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Appendix 1

Metallographic Investigation of Iron Artefacts from EIA Cemetery at Vergina

by Effi Photos, Athens

Seven iron artefacts from Vergina (Lazarides and Malama tombs) excavated in 1970 by K Romiopoulou and presently at Veria Museum were sampled for analysis in January 1988. The objects included three swords, two knives, one spit and one arrowhead in a varying degree of preservation ranging from being substantially corroded (severe flaking) to containing a consolidated corrosion layer. No conservation treatment was undertaken prior to their storage in 1970.

A section was cut across the objects at or near the tip and, in one occasion, at the hilt. The sections were analysed a) metallographically, to establish the degree of steeling (extent of carbon content in the iron and the type of heat treatment the object had undergone) and b) chemically, by Electron Probe Microanalysis (EPMA) to determine the chemical composition of impurities in the metal (other than carbon which can be determined metallographically) and that of slag inclusions trapped in the metal. Chemical analysis is aimed at attempting to establish the type of iron ore and eventually its provenance.

Methodology

The sections were embedded in a cold setting resin, ground with a series of abrasive papers and subsequently polished with three different diamond pastes (6; 1; 1/4 microns). After polishing the samples were etched with 2 % nital and examined optically with the metallographic microscope. The same polished sections were examined chemically in the EPMA, a Cambridge Scientific Instruments Mark V attached to a Link 860 X-ray microanalyser, providing spot elemental analysis.

Analytical Results

I. Metallographic Observations

a. Swords

823. 9th c BC. Length: 75 cm without hilt (10 cm). Width (max): 5 cm. Extensively corroded and broken at two points: a) near the base of the hilt and b) 12 cm from the tip. Metallographic section was cut at 27 cm from the tip.

This section can be divided in two subsections consisting of the cutting edge and the dull edge. The dull edge is primarily ferritic, containing Neumann bands, the result of stress induced on the grains following cold working at temperatures below 500 °C. The section comprising the cutting edge consists of ferrite with pearlite at the grain boundaries (.15—.20 % C). Hardness: $Hv_{(100)} = 132$ (ferrite), $Hv_{(100)} = 158$ (ferrite and pearlite). It is possible that two sheets of metal, one of low carbon and the other of mild steel were forge-welded together in an edge to edge layering. However, there is no clear indication of slag stringers corroborating this fact. In addition, the "weld-line" over the entire length of the section is hardly straight. It is likely that this object was either produced from one piece of the bloom with uneven carbon content or that the same object got decarburised along one edge while at the forge.

833. 9th—8th c BC. Length: 39.5 cm. Width (max): 3 cm. Very good state of preservation. Metallographic section cut 9 cm from the tip.

This is the best preserved artefact. There is evidence for gradual decrease in carburisation from the cutting edge to the dull edge (from .40 % to .15 % C) displaying ferrite of widmanstatten structure (Fig. 49). This effect is the result of fast cooling in air. The cutting edge is ferrite and pearlite (.4 % C), the pearlite being partly spheroidised. Spheroidisation implies prolonged heating between 650—700 °C. The object must have been removed from the forge after having been exposed to the reducing environment of the hearth for some time to allow gradual diffusion of carbon into the blade. $Hv_{(100)} = 174—242$. Smooth gradient in carburisation implies good control of the reducing environment in the forge and suggests a high technical skill from the part of the smith.

853. Late 9th c — early 8th c BC. Length: 80.5 cm with hilt. Width (max): 4 cm. Two metallographic sections were cut, one 3.5 cm from the tip and another at the edge of the hilt.

Uniform carbon content and grain distribution of ferrite and pearlite throughout the section (.20 % C) with the exception of one edge (probably the cutting edge) characterised by elongated grains (Fig. 50) the result of cold working, a function which can impart hardness on the steel. Hardness: $Hv_{(100)} = 196$ (pearlite and ferrite). There exist some long slag inclusions but they are generally few.

853 hilt. The section consists of large equiaxial ferrite grains exhibiting age hardening, namely fine carbide which has come out of the ferrite as a result of prolonged burial. $Hv_{(100)} = 196$ (ferrite and pearlite). There exist small scattered slag inclusions, some of them elongated and consisting of two phases, an iron oxide and a glassy silicate phase.

It is clear that the hilt and blade are metallographically different; the hilt containing very little carbon and the blade containing not only a substantial amount thereof but also distributed in a gradient across the section.

Fig. 49. Sword Inv. Nr. 833. Ferrite grains of widmanstatten structure with pearlite. Scale 400 : 1

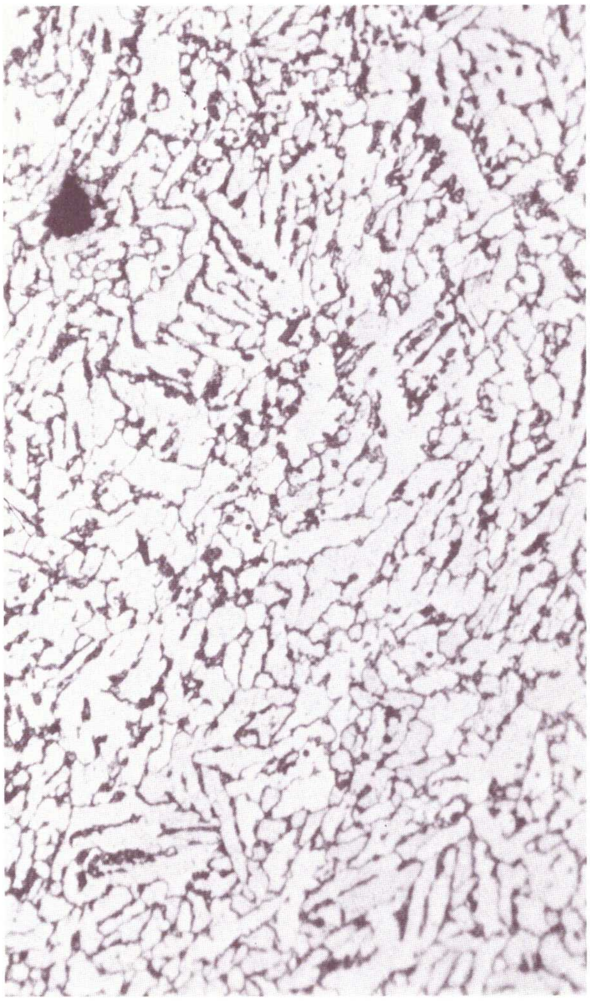

Fig. 50. Sword Inv. Nr. 853. Elongated ferritic grains with pearlite at the grain boundaries. Scale 200 : 1

b. Knives

988. Surface find[236]. Length: 18.5 cm. Width: 2 cm. Metallographic section cut 9.5 cm from the tip.

The section consists of ferrite with pearlite at the grain boundaries, pearlite being spheroidised. The degree of carburisation ranges between .10—.25 % C, while the grain distribution is quite uniform. Spheroidised pearlite is formed when steel is heated for a prolonged period below 700 °C. Heating took place in a well controlled reducing environment ensuring uniform carbon diffusion throughout the sample and equally uniform grain distribution. There exists a large number of slag inclusions, some elongated as slag stringers (Fig. 51). It is more likely that the blade was made from one single sheet of metal rather than two.

854. 9th—8th c BC. Length: 6.4 cm. Width (max): 1.5 cm. Metallographic section cut 9.5 cm from the tip.

The cutting edge consists of martensite produced from fast cooling by quenching into water. Moving towards the dull edge the structure changes gradually to ferrite and pearlite of the widmanstatten structure to a lower carbon area (.15—.20 % C). Martensite suggests quenching by fast cooling but whether this quenching was intentional or not is a matter of debate particularly since there is no evidence for similar structure in any of the other objects analysed here. $Hv_{(200)}$ = 324 (martensite), $Hv_{(200)}$ = 170 (pearlite). Large number of slag inclusions traverse, predominantly, the low carbon area.

c. Miscellaneaous

879. Arrowhead. 9th—8th c BC. Length: 3 cm. Width (max): 1.8 cm. Metallographic section revealed no remaining metal, due to its minimal thickness.

854. Spit. 9th—8th c BC. Length: 7.1 cm. Width: .5 cm. Metallographic section was cut 2.5 cm from one end.

Fine equiaxial ferrite. One corner of the section displays some degree of carburisation with evidence of widmanstatten structure but this is secondary and non

[236] Surface find from the same area of the Early Iron Age cemetery but not found during the excavation the report of which is presented here.

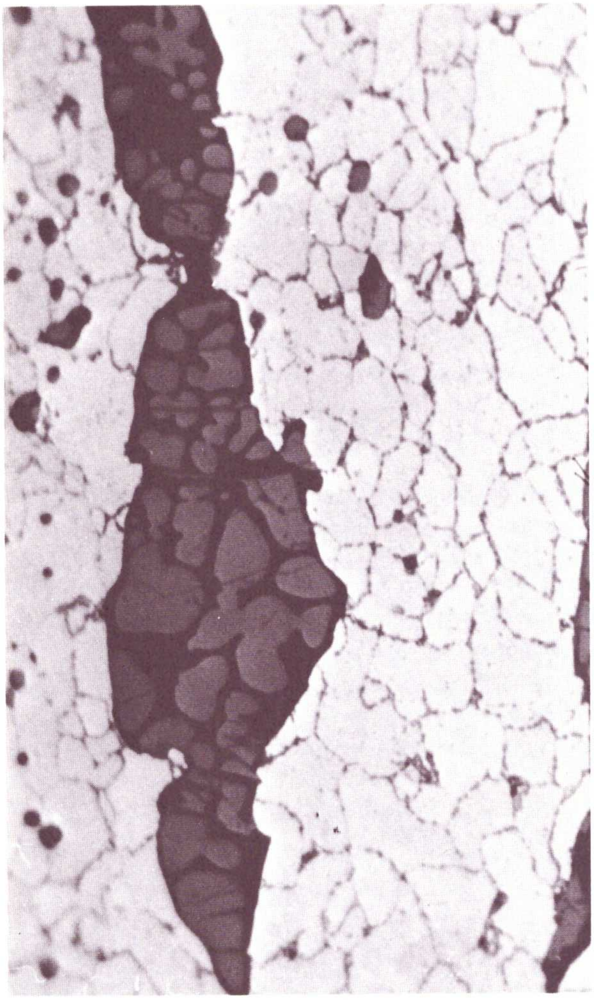

Fig. 51. Knife Inv. Nr. 988. Two phase slag inclusion in ferritic iron. Glassy matrix (dark gray), iron oxide dendrides (light gray). Scale 400 : 1

intentional. Slag inclusions are many, scattered throughout the section. No particular effort seems to have gone into removing them since the object could not have been considered functional. $Hv_{(100)} = 110$.

II. Chemical Analysis

Chemical analysis was carried out with the microprobe to establish the presence of impurities in the metal and the composition of slag inclusions (Fig. 51). The metal revealed absence of phosphorus or sulfur or other metallic elements apart from occasional traces of copper. The presence of traces of copper in the metal is not uncharacteristic and suggests that copper oxide, probably an accidental addition, made its way into the smelting furnace. Slag inclusions can originate either from the smelting cycle — they were never completely removed during the consolidation of the bloom — or during the smithing or in the forge-welding of two pieces of iron. In the latter, joining can be achieved with the addition of sand (SiO_2) which reacts with the oxidised surface of the metal (FeO) to form a slag ($2FeO.SiO_2$).

Table 1 presents the chemical analysis of the two common phases in slag inclusions (Fig. 51), namely iron oxide dendrites (wustite) and a glassy silicate matrix. The composition of these particular phases suggests that they could have arisen from either the smelting or the smithing stage. More important, they do not contain any characteristic trace elements which could direct the investigation to a particular type of ore body. They suggest a hematite/limonite type of ore, one that is widely available at any geographical region. Thus, at this stage of the investigation, it is rather difficult to establish whether the raw metal for the Vergina artefacts was produced locally or was imported.

Discussion

There exist very few published analyses of greek iron artefacts in relation to the plethora of iron excavated in sites post-dating the Mycenean period in Greece (Richardson 1934; Livadefs 1956; Varoufakis 1973; Conofagos and Papadimitriou 1981). Presently, this trend is beginning to reverse and a number of metallographic and chemical analyses of iron objects are currently underway (Photos 1987).

For a period of approximately twenty five centuries (10th c BC to 15th c AD), iron (wrought iron with less than .05 % C) was produced in Europe in small shafted furnaces (bloomeries) via the solid state reduction of iron ore in the presence of a reducing medium like charcoal. That meant that the iron (bloom) was at no stage molten (as is the case in the modern blast furnace) but only the slag was, id est the waste non-metalliferous material which separated from the metal by running to the bottom of the furnace.

As a result of the solid state reduction, the carbon content of the bloom far from being uniform was variable depending on the localised conditions of the furnace. Thus, the smith had to remedy the situation by choosing the right sections according to the type of object he intended to make as well as follow the correct heat

Table 1. Chemical composition of two phases in slag inclusions

phase	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO
wustite	0.38	0.30	0.36	0.12	0.05	0.00	0.00	0.78	97.04
silicate matrix	1.00	8.08	41.87	0.37	3.96	16.99	0.18	1.26	24.37

treatment to achieve the desired properties. In addition he would have to remove the remains of trapped slag which in the long run would act as corrosion nuclei while in the short run would be weak points in the metal fabric given their glassy nature[237].

Steel, an alloy of iron and carbon much harder than iron, contains carbon ranging between .1 and 1.8 % C. Hardness is enhanced if the alloy is cooled quickly from a high temperature in a medium like water or oil. Thus, for steel production both the right carbon content had to be present and the correct heat treatment had to be followed.

Some of the observations presented above in reference to the structure and properties of the iron-carbon alloy seem to have been suprisingly clear to the smiths of the Vergina objects as early as the 9th c BC. The choice of the raw material seemed to have been based on the type of object to be manufactured. Thus, for parts which were not clearly functional like the hilt of a sword (no. 853) and spits (no. 854) sections of bloom characteristic for their low carbon content (ferrite) were chosen. In addition, no effort was made to remove the large number of slag inclusions.

On the other hand, the blades of knives and swords were all chosen for their higher carbon content, although the amount barely surpassed that for mild steel (.5 % C). Often a gradient in carburisation, in decreasing order from the cutting edge to the dull edge, was evident (nos. 833, 854). The preferential carburisation of the cutting edge coupled with uniform grain distribution (nos. 853, 988) throughout the blade also point to a very adequate control of the reducing environment in the forge particularly when some objects seem to have been exposed to prolonged heating periods (spheroidisation in no. 988). In only one sample is there possible evidence for decarburisation (no. 823) in the hearth, the result of local oxidising conditions.

Controlled carburisation is one step towards making functional, good quality steel. The other is enhancing the hardness by the correct heat treatment. In only one occasion (no. 854) is there evidence for possible quenching of the Vergina artefacts (presence of martensite). The cutting edge of this knife seems to have been cooled with care. It is clearly not a case of the smith dipping the object in water just so that he can handle it. Nevertheless, the fact that martensite was absent in all other samples may suggest that hardening via quenching was not yet well understood. However, it is possible that examination of additional artefacts may disprove this preliminary observation.

At his stage of the investigation it is difficult to establish, on chemical grounds, whether the objects were produced locally or were imported. The mineralogy of the slag inclusions do not offer any clues as to a characteristic type of iron deposit other than the widely available limonite/hematite, while the presence of manganese in the slag and some traces of copper in the metal do not give many leads. Furthermore, the absence of slag samples and the presently inavailable information about local ore deposits do not make the task easier. The question will undoubtedly be elucidated in the future with the examination of additional artefacts, analyses of ores and the study of comparative material from other Macedonian cemeteries and settlement sites.

[237] These general observations and a host of other more detailed ones have arisen through the metallographic examination of ancient iron artefacts from various geographical regions in Europe and Asia and the experimental work on bloomery smelting of a variety of iron ores carried out by a number of investigators (Tylecote et al. 1971; Cleere 1972; Tylecote and Gilmour 1986; Tylecote 1987, to mention only a select few).

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