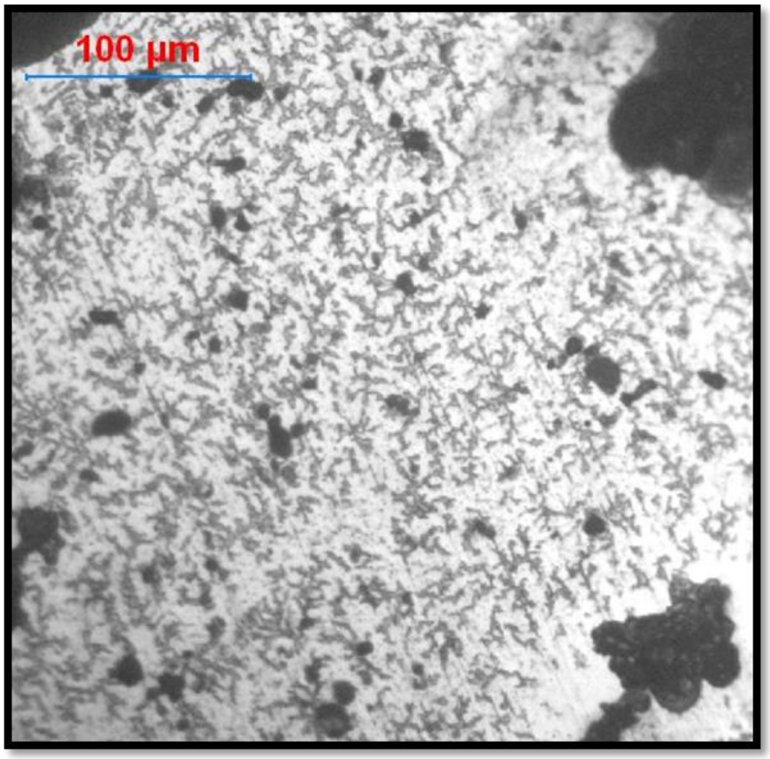


Fig. 2.4.3.1: Optical Micrograph Showing Dendritic Microstructure

Procedure for Casting

Two methods are used for casting procedure; either sand casting is done where the micro-structure is of equi-axed grains of the same size but with varying orientation. This microstructure is formed because the molten metal in the mould looses heat slowly.

Process for Sand Mould Casting

Sand moulds have high resistance to high temperatures. The sand moulds are usually made using red sand which is basically silica particles bonded in clay. For iron casting, coal dust is added to the sand before making the mould as it aids in improving the surface finish of the metal. However this also increases the carbon imbibed by the artefact that is made using the sand mould. The other method of casting is chill mould casting where the metal is poured just above the freezing temperature. The metal in contact with the cold metal mould is instantaneously cooled below its freezing point and the metal at the centre of the mould is least affected. The metal in contact with the chill mould will form chill and columnar crystals and the core would form equi-axed grains. However such mould came to be used only in the post-industrial era (Rollason, 1973). The cast iron artefacts found from the archaeological context were made using the sand mould.

2.4.3.2 Forging

Fashioning of metal artefacts involves different methods of working like hot working, cold working and annealing. Smithery activity involves the process of deformation; the grains suffer from strain either elastic or plastic. In the case of iron smithery plastic deformation takes place which is possible with both hot working and cold working. Hot working processes comprise forging and rolling (Rollason, 1973). However in the archaeological context we have evidence of forging techniques employed by the ancient iron smelters. The process involves of a heavy hammer which is used for repeated striking on the red-hot metal placed on the anvil. Due to the constant striking, deformation takes place. Forging can be done on any metal having a high degree of malleability.

2.4.3.3 Annealing

This is a heat treatment operation. This process involves the heating of the metal strip in a furnace till red-hot condition. Annealing is done to soften the metal so as to increase its machinability. Sometimes the same process is done to reduce the effects of previous treatments such as forging, or uneven cooling. It is to be noted that excessive annealing stimulates increase in ductility and a decrease in the strength of the material.

When the metal artefacts are heated higher than the upper critical temperature, large austenite crystals are formed and slow cooling leads to the formation of Widmanstätten microstructure which leads to the loss of ductility. This is the effect of over-annealing (Rollason, 1973).

2.4.3.4 Quenching

It is the method of hardening steel. Quenching suppresses the breakdown of austenite grain into ferrite and cementite. Water is the most efficient quenching medium because of its ability to attain maximum hardness as the quenching velocity of water is higher than oil which is the other medium used for quenching. However water quenching sometimes results in cracking of the surface of the object. Oil is also used for quenching which has a lower quenching velocity than water and hardness achieved is lower than what is achieved in the case of water quenching (Rollason, 1973).

.

2.4.3.5 Tempering

The quenching process makes a steel tool highly brittle and is highly prone to cracking and deformation of the object. To solve this issue, it is essential that the artefact is again heated to below the critical range so as to relieve the stress and initiate the reaction of cementite precipitation. This process is known as tempering. The tempering process restores a part of the lost ductility. The degree of tempering is measured by the colour achieved by the tempered section (Rollason, 1973).

2.4.3.6 Carburisation

It is the process by which the carbon content absorbed by the surface of the metal is increased by heating it in a furnace in association with carbonaceous metal such as wood charcoal, bone charcoal, charred leather etc. the absorption of carbon during this process is due to the decomposition of carbon monoxide . In the archaeological context, we do have artefacts case hardened on the working edges, however uniform carburization is a rare find (Tylecote, 1979).

2.5 Importance of Microstructure Interpretation in the Field of Archaeo-Metallurgy

The manufacturing of iron artefacts entails a series of complex mechanism such as mining, ore preparation, smelting and smithery activities. To understand these mechanisms it is important to undertake microstructural analysis and study the grain structures present within the corroded artefacts. The metallographic analysis also aids in understanding the methods of extraction of metal and also the proficiency of the early iron smelters in ore dressing and smelting activity.