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Surface studies of a 2400-year old corrosion resistant ancient Indian Iron Artifact

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Surface morphology and chemical analysis of 2400 year old sickle-blade excavated in early 1940s from the ancient city Hastinapur, Uttar Pradesh, India has been carried out. The discovery of sickle blade is important archaeological evidence that demonstrates the effective role of iron in agricultural operations. Despite being buried over 2300 years, the blade has survived in good condition. Hence it became essential to determine its fabrication technique and corrosion behavior. The study is carried out in order to investigate the corrosion behavior of this ancient Indian iron. Detailed analysis of the characterization results revealed the valuable information about the production technology of the associated culture. The sickle blade is analyzed by using optical microscopy (OM), scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS), and x-ray diffractometer (XRD). Characterization results lead to the fact that the sickle blade shows heterogeneous microstructure consisting of ferrite, widmanstätten and pearlite structures which is typical of ancient Indian wrought iron produced by bloomery process. Relatively high amount of Phosphorous has been observed which may be responsible for the corrosion resistance behavior of sickle blade. The study reveal the valuable information about the technology and the materials used in the development of iron-based artifacts in India during the ancient period.

Keywords: Ancient Indian iron, Sickle, Wrought iron, Metallography, Microstructure, Scanning electron microscopy, Energy dispersive spectrometer, Archaeometallurgy

Agriculture tools are as old as Stone Age. Tools made of stone, wood, bamboo etc were used by ancient farmers or craftsmen, but most of them became extinct with the introduction of iron The earliest date for iron in the Indian subcontinent is about 1800 BC[1]. India played a key role in the invention of iron and discovered the useful aspects of intentionally alloying carbon into iron, thereby producing stronger steel. Technically, steel is defined as an alloy of carbon and iron. This steeling of iron, which was discovered in the Indian sub-continent sometime in 800 BC, played a significant role in the manufacturing of agricultural implements which led to a big revolution in civilization. Production of iron and steel implements resulted in clearing of dense forests leading to the subsequent second urbanization of India along the banks of the Ganga and the Yamuna rivers thus pushing forward technological development and promoting social progress.

To ascertain the technological development during ancient period an agriculture implement, a sickle blade excavated from the ancient city of Hastinapur (Meerut, Uttar Pradesh) located on the earlier course of the holy river Ganga was examined. The blade is a curved, hand-held agricultural tool typically used for harvesting cereal crops or cutting grass for hay (Fig.1a). Combining 14C dating with typological study of the pottery, the sickle was dated to the late level of Period III (between the early fourth and the end of third centuries BC)[2]. It is noteworthy that regular use of iron is observed for the first time in this period (400 - 300 BC).

A sickle typically has a short handle and a crescent- shaped blade and is used for reaping during harvesting. This is one of the most popular multi-used tools that our ancestors used in agriculture. Some of these tools are still in abundant use either in original form or with some modification as we can see in fig. 1b. Agricultural implements excavated from Hastinapur site are not many, but the discovery of sickle blade demonstrates that iron had an effective role to play in agricultural operations during that period. This signifies a considerable advancement on the technological side and points towards a revolution in the economic condition of the people since the previous period. This is further supported by archeological data that points towards evidence for rice cultivation at Hastinapur.

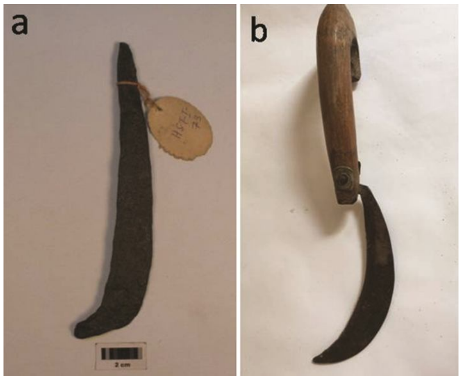


Fig. 1 — Photo of (a) an ancient sickle blade and (b) a modern day sickle blade with handle shown as a comparison

The aim of the present communication is to obtain insights into manufacturing techniques and corrosion behavior of the ancient sickle blade. Therefore, surface microstructure and chemical compositions of sickle blade were studied in order to elucidate its characteristic features.

Experimental Section

An extremely small sample (approximately 1.0 mm^2) was extracted from the as excavated object, without disturbing its antique look and further used for all the scientific studies reported here. The preparation of the sample surface consisted of grinding with silicon carbide papers (120 -1000 and 0 grit), followed by polishing with alumina paste from 5 mm to 0.05 mm. The sample was then cleaned with ethanol and dried. The sample was then etched using 2% Nital (98 mL ethyl alcohol and 2 mL nitric acid). The metallographic samples were examined under an OM (Nikon, Epiphot 200) attached to an image analyzer system (LECO, IA-32) up to 1000X magnification. Surface morphology of the sample was examined using SEM and elemental compositional analysis was performed using EDS attached with SEM. Imaging was done with a EVO MA10 Variable Pressure Scanning Electron Microscope (VPSEM), using a Si (Li) detector with a thin beryllium window. Scanning Analytical parameters were kept constant at an accelerating voltage of 20 kV, probe current of 400-600pA for morphology and 1.5 nA for elemental analysis. All the compositional data are reported in this paper as weight percentages (wt %). In addition, quantitative elemental X-ray mapping was done to identify the distribution of the major elemental concentrations in the spectral image data set. Finally, phase identification of the sample was done by advanced fourth generation benchtop X-ray diffractometer (XRD) system, the Rigaku MiniFlex II.

Results and Discussion

Surface morphology

As excavated sickle blade was found to be in an excellent state of preservation and contained a black adherent rust layer (Fig. 1). Observations of the metallographic sample revealed a heterogeneous microstructure throughout. At the outer edge equiaxed grain structures of irregular orientation exist while in the central region, bigger and coarser grains with higher amount of carbon exist (Fig. 2a). Presence of equiaxed grain structure shows that the blade was hot-worked, followed by, recrystallization of the metallic grains in the forge-welding process. This type of heterogeneous microstructure is a result of high separation in the carbon content and is typical of wrought iron made in ancient bloomeries[3, 4].

Widmanstätten ferrite plates having an acicular or wedge-shaped structure are present in many areas (Fig. 2b). The outstanding crystalline microstructure is formed when steels are cooled from extremely elevated temperatures at a critical cooling rate[5, 6]. Therefore, presence of a Widmanstätten ferrite structure is an indication of prolonged heating of the austenitic phase followed by rapid air-cooling The main factors affecting the formation of Widmanstätten structure in steels are the chemical composition, cooling rate and the size of austenite grains[7,8]. Low C steels, which contain less than 0.3 wt% C, tend to form a Widmanstätten pattern, when they have a coarse austenitic grain, and have been rapidly cooled from austenitic phase[8].

No shape of corrosion is detected on the surface of the sample in SEM observations (Fig. 3a). Iron alloys containing 0.008–2.14 wt% C include a combination of α ferrite and an intermediate compound called cementite (Fe$_3$C) and are defined as steel. The alternating microstructure between α ferrite and Fe$_3$C gives the pearlite phase. Fig. 3 b is a SEM image of the pearlite zone of the ancient sickle blade with wide interlamellar spaces embedded in a matrix of ferrite grains. On one end these cementite layers join the adjacent ferrite grains exhibiting, a somewhat wavy morphology with crust formation at the end of the lamellae. This type of morphological feature is associated with the aging and typical characteristic of ancient hypo eutectoid steel[9].

Elemental compositional analysis

Elemental compositional characterization was carried out at various locations of the sickle sample using energy dispersive spectrometer (EDS). Typical EDS spectra of four regions of the sample is shown in

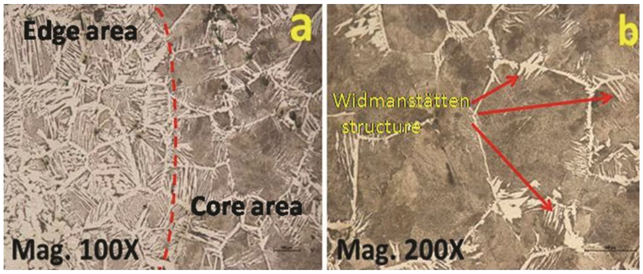


Fig. 2 — Metallographic image showing (a) pearlite matrix with Widmanstätten thin plates and ferrite; (b) Widmanstätten ferrite growth and pearlite phase

Fig.4. Sample surface revealed mainly the presence of iron, oxygen, phosphorus, carbon, aluminum, sodium and chlorine. The purity of the iron observed in the EDS spectra seems to be very high, indicating high quality manufacturing process during the period. The phosphorous content of the metallic matrix at various locations was found to be vary in the range 0.15 wt% - 0.41 wt%. Earlier studies on the ancient Indian iron including Delhi iron pillar also revealed the presence of high phosphorus content (up to 0.25 %)[10, 11]. One probable reason for the high phosphorus contents in the sickle sample could be the use of phosphorus containing ore because Indian iron ores are relatively rich in P_2O_5 [12]. Kumar and Balasubramaniam[13,14] investigated the nature of rust of the 1600 years old Delhi iron pillar and observed that the presence of small amount of phosphorus had an important effect on the corrosion resistance to the atmosphere. The atmospheric corrosion rate of the matrix material accelerated initially, in the presence of slag particles, leading to the enhancement of phosphorus concentration near the surface. With the increase in the phosphorus concentration, the formation of one of the oxyhydroxides of iron, δ -FeOOH as a continuous layer next to the metal surface is catalyzed and it should form as an amorphous compact layer next to the metal surface. The presence of this amorphous layer is the reason for the excellent corrosion resistance of the weathering steels[15]. The enhancement of phosphorus on the surface leads to the precipitation of iron phosphates as they are thermodynamically stable even at phosphorus contents as low as 0.2%[16]. Therefore, it appears that the presence of phosphorus is crucial to the corrosion

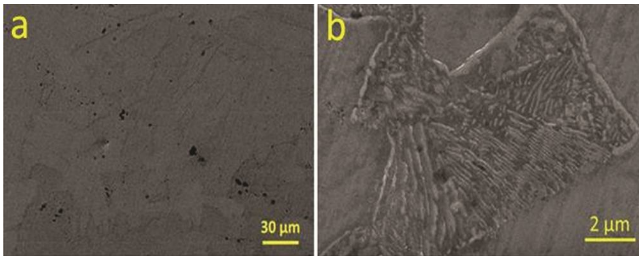
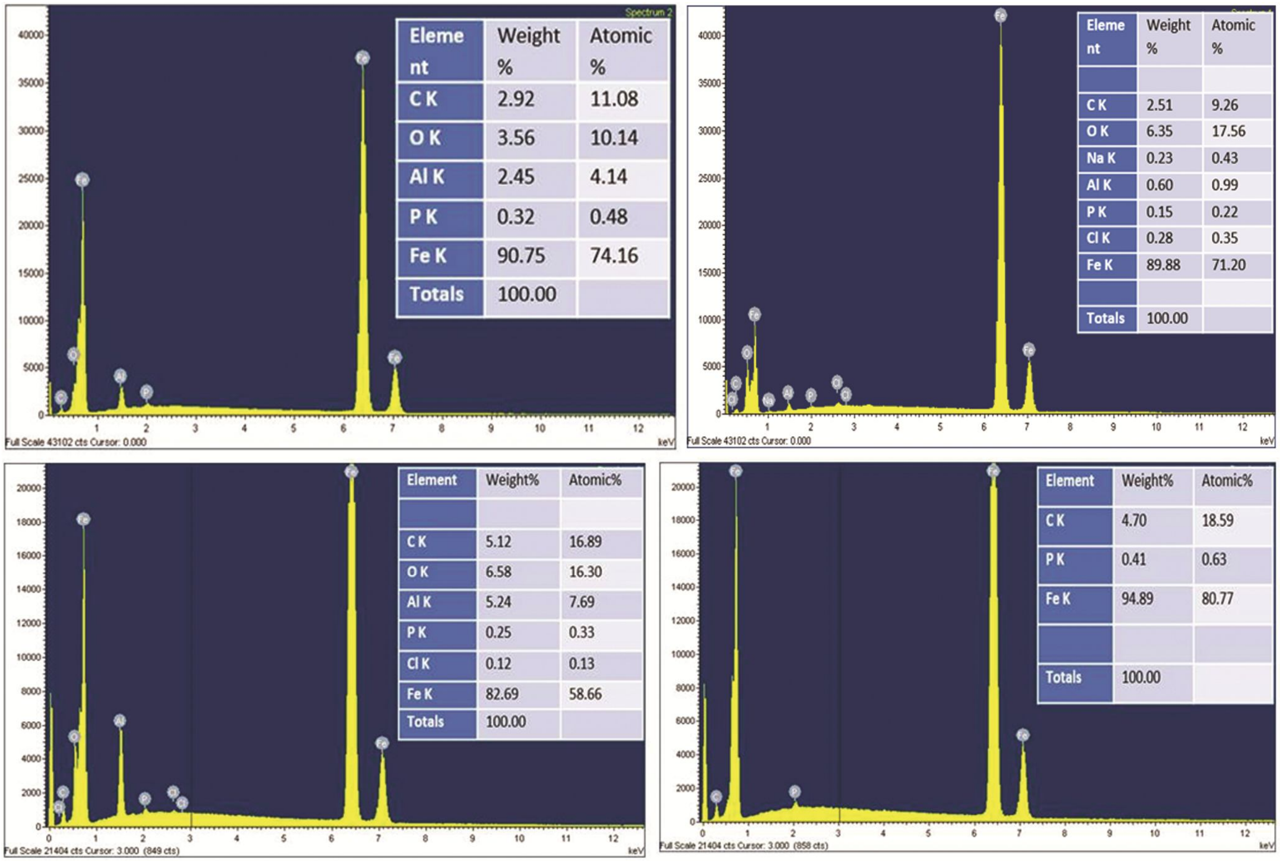


Fig. 3 — a) SEM image of the polished and etched section exhibiting a thin adherent oxide layer; b) showing sinuous (wavy) morphology pearlite structure, consists of the phases cementite (light) and ferrite (dark)



Element	Weight %	Atomic %
C K	2.92	11.08
O K	3.56	10.14
Al K	2.45	4.14
P K	0.32	0.48
Fe K	90.75	74.16
Totals	100.00	

Element	Weight %	Atomic %
C K	2.51	9.26
O K	6.35	17.56
Na K	0.23	0.43
Al K	0.60	0.99
P K	0.15	0.22
Cl K	0.28	0.35
Fe K	89.88	71.20
Totals	100.00	

Element	Weight%	Atomic%
C K	5.12	16.89
O K	6.58	16.30
Al K	5.24	7.69
P K	0.25	0.33
Cl K	0.12	0.13
Fe K	82.69	58.66
Totals	100.00	

Element	Weight%	Atomic%
C K	4.70	18.59
P K	0.41	0.63
Fe K	94.89	80.77
Totals	100.00	

Fig. 4 — EDS spectra of the sample surface depicting presence of phosphorus. Table shown as inset depicting the percentage of various elements.

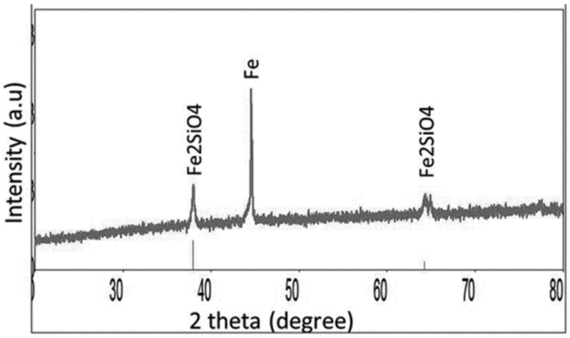


Fig.5 — X-ray diffraction pattern of sickle sample recorded for $2\theta = 20\text{-}80^0$

resistance of the ancient Indian iron.

XRD measurements analysis

Phase identification of the sample was done by using an advance fourth generation benchtop X-ray diffractometer. The sample was found to contain prominently of ferrite (ά-Fe) and iron silicate (Fe_2SiO_4) phase as depicted in Fig.5. These are confirmed by comparing the observed d-spacing with standard data (JCPDF no. 006-0696 and 044-1385). High intensity peak of ferritic iron (ά-Fe) indicates significant amount of iron in the matrix and hence its sound condition. At room temperature, pure iron is composed of a ferrite phase, which is an α iron body-centered cubic (BCC) unit cell. For pure iron manufacturing, iron ore is reduced to a spongy matter called bloom. This bloom is then hammered. The result is a heterogeneous, ductile, malleable, and easily welded material named 'wrought iron'. Second phase particles (slags) which had the composition of Fe_2SiO_4 (fayelite) are the results of extraction technique used for obtaining bloomery iron. Presence of iron silicate (Fe_2SiO_4) in the matrix is another characteristic feature of ancient Indian iron[10]. Both EDS and XRD observations are in good agreement with earlier studies on ancient Indian irons.

Conclusion

Surface morphology studies reveal no shape of corrosion on the surface of the sickle blade. Metallographic results show that sickle blade is made of hypoeutectoid steel consisting of ferrite, widmanstätten and pearlite structures. Elemental compositional analysis of the surface of as excavated sickle blade reveal that the purity of iron in the matrix is found to be about 92% along with high phosphorus content and slag particles (fayelite). It is important to mention here that the sickle blade produced approximately 800 years earlier than the Delhi Iron Pillar found to possess similar microstructures and compositional elements. XRD measurement revealed no iron oxide and iron oxyhydroxide phase which are responsible for corrosion. Hence the atmospheric corrosion resistance of the ancient Indian iron may be due to the formation of a protective passive film on the surface of the object that does not allow corrosion of the underlying metal. Thus, relatively high phosphorus content of the sickle blade play a major role in preventing the sickle blade from corrosion. The obtained results are in good agreement with the previous study and allowed to approach better the mechanism of corrosion resistance of phosphorous containing ancient Indian irons. This signifies that a considerable advancement on the technological point of view was available even before 2300 years ago in the particular region of civilization.

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