Ancient Monuments Laboratory
Report 52/96

METALLURGICAL STUDIES OF MISCELLANEOUS ARTEFACTS AND DEBRIS 1995

D Starley

Ancient Monuments Laboratory Report 52/96

METALLURGICAL STUDIES OF MISCELLANEOUS ARTEFACTS AND DEBRIS 1995

D Starley

Summary

A range of analytical techniques was used to investigate five different groups of material: iron nails from Peterborough Cathedral; non-ferrous nails from Plymouth Dockyard; vitrified stone from Lanercost Priory, Cumbria; and an experimental iron bloom and slag from Top Forge at Wortley, South Yorkshire.

Author's address :-

Dr D Starley
ENGLISH HERITAGE
23 Savile Row
London
W1X 1AB

METALLURGICAL STUDIES OF MISCELLANEOUS ARTEFACTS AND DEBRIS 1995

David Starley
Ancient Monuments Laboratory

Introduction

This report provides details of a number of studies of metal artefacts and debris from high temperature processes examined at The Ancient Monuments Laboratory during 1995.

	Page
1. Peterborough Cathedral, ferrous nails, metallographic examination	2
2. Plymouth dockyard non-ferrous nails, X-ray fluorescence analysis	5
3. Lanercost Priory, vitrified stone, visual identification	8
4. Experimental iron bloom, metallographic examination	9
5. Wortley Top Forge slag analysis, SEM based microanalysis	12

The Examination of Ferrous Nails from Peterborough Cathedral

Background

Three nails were submitted by Julian Limentani, Cathedral Architect to the Dean and Chapter of Peterborough for "analysis and dating". The nails had been removed from the east end of the nave ceiling where they were considered to be the oldest type. Because of the restricted benefits of such a study, the investigation was restricted to visual examination and metallographic examination of the tip of one nail only.

Macro Examination

Nail No. 3 was a hand forged clout nail of 6cm length with rectangular sectioned shaft, tapering from 6mm x 3.5mm to a point. The head had a maximum dimension of 16mm. The nail was superficially corroded.

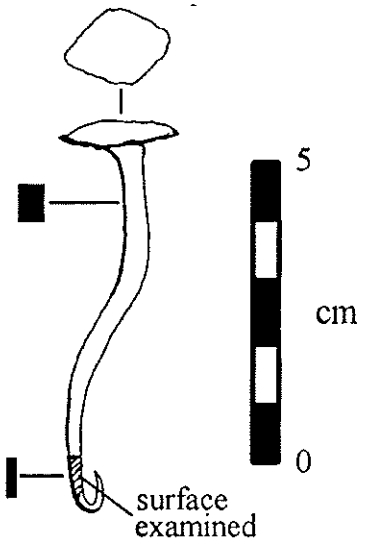

Figure 1.1
Peterborough Cathedral nail No. 3

Metallographic Preparation

No sample was removed. A small area near the point of the nail was prepared using standard metallographic techniques: grinding on successively finer abrasive papers then polishing with diamond impregnated cloths. The specimen was examined on a metallurgical microscope in both the "as polished", *i.e.* unetched, condition and after etching in 2% nital (nitric acid in alcohol).

Metallographic Structure

Viewed in the **unetched** condition dual phase slag stringers were seen to comprise 2% of the polished area. **Etching** in 2% nital revealed the grain structure to be entirely ferritic of very fine grain size (ASTM 8). The ferrite grains showed some evidence of phosphorus ghosting.

Interpretation of the Structure

The metallographic structure is that of a phosphoric iron. The lack of any carbon in the structure prevents any detail on any hot working / quenching being deduced. Without a significant carbon content such heat treatment would have provided little additional strengthening. The presence of small concentrations of phosphorus in the metal would have hardened it slightly, probably without significant embrittlement. It must be stressed that the mechanical properties required of nail making stock are not great and the phosphoric iron used in these nails would have been quite adequate for the task.

Dating

It is almost impossible to specify a date for such nails. **Typologically**, similar hand forged nails are known over a very wide period of time: from at least the Roman period through to (and probably beyond for specific purposes) the advent of the more rapid production of cut nails in the eighteenth century.

Analytically, the dating of ironwork is unpromising. Use of wavelength dispersive microanalysis techniques might detect high levels of sulphur deriving from coke smelting techniques. However, this fuel was not used until after the early eighteenth century.

An alternative approach would be to examine the iron to determine whether it was produced by the direct (bloomery) process or indirect (blast furnace and finery) process. Such dating, on **technological** criteria, presents difficulties on methodological and historical grounds. Firstly, both processes produced iron with wide ranges of compositions, but having similar structures *i.e.* heterogeneous with a large number of slag inclusions, such that there is no simple means of differentiating between materials from the two processes. A research project at the Ancient Monuments Laboratory is currently investigating this problem but much work, including extensive analysis, remains to be done.

However, even if it were possible to determine the technology of production, its value as a means of dating would be limited. In the United Kingdom, there is at least a *terminus post quem* for the production of iron by the blast furnace, which was introduced to the Sussex Weald in 1496. However, elsewhere in the country bloomery production continued until the eighteenth century. In Europe the period of overlap is much greater. Recent archaeological research at Lapphyttan in Sweden and the Jubach, Germany has shown early indirect production of iron, apparently from the thirteenth century. However, the products of more primitive methods of production competed on the European market until the nineteenth centuries, the best known example being iron from "Catalan hearths" in the Basque country of Spain. All three locations are known to have be important sources of iron for medieval and

post-medieval Britain. Therefore, knowing the technology of the process will not necessarily allow the determination of the age of these objects.

Finally, it should be mentioned that although it is theoretically feasible to date iron by the **radiocarbon dating** technique, there are a number of problems associated with the application of the method. These include the possible re-cycling of scrap iron and the use of coal-derived fuels (of geological age) at any stage in the production process. Moreover, extraction of sufficient carbon from iron artefacts, which is problematic under most circumstances, would be precluded by the extremely low levels of carbon in the phosphoric iron of the Peterborough nails.

Further examination

Given the limited potential of further work on the nails, this is not considered to be justified.

Qualitative Analysis of Non-Ferrous Roofing Nails from Plymouth Dockyard

Background

Nine copper alloy nails from the slate roofs of the 1838 Plymouth dockyard buildings were submitted for analysis by Sasha Barnes of Architectural Conservation Branch. It was hoped examination of the nails would help to determine whether the nails (and the slates which they held in place) were original or from a later refurbishment of the building.

Methodology

Small areas of the surface were cleaned with abrasive paper, to remove surface contamination and corrosion, then examined by X-ray fluorescence (XRF) analysis. Visual examination of the nails showed that most had been cast. Nail 951381 (see Fig. 2.1) appeared to have been mechanically cut and headed. The manufacturing origin of the largest nail (951380) was unclear although striations along the length suggested it had been wrought (or at least produced from rolled bar). No metallographic examination was carried out to confirm the method of manufacture.

Results

The results of the analysis are given in Table 2.1. The presence of elements are recorded as having been either strongly detected, weakly detected, detected or uncertain. These are based on the peak height of the fluorescence spectrum. It should be noted that peak height will not necessarily be proportional to percentage of element presence and the results are only able to give the type of alloy used:

951380 was a copper-zinc alloy containing a small amount of tin and a smaller quantity of lead. Probably best classified as a brass rather than a gunmetal.

951381 was copper of reasonable purity.

951382, 3 & 4 were of a similar composition of impure copper / low tin bronze (some of the impurity elements probably resulting from the use of unrefined copper rather than remelted scrap).

951385, 6, 7 & 8 were of low zinc brass (copper + zinc)
Some grey metallic deposit adhering to the tip of 951385 was found to be zinc. The purpose or reason for its presence (on a brass nail) is unclear.

With no comparative material it is not easy to say how closely these nails conform to the "mixed alloy nails" which are believed to have been specified in the original contract. However, one possible indicator of an early date for the nails is presence of small concentrations of nickel in nails 951382, 3, 4, 6 &7. This would not be expected in later nineteenth century artefacts (probably beyond 1880) as the element was extracted from copper.

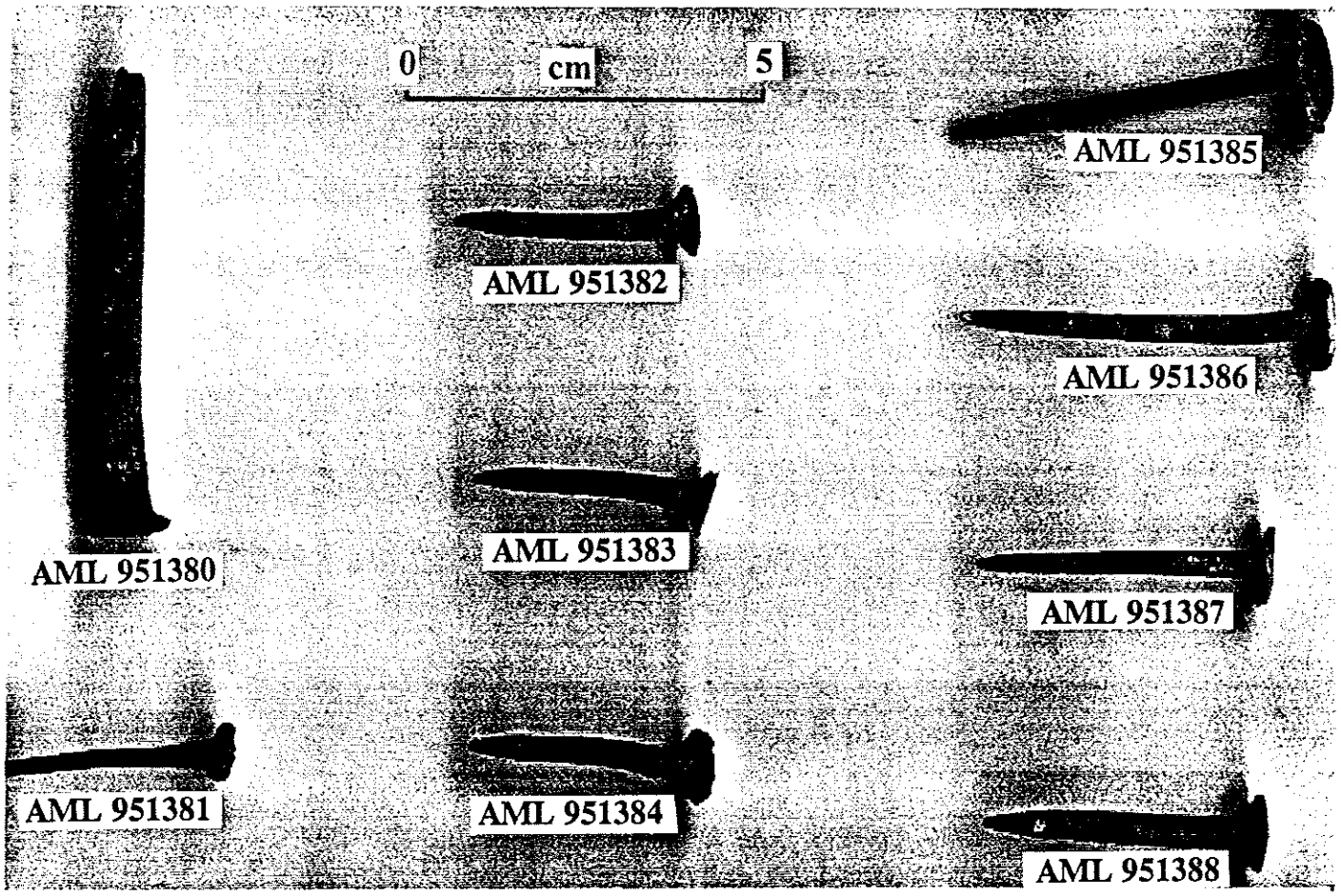

Fig. 2.1 Plymouth Dockyard Nails

Table 2.1 Analysis and Examination of Roofing Nails from Plymouth Dockyard

AML No.	Weight (g)	Shaft section	Manufacture	Elements detected by X-ray fluorescence analysis				comments
				strong	weak	detected	uncertain	
951380	15.64	square/rectangular	uncertain rolled bar?	Cu, Zn	Fe, Sn, Pb		Ca, As	brass
951381	1.82	irregular rectangular	mechanical	Cu	Fe, Pb			impure copper
951382	3.48	square	cast	Cu	Fe, Ni, As, Sn, Pb, Bi			impure copper
951383	3.67	square	cast	Cu	Fe, Ni, As, Sn, Bi			impure copper
951384	3.52	square	cast	Cu	Fe, Ni, As, Sn, Pb, Bi	Ti		impure copper
951385	6.28	rounded square	cast	Cu, Zn	Fe, Pb	Ca, Ti, Mn		brass
951385	(analysis of grey metal on tip)			Cu, Zn	Fe, Pb	Sn	As	zinc coating on tip
951386	6.24	rounded square	cast	Cu, Zn	Fe, Ni, Pb			brass
951387	3.65	rounded square	cast	Cu, Zn	Fe, Ni, Pb		Sn	brass
951388	5.15	round	cast	Cu, Zn	Fe, Pb		Sn	brass

Investigation of Possible Technological Debris from Lanercost Priory, Cumbria

Background

A glazed material of possibly twelfth to thirteenth century date from Trench 2 Context 2026 of the 1994 excavation of the priory (NGR NY 557637) was submitted by Alan Whitworth (English Heritage, Conservation North). The sample was examined visually and by X-ray fluorescence (XRF) analysis to determine whether it derived from a metal working process.

Results

Examination of the sample showed the base material to be a sedimentary rock, the surface of which had been vitrified at a high temperature, probably with alkali fuel ashes acting as a flux. This is a common reaction when fuel, heat and a strong blast of air (applied or naturally induced) occur in the presence of a siliceous material. Although it was thought possible that the sample resulted from some form of industrial process, qualitative XRF analysis failed to detect significant levels of elements such as copper, tin or zinc which might have linked the material to non-ferrous metal working. The vitrification is more likely to be an accidental product, for instance formed during an intense conflagration.

The Examination of an Experimental Iron Bloom

Background

A sample of a 6.5kg iron bloom produced in a reconstructed shaft furnace by John Anstee was submitted to the Laboratory by Leo Biek. A section of the sample measuring approximately 45mm x 20mm was prepared by mounting in cold-setting resin then grinding and polishing. Metallographic examination was carried out in both the as-polished condition (Plates 4.1&2) and after etching in 2% nital (Plate 4.3&4).

Results

Examination of the unetched sample showed it to contain up to 20% of large pores (Plate 4.1), but relatively few slag inclusions (Plate 4.2). These were restricted to a couple of discrete areas and were of a single dark grey phase.

Etching revealed an inhomogeneous, but generally high carbon structure containing a range of constituents;

Ferrite (50%) and pearlite in Widmanstätten morphology (Plate 4.4)

100% coarse pearlite and 95% pearlite + 5% grain boundary cementite (Plate 4.3), towards outer portions of the bloom.

100% ferrite (Plate 4.4), on surface only.

Metallurgical interpretation

Although the bloom had undergone some localised surface decarburisation, the overall carbon content was high, reaching hypereutectoid (greater than 0.8% carbon) composition, *i.e.* a high carbon steel, in places. Whilst such a composition is richer in carbon than most archaeological artefacts, such compositions are not exceptional and it is widely recognised that the operating conditions of most ancient bloomery furnaces could be manipulated to produce steels, although achieving a homogeneous product would have been difficult.

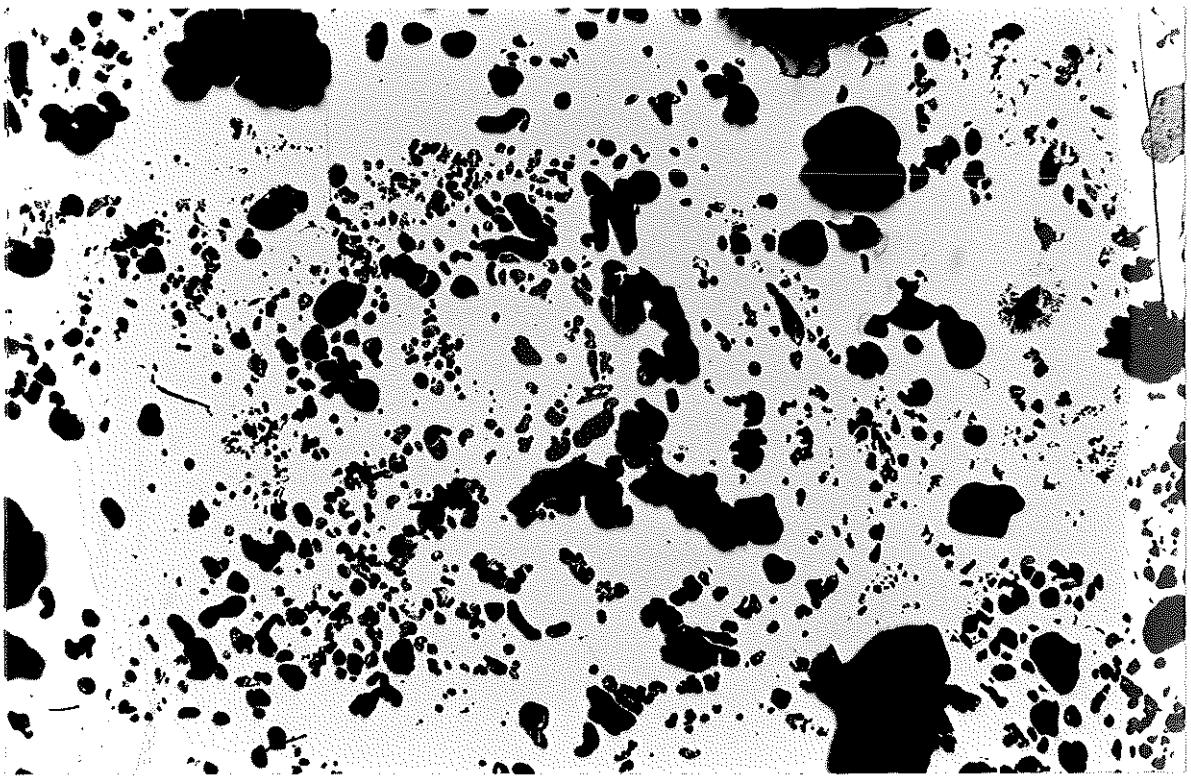

Plate 4.1 Micrograph of unetched bloom sample x15 showing high porosity

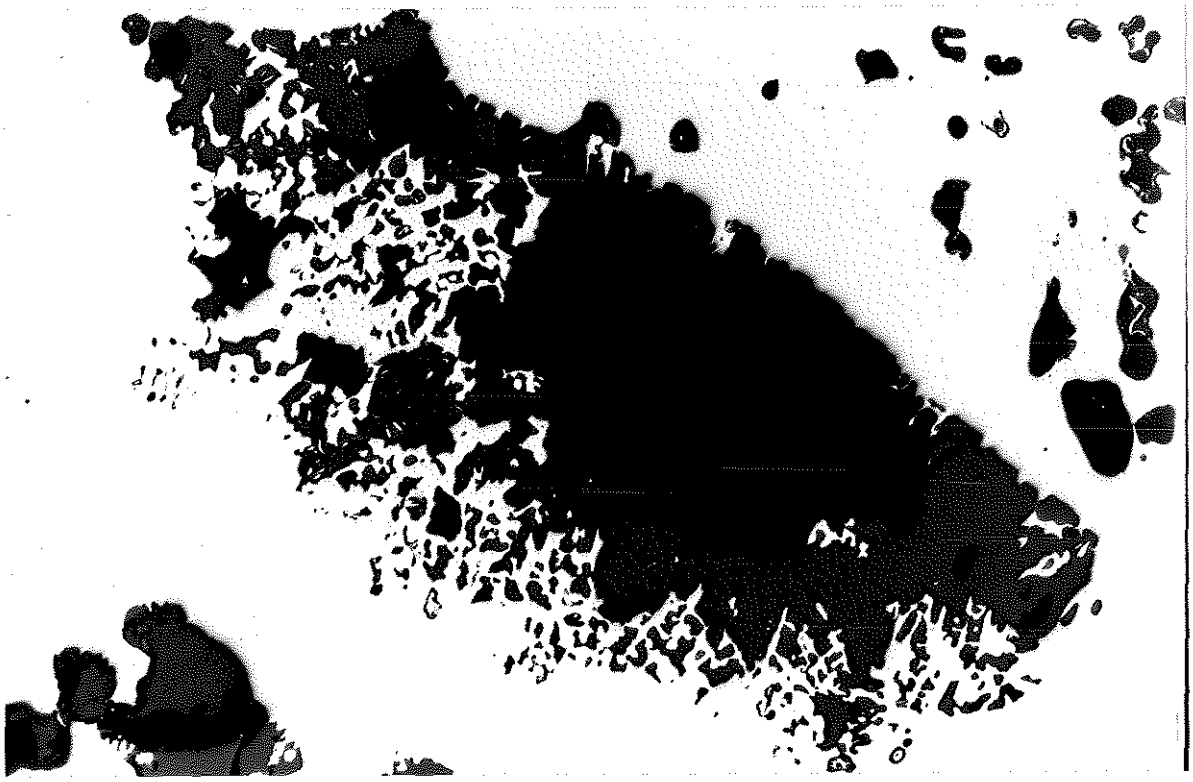

Plate 4.2 Micrograph of unetched bloom sample x50, showing large slag inclusion

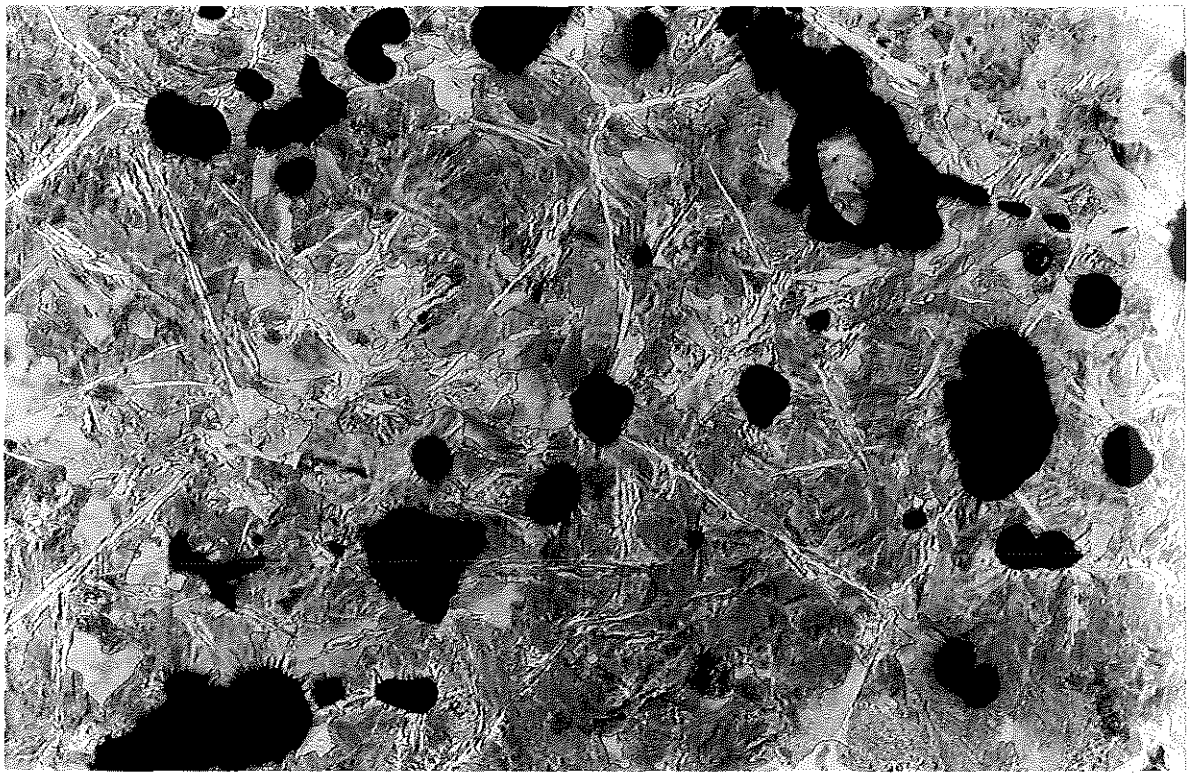

Plate 4.3 Etched bloom sample x50, high carbon (pearlite +cementite) structure

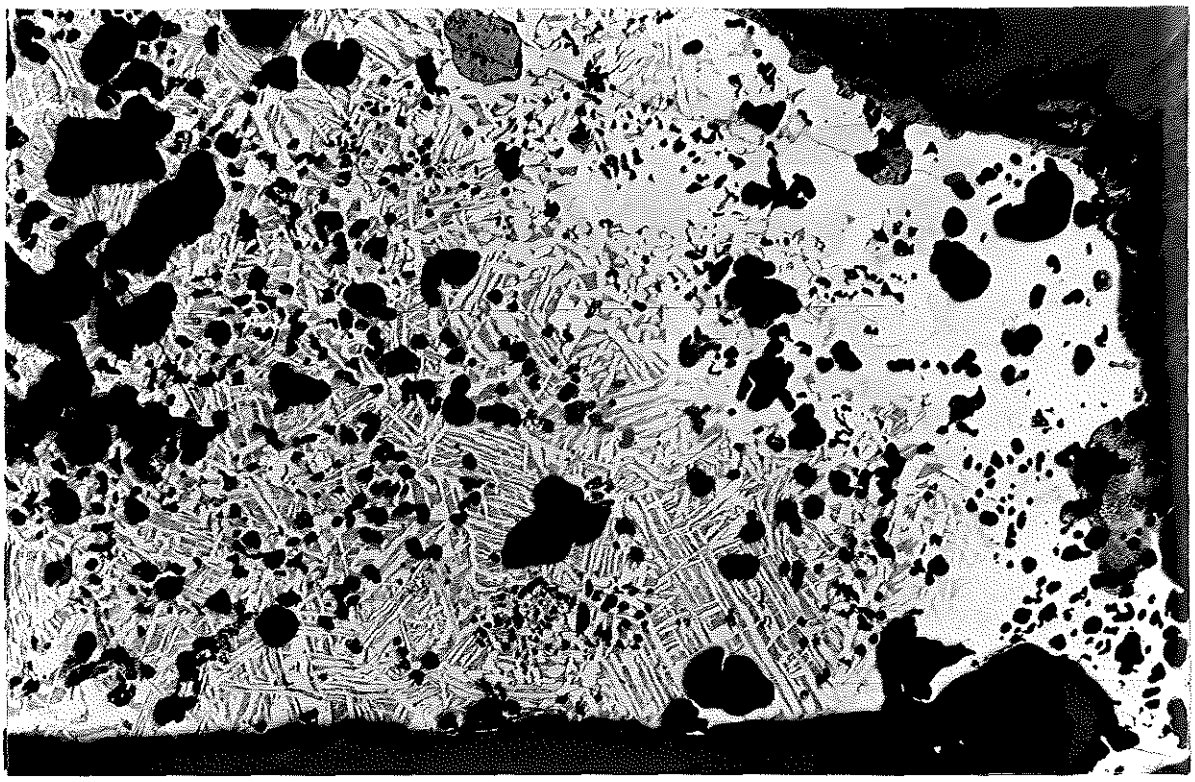

Plate 4.4 Etched bloom sample x15, widmanstätten and decarburised (ferritic) zones

Analysis of Slag from Wortley Top Forge, South Yorkshire

Background

A piece of slag from this historic site was submitted for analysis by David Crossley of Sheffield University. The earliest reference to iron working at Wortley[1] dates from 1621 and refers to iron smithies, but the estate also included a bloomery. By 1658 "Wortley forges" included fineries, a chafery and a hammer. It is believed[2] that in the late eighteenth century John Cockshutt introduced his patent method (patent no 988) for the manufacture of iron to the site, but that he later also introduced Cort's puddling process there. It is recorded[3] that work finally ceased on the site in 1912.

Sample Provenance

The sample was reported to have been removed from behind the tail race during consolidation of the site.

Methodology (preparation and analysis by T. Finney)

A piece of the sample was detached, mounted in conductive thermosetting resin then ground and polished to provide a flat surface for analysis. Microanalysis was carried out using a scanning electron microscope (SEM) with an energy dispersive X-ray (EDX) analysis system. Conditions for the analysis were 20 kV, 1500pA and a working distance of 25mm. Plate 5.1 shows an image of the sample in backscattered electron mode and locates the phases analysed in Table 5.1. In addition a bulk analysis of a larger area of the sample was made.

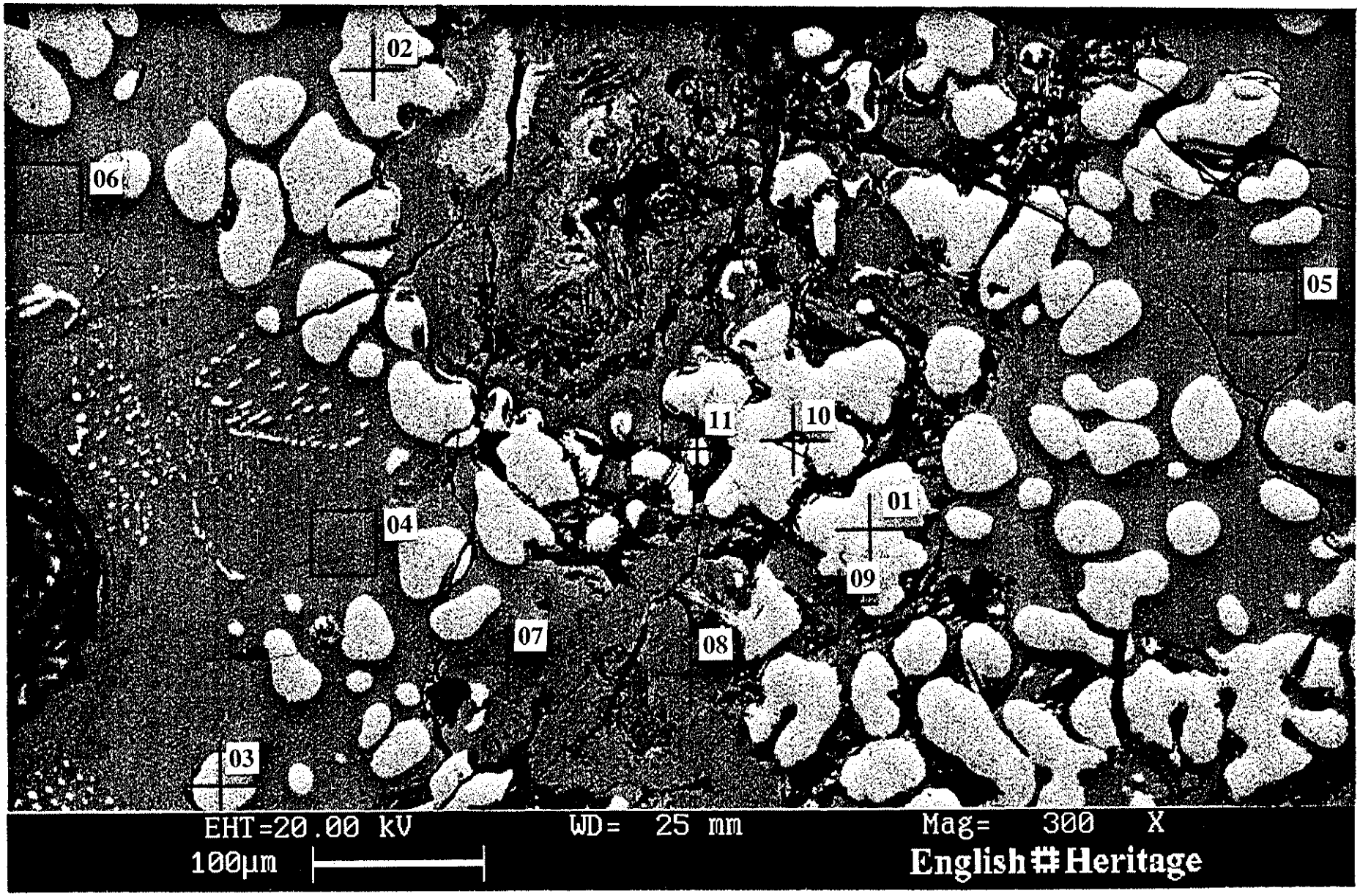

Plate 5.1 Backscattered electron image of Wortley slag showing points and areas of analysis

Table 5.1 Oxide wt% of phases in Wortley slag sample

analysis	feature	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	S	K_2O	CaO	TiO_2	MnO	FeO	spectrum
01	light coloured dendrite	0.8	0.0	0.8	0.5	0.2	nd	nd	0.1	0.5	1.2	96.0	wat/01
02	light coloured dendrite	0.8	0.1	0.8	0.3	nd	nd	nd	0.1	0.4	1.3	96.3	wat/02
03	light coloured dendrite	0.8	nd	0.4	0.5	nd	nd	nd	nd	0.2	1.5	96.7	wat/03
04	grey matrix	0.5	1.0	0.4	25.9	1.4	nd	0.1	0.6	nd	4.3	65.8	wat/04
05	grey matrix	0.7	0.3	0.3	22.3	0.9	nd	nd	0.3	0.1	3.7	71.4	wat/05
06	grey matrix	0.5	1.2	0.4	24.0	0.7	nd	nd	0.3	0.0	3.8	69.1	wat/06
07	light coloured dendrite	0.8	0.1	0.2	1.6	0.8	nd	0.0	0.0	nd	0.4	95.8	wat/07
08	light coloured dendrite	1.0	0.1	0.3	1.4	2.4	nd	nd	0.2	nd	0.4	94.3	wat/08
09	light coloured dendrite	1.0	0.2	0.2	2.6	7.8	nd	0.1	0.2	nd	0.3	87.6	wat/09
10	light coloured inclusion	0.9	0.1	0.1	0.1	0.1	nd	nd	0.1	0.1	nd	98.4	wat/10
11	light coloured inclusion	0.8	0.1	0.1	0.2	0.1	nd	nd	0.1	0.1	nd	98.7	wat/11
12	bulk specimen	0.6	0.3	1.0	11.3	2.3	nd	0.1	0.9	0.3	2.2	80.8	wat/12

nd = not detected

Interpretation

The structure predominantly comprises wustite (FeO) dendrites in an impure fayalitic ($2FeO.SiO_2$) matrix. Occasional inclusions of purer iron oxide were also identified, perhaps resulting from partly reduced iron scale.

Sulphur contents below the limit of detection may indicate that the debris derived from a process using charcoal rather than coke. However, the compositions of bloomery, finery and puddling slags overlap to such a degree that it is not possible to distinguish from which process this sample derives.

References

1. Barraclough, K. C., Top Forge, Wortley *Bull HMG* 4.2 (1970) p83.

2. Morris, J. pers comm (arch-metals) electronic mail base, 10/6/96.

3.Barraclough *op sit.*