



Characterization of Corrosion Behavior of Archaeological Iron Spear from Sanur (300 BC – 50 AD) – A Megalithic Site in Southern India

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DOI : 10.2478/acmy-2019-0003

Abstract:

This investigation deals with the chemical composition and microstructural analysis of the iron object, a spear excavated from Sanur, Tamil Nadu- a megalithic site dated 300 B.C. to 50 A.D. Phase analysis and microstructural examination were carried using XRD, optical and variable pressure scanning electron microscope (VP-SEM). Optical micrograph shows the equiaxed grain structure along with the Newman bands. Formation of Newman bands suggests that the original artifact was forged at high temperature followed by cooling, although not so rapid to produce the marked hardening. The absence of carbides at the grain boundary, within the grains and lower value of micro-hardness indicates that the iron spear was not subjected to the carburizing treatment. Results of corrosion characterization revealed that deterioration of excavated iron artifact is associated with the presence of chlorine in corrosion products. However, compact nature of the outer rust (goethite) was helpful in protecting the object. The formation of goethite [α -FeOOH] layer may prevent the iron matrix suffering from attacks by other environmental factors due to its good continuity. In addition, less aerated environment of storage and no history of any cleaning of object were also helpful in preventing the iron spear from further deterioration.

Keywords: Megalithic iron; Sanur; Slag inclusion; Goethite; Carburization.

1. INTRODUCTION

Scientific studies on iron metallurgy from Northern Gangetic plains of India revealed that the ancient settlers in the region develop a skill of iron tool manufacturing without a long antecedent gestation period. During Early Iron Age (from the beginning to 7th-6th century BCE) the Indian iron industry was in an uncertain experimental stage. This age is followed by improvisation in technology in Middle Iron Age (7/600BC to 100BCE). An improvement in Late Iron Age (2nd – 1st cen. BCE to the historical period) was continuously maintained until the 18th century. Thus, evidences from 700- 100 BCE are very important since appearance of iron marks a phase of second urbanization in Northern India. By this time, ancient Indian blacksmiths realized the superior quality of iron and there was a gradual growth in iron technology resulting in an entirely new technological pattern in the Northern Ganga plains. However, in Southern India Iron Age, deposits had numerous iron objects, along with a plethora of pottery and other objects and yet iron did not lead to urbanization [1]. Archaeology of Southern India was full-fledged Iron Age culture and dominated by megalithic culture since its inception [2]. The megalithic period in India is notable for the emergence and development of iron metallurgy and the appearance of new burials known as megaliths [3]. Based on radiocarbon dating and typological studies megalithic cultures in South India may be placed between 1100 B.C and A.D 100. However, the available archaeological data suggests that the period of their existence lies between somewhere between 600 B.C and 100 A.D [4].



Figure 1: The location fo Chengalpattu

The south Indian sites having evidence of iron can be grouped under habitational sites and cemetery sites. The iron objects found in habitations and burials prove their high achievements in forging this metal into perfect shape. There are many megalithic sites, which were production center for metals like iron, copper, gold, silver etc. The megalithic culture in South India was full-fledged Iron Age culture, when the people [5] finally realized the great benefits in the use of this metal. The iron artifact selected for this study is a spear (300 BC- 50 AD), excavated from the Sanur, Chengalpattu, Tamil Nadu associated with the megalithic culture of South India. Sanur ($12^{\circ} 33' 5''$ Latitude and $79^{\circ} 55' 0''$ Longitude) is situated in district Chengalpattu in the southern India state of Tamil Nadu (Figure 1). The excavation of megalithic burial and extensive exploration all over the Tamil Nadu state provides an excellent picture about the typology and distribution of iron age /megalithic monuments in Tamil Nadu [6]. It has an extensive high ground about 18 hectares, lying to the west of Madras Trunk Road flanked by the hills on the west. During the exploration, in this region in 1944-45, large numbers of megalithic fields were discovered. N.R. Banerjee & K.V. Soundararajan excavated the site Sanur in 1952 and found that interments or grave goods are spears tanged draggers, knives, hooks, bars, wedge, tangs, arrowheads, sickles and horse bits placed inside the chamber at different levels [7]. The brown clayey soil is the most predominant covering for the burial sites. High relative humidity between 58 to 84% prevails in the region throughout the year due to coastal proximity and impact the metal corrosion.

Some iron objects from Sanur area were studied earlier [8] revealing that the artifacts were free from metallic iron and it was transformed into ore due to vagaries of the nature-defying protective condition of its preservation [9]. It has been proposed that the artifacts first get oxidized by corrosion and then transform into silicate of iron due to its close contact with silica slag embedded within the iron piece. The determination of corrosion behavior is very important for knowing the microstructure and chemical element concentration in the object [10]. Based on metallurgical studies of 18 iron artifacts from 8 excavated sites of Tamil Nadu from early historic period [11], it was concluded that most of the artifacts were reduced to minerals as they were in close contact with earth for a long time. Some earlier studies were made on iron objects from Northern India excavated sites of Rajghat and southern megalith site of Sanur, although their microscopic composition, structural variations and corrosion studies were not studied in detail [11-13]. In the past, wootz steel from South India has been studied for its metallurgical aspects [14-17]. The hardening of carbon steels as well as many alloy steels is based on the difference in the solubility of carbon in α -iron (ferrite) and γ -iron (austenite). In pure iron, austenite transforms to ferrite on cooling to 912°C . The continuous network of polyhedral grains is characteristic of pure iron. If impurities are present in considerable quantity, it may be retained and dissolved in the form of mechanical inclusions. Slags may often be observed and flaking of the ferrite grains is a source of weakness, rendering the iron brittle. The heterogeneous distribution of entrapped slag inclusions is a typical feature of ancient iron manufacture [18]. The slag inclusion in ancient iron is mostly composed of fayalite along with wüstite and glass phase [19]. Examination of slag gives us good indication about the ores used and smelting process. The presence or absence of *wüstite* in the slag also depends on the types of ores used in smelting.

Deterioration after excavation of archaeological iron artifacts buried in soil is often associated with the presence of chlorine in corrosion products, leading to serious problems for conservation of metallic objects of cultural heritage. This leads to a locally accelerated dissolution of metal. Broad pits often observed on the surface were attributed to the presence of Chlorine. Therefore, to obtain micro scale information on different corrosion products within

archaeological iron artifacts buried in soil, advance techniques: optical microscope (OM), variable pressure- Scanning Electron Microscope (VP-SEM), Energy Dispersive spectroscopy and X-ray diffraction, of material characterization are implemented. The analyses are realized on cross sections of corroded iron object. The iron corrosion process after excavation is related to the presence of chlorine, and knowledge about it is particularly important for restoration and conservation of metallic artifacts.

The chemical composition analysis and microstructural characterization of metal objects enable to understand the technology adopted in ancient time. Also, understanding the corrosion mechanism and the corrosion characterization forms an important step in the studies of the behavior of corrosion [20]. The objective of the present investigation deals with the microstructural and corrosion product analysis of the iron spear object to understand the manufacturing methodology adopted and its conservation problem.

2. MATERIAL AND METHODS

Table 1: EDS analysis of the Corrosion layer

Element	wt%
O	30.08
Fe	3.08
Cl	66.24

The iron objects studied in the present investigation was excavated from the Sanur, Tamil Nadu- a megalithic site dated from 300 B.C. to 50 A.D. and it was the part of Central Antiquity Collection of Archaeological Survey of India. Presently, the sample is stored in New Delhi fort known as Purana Qila having thick walls built in red sandstone. The storage space is not environmentally controlled in any active way and only ventilation (outlet) is provided by planned air exchange internally and through original ventilation in the building fabric. The storage area is quite damp. The storage has 60% relative humidity with almost $\pm 20\%$ seasonal fluctuations. New Delhi has a continental climate with severe summer from March to May (Temperature: 45°C) that alternates with cold temperature when the temperature plunges to freezing point. In monsoon (June to September), the relative humidity varies from 60-80% due to heavy rainfall. Such kind of climatic variations exerts a tremendous influence on objects housed in the uncontrolled environment as they are vulnerable to climatic variations. The storage materials are a hybrid system of wooden and metal shelving, display cases and steel trunks. The interior of each store room has a varied microclimate. The iron spear placed in wooden shelves was found covered in thick layers of dust. The shape of the untreated iron spear retained completely. However, other previously treated iron objects from the same site have flakes so badly that they have disintegrated completely. In the similar way iron objects excavated from the site of Rajghat was placed.

2.1 Condition of the object



Figure 2 (a, b and c): Iron Spear

The iron spear excavated from Sanur (Figure 2 A & B) was stored in wooden shelves (Figure-2 C) The iron spear placed in wooden shelf was found covered in thick layers of dust. The shape of the untreated iron spear retained completely without any sign of active corrosion. Unfortunately, the other previously treated objects from the same excavation site stored in the similar way as untreated iron spear have flakes so badly that they have disintegrated completely. They were found severely corroded and no core metal remains.

2.2 XRD analysis

The corrosion product/phase analysis was carried out using X-ray diffractometer (Model: Bruker AXS D8) with copper target material.

2.3 Optical Microscopy

A very tiny piece of sample with dimension 1 mm \times 1 mm was sectioned from the object without disturbing its visual appearance for microstructural characterization and hardness determination. The sample was mounted in epoxy resin and mechanically ground successively polished with emery papers of different grades such as 120, 400, 600 to 1200 followed by cloth polishing with diamond pastes (1 μ m, 3 μ m and 8 μ m) to obtain mirror like finish. The surface was rinsed with distilled water and degreased with acetone. The sample was etched with 2% nital (2% HNO₃ in ethyl alcohol) for 10 seconds to reveal its microstructural details. The optical microscopy was carried out using the metallurgical optical microscope (Model: Nikon Epiphot -200) attached to an image analyzer system (LECO IA-32).

2.4 Scanning Electron Microscopy

In the present investigation variable pressure scanning electron microscope (VP-SEM) (Model: EVO MA 10) was used to examine the morphology of the corrosion product. VP-SEM technique was used in this investigation because it does not require any type of coating in contrast to the conventional scanning

electron microscope and field emission scanning electron microscope (FESEM). The elemental analysis was carried using energy disruptive X-ray analyzer (EDX) (Model: OXFORD/MCA ENERGY 250).

2.5 Microhardness

Vickers microhardness tester (Model: Future –Tech FM7 Micro) with a diamond indenter was used to determine the microhardness. Sample with mirror polished was used for microhardness determination. Dwell time for each indent was 10 seconds. The applied force was 100 gram. The value of the microhardness lies in the range from 135 to 173 Hv.

3. RESULTS

3.1 X-ray diffraction analysis

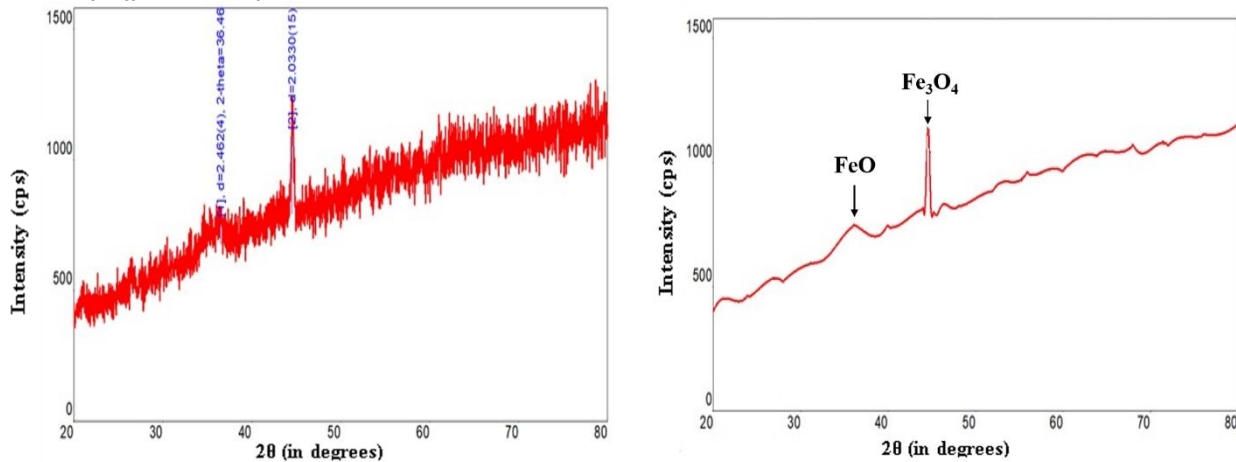


Figure 3: XRD pattern

XRD pattern of the sample is displayed in Figure 3. The XRD revealed the presence of magnetite (Fe₃O₄), iron oxide (FeO) and iron silicate. It may be clearly seen from the figure that intensity of the peak is very less & diffused and this may be due to the amorphous nature of the sample.

3.2 Microscopy

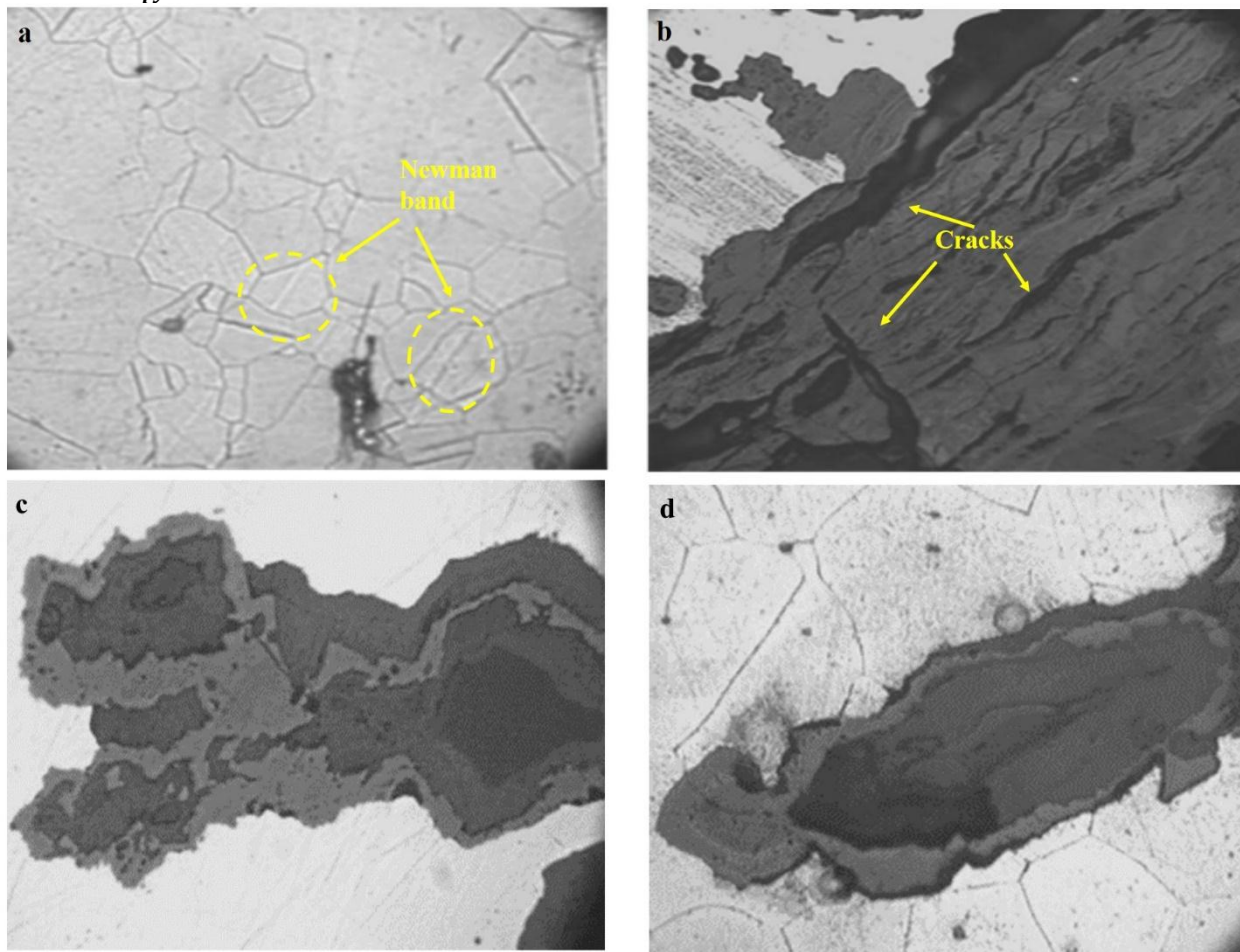


Figure 4 (a, b, c and d): The optical micrographs shows grey veins in a dense corrosion product layer

The optical micrographs of the investigated sample are shown in Figure 4. It may be clearly seen from the fig.3a that there is equiaxed grain structure without any evidence of carburization. The Newman bands may be clearly seen in grains and encircled in Figure.4a. Figure 4b shows light grey veins embedded in a dense corrosion product layer, which appears like a marble structure with typical characteristics of magnetite morphology [21]. The corrosion products layer shows numerous cracks several tenths of micrometer thick, which are easily identified under an optical microscope. The cracks are relatively parallel to the metal-corrosion product interface but sometimes also perpendicular. The metal matrix is rather clean but some slag inclusions are heterogeneously distributed in the metal core (Figure 4 c & d). It may be understood that iron spear is manufactured from wrought iron fabricated in bloomery furnace. Coarse grain size due to overheating has caused the iron to break with a crystalline fracture and low elongation. The microstructure suggests that the original artifacts were forged at a high temperature and then cooled rapidly, although not so rapid enough to produce the marked hardening. This resulted in the formation of Neumann bands.

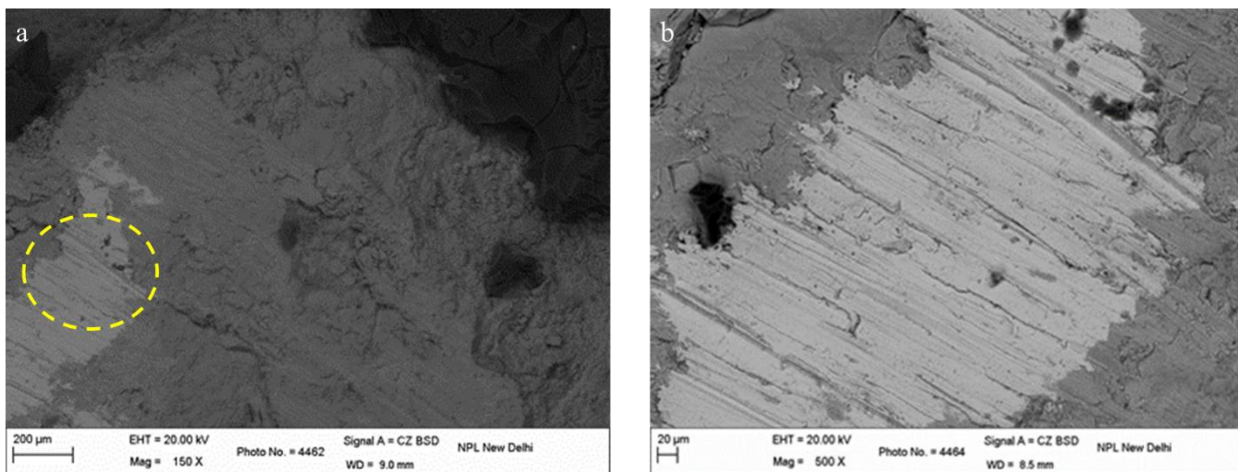


Figure 5 (a and b): SEM micrograph of the corrosion surrounded thin metallic

SEM micrograph of the cross-section portion of studied sample is shown in Figure 5 (a & b). The micrograph revealed that corrosion products have surrounded thin metallic core distinct layers. A dark grey inner layer, light grey intermediate layer and an outer layer, which penetrates deep in the bulk, can define the structure of the sample. It may be clearly seen that the sample is mostly corroded and only the island of ferritic grains is visible. The shape of the spear was retained almost completely although metallic iron appears to be fully transformed to oxides. The sites of origin of corrosion seem to be embedded slag inclusions identified in the samples.

3.3 X-ray Mapping

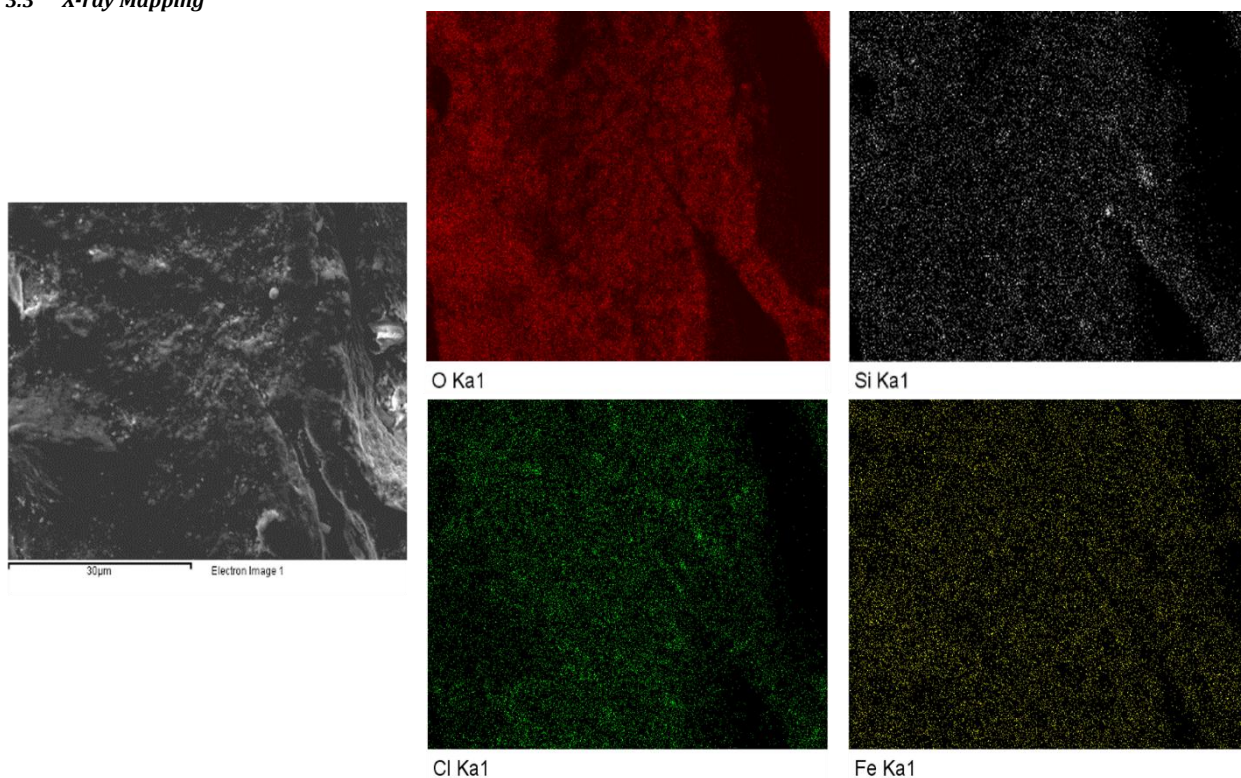


Figure 6: Distribution of various elements like oxygen, silicon, iron and chlorine

X-ray mapping of cross-section sample of the sample is presented in Figure 6. Distribution of various elements like oxygen, silicon, iron and chlorine may be seen. It is evident from the X-ray mapping images that a sufficient amount of silicon and chlorine is present on the top surface which is responsible for the initiation of corrosion and degradation of the iron spear during the course of time. Ongoing corrosion problems occur in iron objects after excavation if they still contain an iron core and are contaminated with salts, especially an acidic iron (II) chloride [20] [22]. When freshly excavated iron objects are exposed to a new environment above ground, it generally experiences lower relative humidity (RH) and higher oxygen concentration relative to the burial environment. As the iron dries, the contaminating acidic $FeCl_2$ and other salts concentrate and the corrosion layer cracks, allowing greater access of oxygen to remaining metal. Rapid drying of freshly excavated iron objects may also result in the formation of yellow crystals of $FeCl_2$ [23]. The solids or dissolved ions that were stable in the burial environment may no longer be stable in the air and may oxidize to new corrosion product. The acidic solution of Fe^{2+} ion can undergo hydrolysis in exposed air and oxidize to Fe^{3+} ion. This corrosion process causes physical damage to the shape of the object and chemical damage to any remaining metal. Laboratory studies of the oxidation and hydrolysis of $FeCl_2$ found that at low Cl^- ion concentration, goethite $\alpha-FeO(OH)$ and/or lepidocrocite $\gamma-FeO(OH)$ precipitate, at high Cl^- concentration, akaganeite $\beta-FeO(OH)$ formation takes place [22]. Formation of ferric oxyhydroxide is associated with volume expansion, which causes cracks, and exfoliation of corrosion layer or even the whole artifacts may accelerate to the deterioration. The presence of significant number of cracks is also seen in the studied objects. At the point of fracture, an orange powder may be observed which can be identified asakaganeite on several artifacts [24].

3.4 EDS analysis

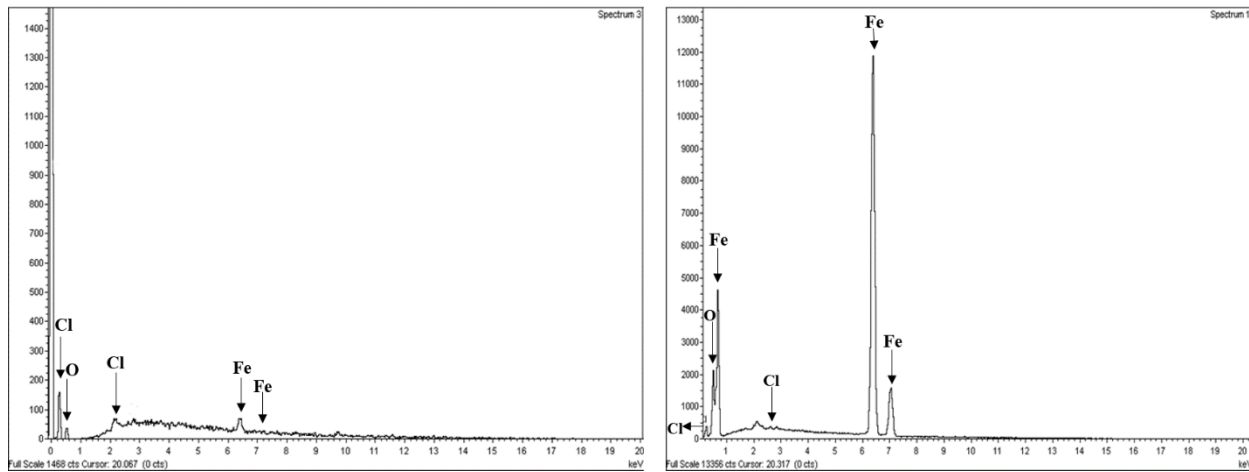


Figure 7: EDS analysis

EDS analysis was carried out to determine the elemental composition of different corrosion compound. It may be clearly seen from the EDS spectrum that there is presence of iron, oxygen and chloride (Figure. 7). Quantitative data for the elements present in the corrosion layer is displayed in Table 1. It is quite obvious from the table that the chlorine percentage is high i.e. 3.68% and this percentage is sufficient for causing the deterioration of the object. Most of the chlorides were detected at the interface of the metal matrix and corrosion layer.

3.4 Morphology of corrosion products

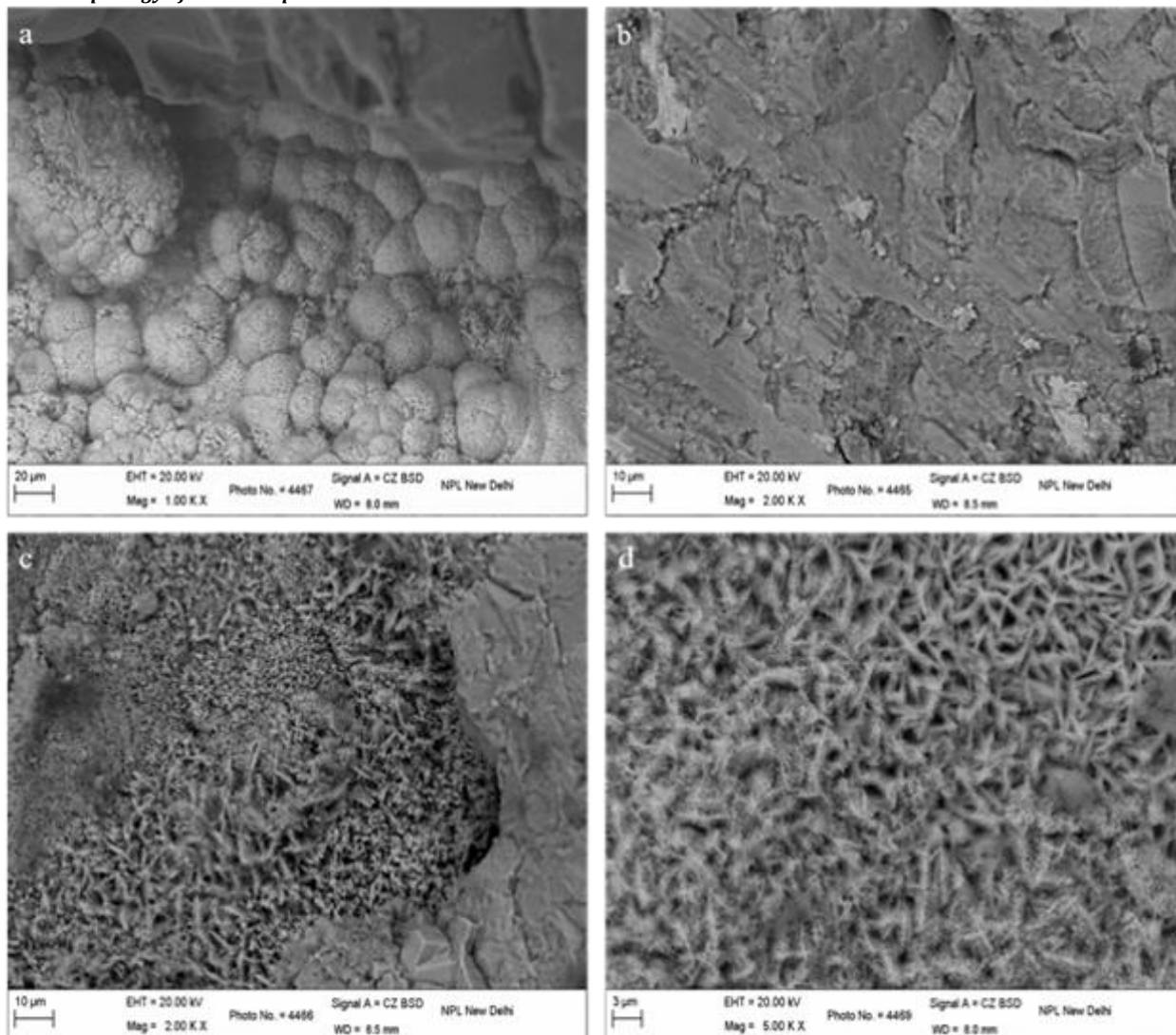


Figure 8: The morphology of the corrosion product

The morphology of the corrosion product was examined by VP-SEM and shown in figure 8. It may be clearly seen that there are different type of corrosion product with different morphology in the investigated sample. There is formation of globular (cotton ball) structures at the outer surface (Figure 8a). The cotton ball structure typically resembles semi-crystalline goethite [24] interconnected by formation like a nest and compact iron oxide layers were found on the outer surface of the specimen analyzed. The corrosion products formed on the outer layer are more compact in comparison to the inner region. The micrograph of the sample shows the typical structure of goethite and the nest formation interconnecting the cotton balls (Figure 8c & d).

The corrosion of the chloride infested wrought iron in the atmosphere involves the formation of various FeO(OH) polymorphs and Fe₃O₄. The presence of crystalline magnetite (Fe₃O₄) in the rust and it is also confirmed through the XRD analysis of the sample (Figure 3). Magnetite occurred at the less aerated

metal/corrosion products layer interface, in the reduced oxygen environments beneath the corrosion layer [25–27] and requires alkaline environments for best results [23,28]. Morphology shows the compact nature of corrosion products (goethite) formed on the surface, which can stop the diffusion of oxygen and moisture into the metal, thus preventing further corrosion. It was earlier established [29] that goethite irons are one of the most stable corrosion product found on iron. However, the orientation of the particles can cause cracking and flaking on the surface [30]. The formation of goethite instead of akaganeite may be due to low chloride ion concentration. Existing literature [31] suggests that akaganeite can form at high chloride ion level ($Cl^-/OH^- > 8$) and goethite forms at low Cl^- level ($Cl^-/OH^- > 6$) [30].

4. DISCUSSIONS

On the basis of metallographic analysis of Sanur excavated iron object, it was revealed that iron spear is wrought iron fabricated in bloomery furnace. An excessively coarse grain size due to overheating has caused the iron to break with a crystalline fracture and low elongation. As a rule, higher the temperature above Ac_3 , to which iron has been heated, the larger will be the grain size. The structure suggests that the original artifacts were forged at a high temperature and then cooled rapidly, although not so rapid enough to produce the marked hardening. This resulted in the formation of Neumann bands. Neumann bands are probably regions of severely distributed orientation.

The shape of the spear was retained almost completely. However, macro and microscopic images show that metallic iron appears to be fully transformed into iron oxides. The presence of a significant quantity of chlorides at metal corrosion products interface is an indicator of the corrosion process in the iron sample. Morphology shows that the layer of goethite, with the crust like stalactite, has a good continuity and compactness in texture. It is a non-reactive phase with an important protection owing to its ability to effectively prevent the iron matrix suffering from attacks of other environmental factors such as oxygen, moisture as well as polluted gases. Thus formation of goethite is preventing further corrosion in an iron spear.

From the comparison of iron objects from southern megalithic site to that of Gangetic plains iron object, we get a clear indication of the status of metallurgy. All the iron objects excavated from northern India Ganga plain have a high percentage of metallic iron (94-99%) that indicate low degree oxidation of the sample inspite of time which has elapsed since they were fabricated. All the samples analyzed from Ganga plains were normalized, hypoeutectoid steel made by direct reduction process (bloomery process).

The megalithic iron objects from Sanur were without the possibility of being identified. On the basis of analytical investigations carried on the southern megalithic object, it can be said that the technique of carburization was not used by Sanur blacksmiths and hence no heat treatment was done on the object to increase its strength. In addition, there are no evidence of the use of phosphoric ores in manufacturing. That is why the southern megalithic irons show less corrosion resistance than Gangetic irons.

Based on microstructure and microanalysis of an iron spear from Sanur, Tamil Nadu (300 BCE-50 AD), it can be revealed that object is made of chloride infested wrought iron which is responsible for the conversion of metal matrix into minerals during post-excavation. Results also suggest that goethite is the main corrosion products that form on corroded sample. The formation of a compact corrosion product layer (goethite), in a longer perspective may be protective and lead to a lower corrosion rate. Thus, a compact corrosion crust on the surface can stop diffusion of oxygen and moisture into the metal, thus corrosion. The less aerated environment and compact nature of the rust can be helpful in protecting the object.

5. CONCLUSION

The following conclusions may be drawn from the present investigations:

- It may be understood from the formation of Newman bands that the original artifacts was manufactured by forging at high temperature followed by the medium cooling.
- The absence of carbides at the grain boundary, within the grains and lower value of micro hardness indicates that the iron spear object was not subjected to the carburizing treatment.
- Presence of chloride was confirmed by the EDS analysis and amount of chloride is sufficient for causing the severe corrosion. The chloride bearing corrosion products are responsible for accelerated corrosion during post-excavation.
- In our earlier investigation, iron objects excavated from the northern India (Rajghat, Varanasi) is having higher percentage of metallic iron (94-99%) and shows lower rate of corrosion. All the samples analyzed from Ganga plains were normalized, hypoeutectoid steel made by direct reduction process (bloomery process) [32]. The megalithic iron objects from Sanur were without the possibility of being identified.
- There is no evidence of the use of phosphoric ores in manufacturing and this is why southern megalithic irons show less corrosion resistance in comparison to the Gangetic iron objects.
- The formation of layer of goethite [α -FeOOH] may prevent the iron matrix suffering from attacks by other environmental factors due to its good continuity and compactness. The less aerated environment and compact nature of the rust are helpful in protecting the object.
- Any mechanical cleaning could expose the chloride ions and the metal to air which may accelerate the corrosion of the object. Therefore, the cleaning of the iron object may not be advisable if environmental control is not in place for the storage of the object.

6. ACKNOWLEDGMENT

The authors are thankful for the help extended by the scientists of National Physical Laboratory, New Delhi. We are thankful to Dr. B.R. Mani for all his support and interest in the work. The authors are thankful to Ms. Tahseen Karche for all her help extended for the manuscript.

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