Why pay more? An archaeometallurgical investigation of 19th-century Swedish wrought iron and Sheffield blister steel

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ABSTRACT: For their best quality steel, Sheffield cementation steelmakers preferred iron from a small number of finery forges in Sweden and were prepared to pay a premium price for it. This study aimed to determine whether there was a scientific explanation for the steelmakers' preference. The abundance and composition of slag inclusions from 10 samples of premium and common grades of Swedish wrought iron and 10 samples of blister steel made from both grades of iron were compared. The samples were analysed using optical and electron microscopy, SEM-EDS, quantitative metallography and, where possible, bulk chemical analysis. Analysis found that premium brands of wrought iron had a lower volume of slag inclusions and a higher proportion of wüstite within the inclusions. These characteristics meant that the premium brands of wrought iron would give a 'cleaner' blister steel. The results suggest that Sheffield cementation steelmakers had a valid reason for paying more for premium brands.

Introduction

The main aim of this study has been to determine whether there was a scientific explanation for Sheffield steelmakers' preferences, or whether their choices were based on conservatism. The approach taken has been to investigate the abundance and composition of slag inclusions in Swedish wrought iron to see if any differences exist between the cheap and expensive brands, and to see if these differences are reflected in the blister steel. The study was not intended as a characterisation of finery iron or blister steel, and focused on areas of difference rather than of similarity.

The choice of samples for analysis was dictated largely by the availability of the material. Although archaeologically the metal is relatively young, it is already rare. Bars of Swedish wrought iron and blister steel can be regarded as material in an intermediate stage of production. The Swedish wrought iron bars were brought to Sheffield specifically for conversion into blister steel. The blister steel bars would then have been reheated and worked into finished products, or broken into small pieces to be melted down to make crucible steel. Both the wrought iron and steel were relatively expensive and it seems unlikely that large numbers of bars would have been left lying around, even after the advent of new technologies or the closure of works. This may explain why it is very unusual to find wrought iron or blister steel bars in their original state, and why recent excavations of cementation and crucible steelmaking sites in Sheffield have found little in the way of wrought-iron or blister-steel bars.

The cementation process

In the cementation process, bars of wrought iron were packed in layers interspersed with charcoal in large refractory chests. The chests were then sealed, and heated for several days at around 1100˚C. With the gradual heating and cooling of the furnace, a typical firing or 'campaign' would take up to four weeks to complete. During the process, the bars stayed in a solid state and would slowly absorb carbon by diffusion from the surrounding charcoal. Because of the way carbon diffuses during cementation, the carbon content of blister steel generally decreased towards the centre of the bars. The traditional term used to describe this low-carbon region was 'sap'. The degree of carburization was controlled by the time and temperature of the firing. During cementation, the reducing atmosphere caused the oxide component of the slag inclusions within the bars to react with carbon, forming carbon monoxide. The pressure of this gas within the metal would open up voids and some of these appeared as blisters on the surface of the bars, giving the steel its name. Within Sheffield, cementation steelmaking was also known as 'converting'.

Swedish ironmaking for the Sheffield market

From the 16th century through to the middle of the 19th century, the iron industry in Sweden was highly regulated (Rydén and Evans 1995; Eriksson 1987). Swedish bar iron was produced within a strict quota system that limited the production of individual forges. Forges were issued with brand marks; these were stamped on to bars before they left the forge, and this meant that inferior-quality iron could be traced back to the producer. These brand marks are invaluable for dating and provenancing bars. Archive copies of 19th-century catalogues of Swedish iron brand marks (*Stampelboks*) sometimes give details of individual forges, such as the finery method used, the date that marks were registered, and the annual permitted production of the forges.

The high-quality wrought iron produced by the Swedish Walloon finery forges made ideal feedstock for cementation furnaces. 'Nobody has so far succeeded in making blister steel with the combination of all the desired properties from any kind of wrought iron other than the Walloon iron' (Andersson 1767, 176).

The most prestigious brands of Swedish wrought iron were all made using magnetite ore from the Dannemora mine; this was a particularly iron-rich ore with a relatively high manganese and low phosphorus and sulphur content (Eriksson 1987, 14). Walloon iron was also known as Dannemora iron or Oregrund iron as the iron was shipped through the port of Oregrund.

The Walloon Forge (WF)

The Walloon forge consisted of three basic elements: a finery hearth in which cast iron was decarburized to form a bloom of malleable iron, a water-powered hammer for consolidating the bloom and shaping it into finished bars, and a chafery hearth to reheat the bloom and bars during forging. The finery hearth itself was a relatively simple design; a general view of a typical Walloon finery hearth is shown in Figure 1.

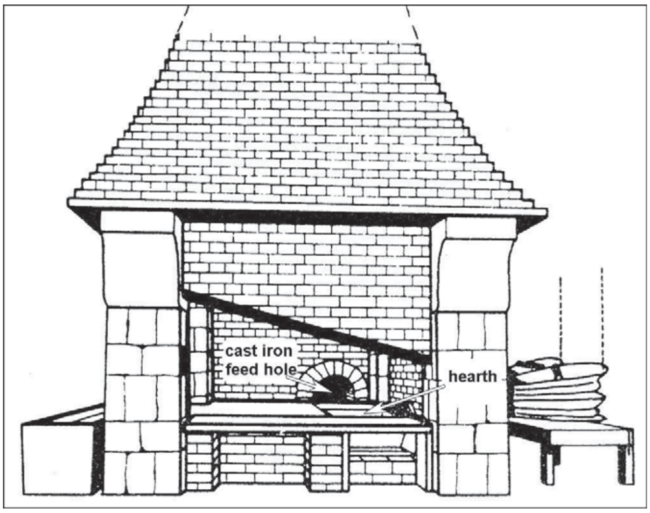

Figure 1: General view of Walloon finery hearth (after den Ouden 1981, 67).

Charcoal was used as fuel and cast-iron 'sows' were fed into the hearth using a system of rollers. As the end of the cast-iron sow melted, drips of iron would fall through the charcoal and pass through the oxidizing zone in front of the tuyère(s). The hearth itself, where the iron collected, was a rectangular well, measuring around 650mm long, 450mm wide and 300mm deep (den Ouden 1981, 69). A pool of liquid slag was maintained in the bottom of the hearth to protect the re-melted iron from further oxidization. The fining process itself produced only a small amount of slag, so the slag pool was created in the first instance by adding lumps of blast-furnace slag, hammerscale and sand. The hearth was lined with cast-iron plates which protected the brickwork of the structure from the slag.

Although no historical records of the operating temperatures for Walloon finery hearths exist, previous researchers have suggested that the melting zone of finery hearths lies within the range 1300°C to 1350°C (Barraclough 1991, 310) with a maximum temperature of 1450°C directly in front of the tuyère (Morton and Wingrove 1971, 25). As Walloon hearths were not enclosed, and used a cold air blast (Percy 1864, 600), it seems likely that they operated at the lower end of this temperature range.

The Swedish Lancashire finery hearth (SLH)

As the demand for bar iron and the cost of charcoal in Sweden rose, iron-makers began to look at ways to reduce charcoal consumption and increase output. Problems with charcoal shortages had been encountered in England early in the 18th century and this had led to the development of more fuel-efficient finery hearths (Tylecote 1991, 240). In 1828, the Swedish ironmaster Gustav Ekman visited a British ironworks at Ulverston in Lancashire, where he saw Lancashire finery hearths in use. Aware of their potential, Ekman returned to Sweden and built copies of the hearths in his works at Dormsjo and Sodefors (den Ouden 1981, 80) The 'Swedish Lancashire hearths', as they came

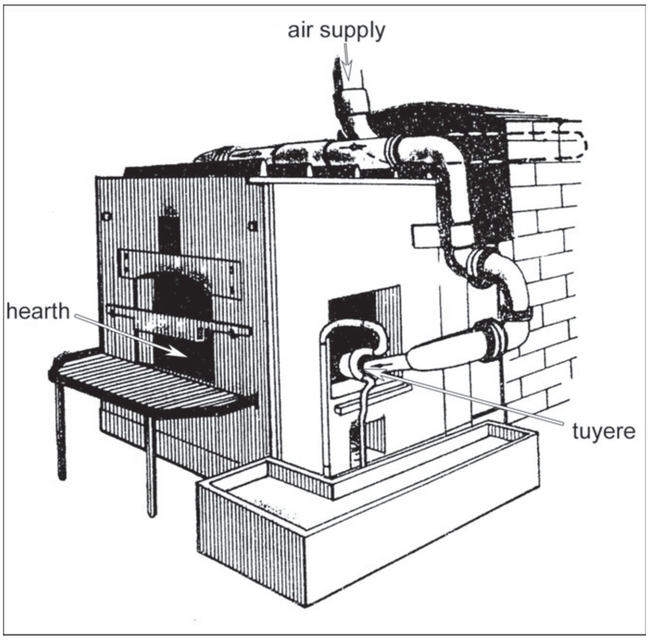

Figure 2: Swedish Lancashire Hearth (after den Ouden 1981, 73).

to be known, were more productive and fuel efficient than the Walloon fineries (Percy 1864, 596–601), and they had the potential to take advantage of increases in blast-furnace output. As early as 1830, Daniel Doncaster sold blister steel made from Swedish Lancashire Hearth iron at about 60% of the price of blister steel made from premium Walloon Finery iron (Barraclough 1990, 16), demonstrating steelmakers' interest in cheaper alternatives to the latter. However, even after the widespread adoption of the Swedish Lancashire hearth, the best qualities of steel continued to be made using Walloon Finery iron.

In principle, the Swedish Lancashire hearth operated in very much the same way as the Walloon hearth, with cast iron being drip melted and decarburized in front of the tuyère(s). However, there were differences in the design and operation of the hearth that improved its efficiency. Figure 2 shows an illustration of a Swedish Lancashire hearth from the middle of the 19th century. The most obvious difference in the design is that the hearth itself is almost completely enclosed within a cast-iron box. The draught for the hearth was induced by a tall chimney (not shown in Figure 2), which had a damper to control the temperature in the hearth.

Although the early hearths used cold blast, it was soon realized that air could be pre-heated by running the supply pipe along the inner roof of the hearth. The resulting reduction in fuel consumption meant that by the middle of the 19th century all the Swedish Lancashire hearths were using hot blast, often delivered using two tuyères, one on each side of the hearth.

Rankings of Swedish iron by Sheffield steelmakers

Previous archaeometallurgical investigations into the quality of wrought iron (Gordon 1984 and 1988) have studied the material from an iron-worker's perspective, rather than as a raw material for cementation steelmaking. Assessing what made a good quality iron for cementation is difficult, as characteristics that are important to an ironworker or end user of wrought iron may not be as relevant to the steelmaker, and vice-versa.

Sheffield steelmakers invented their own terminology to describe the qualities they were looking for. Professor Le Play, who visited Sheffield in 1836 and 1842, described the problems with interpreting terms such as 'body', 'sound', 'strong' and ' tough' (Le Play 1843,178). While these expressions had precise meanings that were perfectly clear to the steelmakers, they found it difficult to explain them to a layman, and Le Play concluded that the price of the iron was the best guide to its quality, implying that a steelmaker would not pay the extra cost without a good reason.

Table 1 shows the categorization of Swedish irons into premium, second rank and common grade, based on listings provided by visitors to Sheffield in the 1840s (cited

Table 1: Ranking of Swedish wrought irons in the 1840s (after Barraclough (1984 and 1990).

Ranking	Forge	Fining Method	Price per ton in 1843 (£)
Premium			
	Leufsta	WF	35.0
	Carlholm	WF	35.0
	Gimo	WF	31.0
	Osterby	WF	30.0
	Ranas	WF	31.0
Second Rank			
	Alfkarleo	WF	21.0
	Soderfors	Forge converted to SLH	18.0
	Gysinge	WF	27.0
	Wattholma	WF	26.0
	Forsmark	WF	28.0
	Skebo	WF	25.0
	Backefors	SLH	18.5
	Lesjofors	SLH	Not listed
	Stromsberg	WF	28.0
	Ullfors	WF	28.0
Common Irons (not all shown)			
	Norberg	SLH	17.5
	Sanna	SLH	15.0
	Thurbo	SLH	15.5
	Avesta	SLH	15.0
	Fagertsa	SLH	14.5
	Larsansjo	SLH	13.0

in Barraclough 1990). Interestingly, some of the Swedish Lancashire Hearth forges are ranked above Walloon finery forges. These rankings were not static; iron from the Carlholm forge that was listed as a premium brand in the 1840s had fallen to a second rank brand by the 1860s, perhaps reflecting problems in quality control at the forge.

Barraclough (1990, 14) discusses the characteristics of wrought iron that were important to cementation steelmakers: he mentions how historical sources continually refer to 'the somewhat indefinable characteristic of "body" in the Oregrund [Walloon Finery] irons'. Barraclough went on to suggest that the term might have described a 'fine-grained structure with a well-disseminated pattern of fine slag streaks… and a resistance within the bar to decarburization when reheated for forging operations'. However, as he did not have access to samples of Walloon Finery iron, he was unable to confirm this view.

The importance of the volume of slag present in the wrought iron depended on the final use of the blister steel. In blister steel that was to be broken up and melted in crucible furnaces, a low slag content was of lesser importance, since melting 'would release it from the metal and it could be prevented from entering the ingot' (Barraclough 1990,19). However, for trades where artefacts were made from rolled blister steel or forged shear steel, the volume of slag remaining in the steel was of critical importance for the finish and performance of their products. Contemporary authors noted that one of the problems associated with blister steel was that the amount of slag present was not apparent from visual inspection of the bar, or even the rough finished articles. It only became visible during the final manufacturing stages of machining and polishing. Cutlers making high-quality items such as knives could reject over a third of their production due to slag streaks, incurring considerable cost (Le Play cited in Barraclough 1984, 182; Crookes and Röhrig 1870, 213).

Given the difficulty of interpreting historical preferences, it seems sensible to work instead from first principles. From the results of cementation experiments conducted by one of the authors (RM), the properties in wrought iron that appear to be most important for production of good quality cementation steel are:

- a low volume of slag
- easily reducible slag
- what slag is present should be finely disseminated through the material
- an even ferritic microstructure.

The samples

The samples of Swedish wrought iron and blister steel used for this study are listed in Table 2. Historical documents were used to trace brand marks (where present)

Table 2: Swedish wrought iron and blister steel samples examined.

Sample Number	Material	Fining Method	Brand	Ranking	Source
S1	wrought iron	Swedish Lancashire Hearth	LG	Common	Excavation of former Jessop's steelworks.
S2	wrought iron	Swedish Lancashire Hearth	LG	Common	Excavation of former Jessop's steelworks.
S3	wrought iron	Swedish Lancashire Hearth	LG	Common	Excavation of former Jessop's steelworks.
S4	wrought iron	Swedish Lancashire Hearth	LG	Common	Excavation of former Jessop's steelworks.
S5	blister steel	Walloon Finery	JB&Crown	Second	Private collection
S6	blister steel	Swedish Lancashire Hearth	DU	Common	Private collection
S7	blister steel	Swedish Lancashire Hearth	DU	Common	Private collection
S8	wrought iron	Swedish Lancashire Hearth	DGL	Common	Private collection
S9	wrought iron	Walloon Finery	Hoop L	Premium	Sheffield Industrial Museums Trust
S10	wrought iron	Walloon Finery	GL	Premium	Sheffield Industrial Museums Trust
S11	wrought iron	Walloon Finery	JB&Crown	Second	Sheffield Industrial Museums Trust
S12	wrought iron	Walloon Finery	OO	Premium	Sheffield Industrial Museums Trust
S13	blister steel	Walloon Finery	Hoop L	Premium	Sheffield Industrial Museums Trust
S14	blister steel	Swedish Lancashire Hearth	DGL	Common	Sheffield Industrial Museums Trust
S15	blister steel	Walloon Finery	Hoop L	Common	Sheffield Industrial Museums Trust
S16	blister steel	Walloon Finery	GL	Premium	Sheffield Industrial Museums Trust
S17	blister steel	Swedish Lancashire Hearth	LG	Common	Experimental conversion of iron from Jessop's steelworks
S18	blister steel	Swedish Lancashire Hearth	LG	Common	Experimental conversion of iron from Jessop's steelworks
S19	wrought iron	Walloon Finery	GL	Premium	Osterbybruk museum, Sweden
S20	blister steel	Walloon Finery	GL	Premium	Osterbybruk museum, Sweden

to individual forges and in most cases the documents also gave information on the type of finery hearth used by each forge. The samples represent a broad range of qualities of bar iron and blister steel.

Finery iron is characterized by its variability and relatively high abundance of non-metallic inclusions. In theory, two samples removed from the same wrought-iron bar can differ substantially in the amount and distribution of both carbon and inclusions. To assess the variability of the material, it was originally intended to take several samples from each bar. However, because of the small size of some of the excavated bar fragments, and sampling conditions imposed by museums and private collections, this could only be done on the two 'full length' bars recovered during the excavation of Jessop's steelworks at Brightside; the pairs of samples from these bars are numbered S1, S2 and S3, S4.

The author converted two samples of SLH finery iron (samples 17 and 18), to increase the number of blister-steel samples and to observe the effects of cementation on Swedish finery iron. The samples were taken from the same wrought-iron bar as samples 1 and 2. Where possible, the experiment used the same materials as the Sheffield process, though modern furnaces and refractory containers were used.

Experimental methods

A combination of optical microscopy, scanning electron microscopy (SEM), microanalysis using energy-dispersive spectrometry (EDS), quantitative metallography and, where possible, bulk chemical analysis were used to answer the key questions raised by this research.

Quantitative analysis was performed on most of the samples listed in Table 2, using: backscattered electron imaging (BSE) in the SEM to produce composition-dependent images of slag inclusions; EDS for the microanalysis of areas of slag inclusions within the bars, and of individual phases within inclusions; and quantitative metallography to determine the volumetric proportion of slag in each sample and the proportions of phases within some of the inclusions for the wrought iron samples. Samples 16, 19 and 20 were obtained at a late stage in the project and it was not possible to perform SEM-EDS analysis on them.

Bulk chemical analysis was carried out using inductively coupled plasma emission spectrometry (ICPES) and a Leco analyser. Because of sampling restrictions imposed by museums, bulk chemical analysis was generally only possible on archaeological material. Where bulk chemical analysis could not be used, the carbon content of the samples was estimated using optical microscopy.

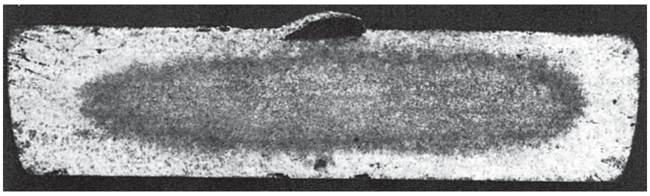

Figure 3: Etched cross-section of a blister-steel bar showing a high-carbon 'envelope' surrounding the lower-carbon centre. Note that this is a negative image, so high-carbon areas appear lighter than low-carbon areas. Scale: 4:3 (Barraclough 1984, plate 3c).

Sample preparation for microscopy

Because of the heterogeneous nature of both the wrought iron and blister steel, it was felt that the best approach would be to remove a transverse section from the bars. Barraclough and Kerr (1973, 470) used a full transverse section in their analysis of a blister-steel bar, and their illustration of the section is useful in demonstrating both inclusion abundance and carbon distribution through the width and depth bar. The etched surface of the same bar is also shown in Barraclough 1984 (pl 3c) and this has been reproduced as Figure 3.

Bars from private and museum collections were sampled so as to remove the minimum amount of material necessary to obtain a full cross-section. With irregularly shaped pieces of bar, removing a full cross-section would have led to an unacceptable loss of material, so the cut was placed to remove as near to 50% of the cross section as possible.

The samples were prepared for analysis following the methods described by Vander Voort (1999). Some of the inclusions within the samples may have been damaged or lost as a result of the grinding and polishing stages of preparation. This is potentially more of a problem in blister steel samples because of the voids opened up during cementation. Any slag remaining in the voids may not be attached to the metal strongly enough to withstand grinding and polishing. However, as all samples were prepared in the same manner, losses should be similar between samples.

Optical microscopy and quantitative metallography

Optical microscopy was used to evaluate microstructures and estimate carbon content. A reflected light microscope equipped with digital camera and PC with image-grabbing software was used for capturing digital

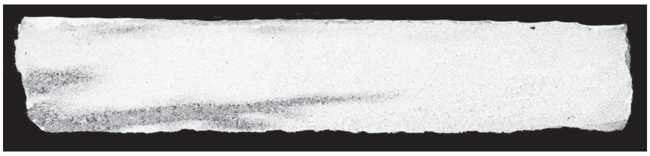

Figure 4: Etched cross-section of wrought-iron bar (sample 1); dark areas are high carbon. Scale 1:1.

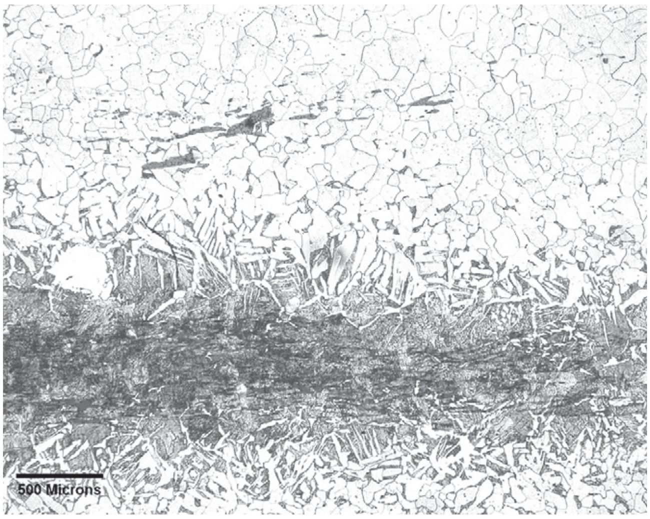

Figure 5: Band of pearlite (dark) within wrought iron (sample 1). Note size and distribution of slag inclusions within top half of the image.

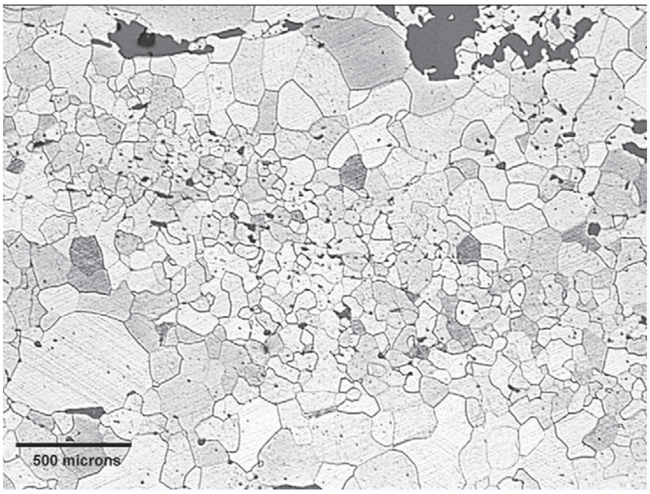

Figure 6: Typical variations in grain size within wrought irons as shown in sample 6. Note size and distribution of slag inclusions (dark grey).

images, which were then used for quantitative metallography. This has been used in two ways: firstly to determine the total volume of slag inclusions present in each sample and secondly to calculate the proportion of phases in the two-phase inclusions within the samples of wrought iron.

The volume fraction of slag inclusions present in each sample was determined by point counting. The interval between points was set to give an even distribution of points across the average full-width cross-section; typically, 500 points were counted for each sample.

Image analysis was used to determine the relative proportions of phases within two-phase inclusions in the wrought-iron bars. Backscattered SEM images were analysed using Zeiss KS400 (version 3.0) computer software. The program uses contrast differences in the image to identify particular phases within an inclusion; the software then calculates the relative volume of the phase of interest by counting the number of points found within each phase.

EDS analysis

Because of the heterogeneous nature of inclusions in wrought iron, Rostoker and Dvorak (1990, 164) recommend analysing ten different slag inclusions in each sample. However, because of time and cost constraints, it was not possible to achieve this for all samples and a minimum of eight inclusions was analysed. To avoid bias the inclusions were initially chosen at random from different areas of the cross-section. The only condition was imposed by the interaction volume of the electron beam; for EDS this is typically 3μm so the inclusions had to be larger than this. As research progressed, a decision was made to focus on two-phase slag inclusions in unconverted bars and about 80% of the inclusions selected for analysis were of this type. The two-phase inclusions contain wüstite, together with fayalite or glass. Single-phase inclusions did not contain wüstite, so would not be so readily modified during cementation. The inclusions were still selected from different areas of the cross-section, to avoid sampling large slag stringers twice.

During analysis, the operating conditions of the SEM were set as follows: Accelerating voltage: 20kV; working distance: 30mm; tilt angle: 0°; take-off angle: 30°; beam current: around 500 nA, adjusted to give a count rate of 2500–2800 per second; analysis time: 60s.

As the inclusions were composed of predictable elements, these settings were selected to avoid having to re-adjust the microscope settings when moving between image acquisition and EDS analysis.

The standards used were silica, alumina, iron and lime. Cobalt was used as a standard to measure count rate. Measured counts were corrected to weight percent using a ZAF programme and components measured to within 5% of content.

Results and discussion of analysis of wrought-iron samples

Microstructure

Almost all of the wrought-iron samples analysed in this research had localized pearlitic areas. Some of these localized areas contain up to 0.7% carbon (Figures 4 and 5). These are probably due to partially-fined iron that had been folded in to the centre of the 'bloom' during fining.

The ferrite grain size was variable within all of the wrought-iron samples. A typical example of the variation in grain size is shown in Figure 6. Phosphorus banding was not observed in any of the wrought-iron samples.

Given the variability in the results for both types of finery iron, it would seem sensible to take a cautious approach and to discount the distribution of carbon and uniformity of grain size as primary reasons for the preference for WF iron by Sheffield steelmakers.

Volume and distribution of slag inclusions

In general, the WF samples contain a lower overall volume of slag inclusions than the SLH samples. The average volume of slag in the WF samples is 5% ±1% compared to an average of 10% ±4% in the SLH samples. The volume of slag in the WF samples is less variable than that in the SLH samples; this is illustrated graphically in Figure 14, which also shows some overlap in values between one of the SLH samples (S4) and two of the WF samples (S9 & S11).

The distribution of inclusions was extremely variable in all of the samples. Individual inclusions typically range in size from <10μm to approximately 5mm across, and there is no apparent reduction in volume of inclusions within areas of high carbon. The samples do not show any evidence of more or less inclusions in certain areas, for example, towards the centre of the bars.

Samples 1, 2, 3 and 4 demonstrate how much the volume and distribution of inclusions can differ, both within individual bars and between bars of the same brand. The bars were found in the same archaeological context during the excavation at the site of Jessop's Brightside works, so it seems likely that they were manufactured around the same time. The pairs of samples taken from the two bars also show how the slag volume and distribution can vary, even within a relatively short section of the same bar. Although this is perhaps not surprising given the nature of wrought iron, it does highlight the fundamental problem in assessing the quality of this highly variable material. Because of the limited availability of samples of the same brand, and the sampling restrictions imposed by museums, it has not been possible to say whether this degree of variability was typical of SLH iron. It would be interesting to know if the slag volume and distribution in WF iron was more consistent; if it were, this may have been a reason for the steelmakers' preference.

If the steelmakers' preference for iron with 'body' is interpreted as iron with a uniform distribution of small slag inclusions, some difference between the distribution of inclusions in WF and SLH samples would be expected. However, the results of this analysis show that, apart from one sample, there is no discernible difference in the distribution of inclusions between the expensive and cheaper brands of wrought iron. The one exception to this is sample 12 (which is a premium WF brand, 'OO'). The sample contains a low volume of slag and most of this is concentrated into two small areas, one near the centre, the other near the surface of the sample. The inclusions outside these concentrations are predominantly small (<30μm) and are, by comparison, evenly-dispersed through the sample. Because of the limited availability of samples, it has not been possible to confirm whether this sample is typical of the 'OO' brand.

As the general method of fining is very similar for both WF and SLH iron, the results seem to suggest that the unpredictable pattern of slag distribution is a feature of Swedish finery irons.

Proportion of wüstite within slag inclusions

Most of the inclusions in the wrought-iron samples consist of two phases, wüstite (FeO) within a fayalite ($2FeO.SiO_2$) or similar silicate matrix (Figs 7 and 8). The amount of wüstite present within the inclusions varies

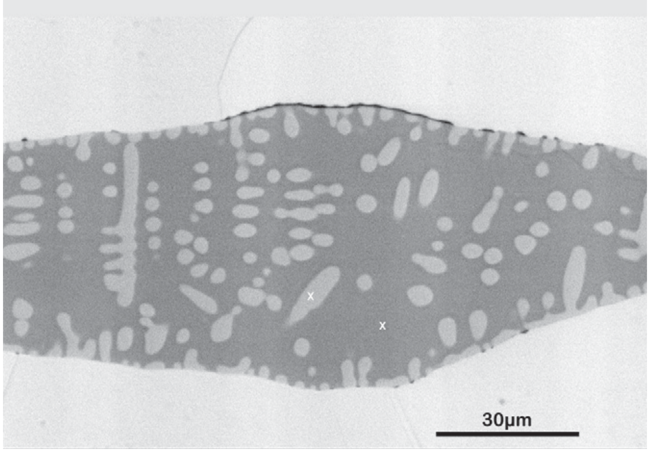

Figure 7: Slag inclusion in SLH wrought iron (sample 4) with low proportion of wüstite.

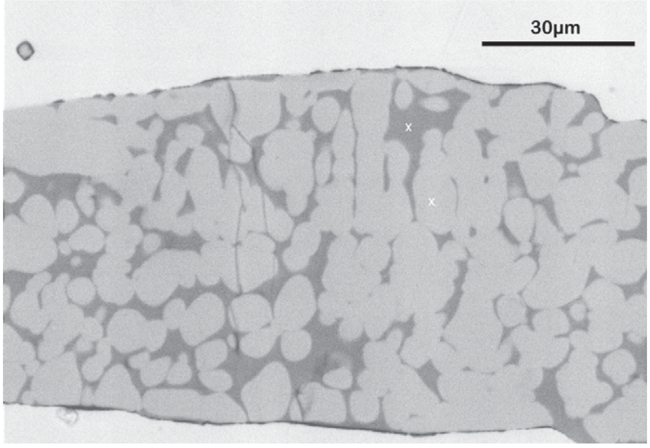

Figure 8: Slag inclusion in SLH wrought iron (sample 4) with high proportion of wüstite.

widely. Within the high-carbon areas of the wrought iron, there were predominantly single-phase silicate inclusions.

The wüstite phase is the most reducible component of the slag inclusions. During the cementation process the reducing atmosphere in effect 'cleans' the material and reduces the volume of slag in the blister steel (Rostoker and Dvorak 1988, 177), so the proportion of wüstite in the wrought iron inclusions is a good indicator of the potential quality of the blister steel.

Image analysis of two-phase inclusions in the two groups of iron showed that on average the WF samples have a higher proportion of wüstite phase than the SLH samples. The mean value of wüstite in the inclusions within the WF samples is 66%, compared with 52% for the SLH samples. The histograms (Figs 9 and 10) show the frequency of wüstite proportions for both groups. The distribution pattern is similar in both sample groups but the most striking feature about the WF samples is the concentration of values in the 70–90% range and the lack of values lower than 20%. Although the general trend within the SLH group is similar to that in the WF group, it is interesting to note that there are no values in the 80–90% range.

The 'normal' curves superimposed on the histograms (Figs 9 and 10) show the skewed distribution of the data. The standard t-test could, therefore, not be used to test the hypothesis that slag in WF iron contains more wüstite than that in SLH. The most suitable statistical test for investigating datasets with 'non-normal' distribution is the Mann-Whitney test (Meyer and Sykes 1996, 127). The results from this test showed that when the variability of the materials is taken into account, there is a statistically-significant difference between the average proportions of wüstite in WF iron and SLH iron.

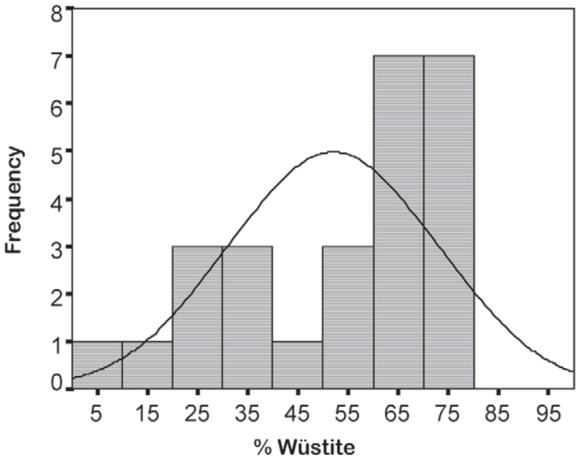

Figure 9: WF iron – percentage of wüstite in two-phase inclusions.

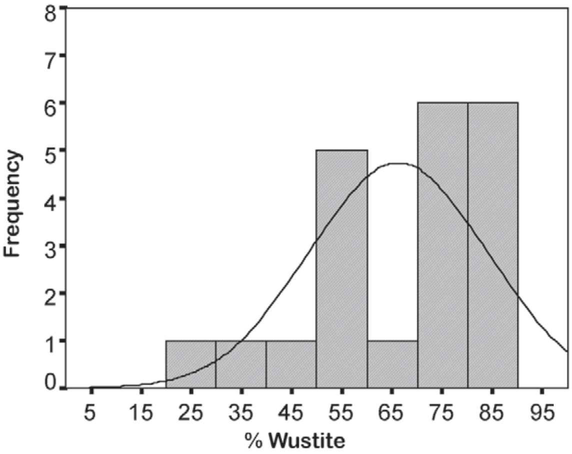

Figure 10: SLH iron – percentage of wüstite in two-phase inclusions.

Although the science of metallurgy was not sufficiently developed in the 19th century for this difference to be observed, one can imagine that cementation steelmakers would have been aware empirically that some irons produced cleaner steel than others.

Other elements in wrought iron samples

The quantities of sulphur, phosphorus and manganese present were investigated to see whether they could have influenced the selection of WF iron over SLH iron.

The results of bulk chemical analysis are shown in Table 3. It revealed that WF and SLH irons both contained very low levels of sulphur (<0.005% ±0.001%) and phosphorus (*c* 0.01% ±0.002%); there was not a significant difference between WF and SLH iron. As mentioned earlier, no phosphorus banding was observed in the microstructure of any of the samples.

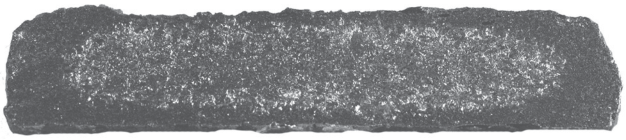

Figure 11: Etched surface of blister steel with area of lower carbon ('sap') in centre of bar, typical of bars with less than around 1.0% overall carbon content. Scale 1:1.

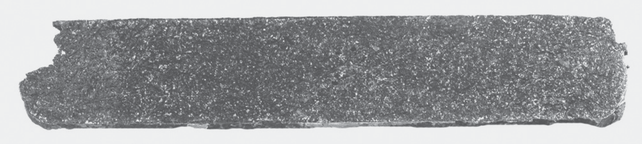

Figure 12: Etched surface of blister steel with more even carbon distribution, typical of bars with more than around 1.0% overall carbon content. Scale 1:1.

Manganese was not present in the iron in significant amounts. Random EDS points within the iron did not find manganese above the limit of detection, which was around 0.25%; bulk chemical analysis found a maximum of 0.12% (±0.02%) in one of the WF samples.

Results and discussion of analysis of blister steel samples

Microstructure

The main factor determining the microstructure of a blister steel is the amount of carbon present. Because carbon is absorbed through the surface of the bars, blister steel bars with an overall carbon content lower than around 1.0% tend to have a higher-carbon outer and a lower-carbon centre (Fig 11). This distribution of carbon gives the distinctive 'sap' that has traditionally been taken as an indicator of blister steel. However, when the overall carbon content of the blister steel is above 1.0% there may be no obvious sap and a more even carbon distribution (Fig 12).

Although the variable distribution of carbon through the thickness of the bar was a feature of blister steel, it was predictable, and for many applications it was not a serious problem – the blister steel was simply forged or rolled to close holes and cracks before being made into artefacts (Cranstone 1997, 4; Giolitti *et al* 1915, 220). Where a more homogenous material was required, the blister steel would be piled and forged to create shear steel, or re-melted in crucible furnaces to make cast steel (Crookes and Röhrig 1870; King 2003).

However, in some of the samples, there are small areas with coarser crystals and slightly higher carbon contents that do not follow the 'sap' pattern. These areas in the blister steel are remnants of the high-carbon inconsistencies in the wrought-iron bars, which have survived cementation. This was also seen during the author's cementation experiments. Sample 2 (wrought iron) and sample 18 (blister steel) were both taken from the same short length of wrought-iron bar. Sample 18 contained a patch with coarser crystals and slightly elevated carbon content, which corresponded with a

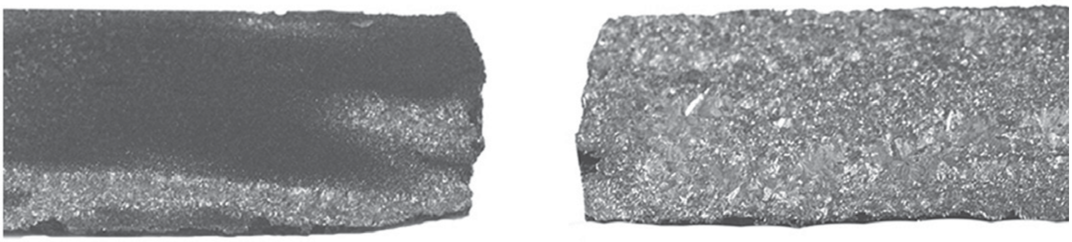

Figure 13: 'mirror image' showing etched surfaces of samples taken from the same bar before and after cementation. The light areas in the wrought iron sample are areas of high carbon. (2 x actual size)

Table 3: Results of ICP analysis of selected iron and blister steel samples (wt%)

Sample Number	Finery Type	Material	C	S	P	Si	Mn
S1	SLH	Iron	0.06	0.004	0.006	0.03	0.03
S3	SLH	Iron	0.12	0.004	0.011	<0.02	0.03
S19	WF	Iron	0.09	0.001	0.011	<0.02	0.12
S6	SLH	Steel	1.45	0.020	0.019	0.03	<0.02
S17	SLH	Steel	0.25	0.003	0.013	<0.02	0.04
S18	SLH	Steel	0.46	0.001	0.011	<0.02	0.05
S20	WF	Steel	1.01	0.001	0.012	<0.02	0.03

Note: Error ± 0.01% for C and Mn, ± 0.002% for P and ±0.001% for other elements

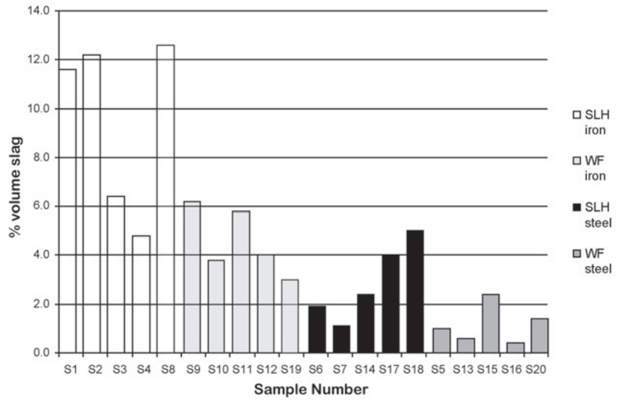

Figure 14: Bar chart showing the average percentage volume of slag by finery type for wrought iron and blister steel samples.

patch of high carbon visible in sample 2. (Fig 13). The corresponding differences in the microstructure of the samples are more obvious to the naked eye.

Although this feature of the cementation process was known to the steelmakers (Le Play cited in Barraclough 1984; Doncaster 1967), it does not seem to have been appreciated by previous researchers. The random patches of high carbon along the length of the blister steel bars were impossible to predict and the resulting variations in hardness only became apparent during forging and later stages of manufacturing (Le Play *op cit*). Doncaster (1967, 187) describes how the carbon content (temper) varied not only between bars converted at the same time, but also '… from foot to foot in each bar. To get uniformity, bars were broken up into the shortest usable lengths and the fracture examined. The old examiners knew their job and could judge the carbon content very accurately, but the results were never really satisfactory.'

Doncaster (*ibid*) suggests that it was this variation in carbon content along the length of the blister-steel bar, rather than the variation through the cross-section or slag inclusions, that led Huntsman to develop his crucible process.

Volume of slag inclusions

The average value of slag volume in the samples of WF blister steel is 1.2% compared with an average volume of 2.5% for the SLH blister steel samples. But, there is an overlap in the values for the two types of blister steel, as illustrated in Figure 14.

The lower average volume of slag in the WF blister steel is unsurprising given the lower average volume of slag in the WF iron. Given the variable nature of the material and the small number of samples, it is not possible to state conclusively that WF blister steel will always be cleaner than the equivalent SLH blister steel, although the results do reflect the trend found in the wrought-iron samples analysed.

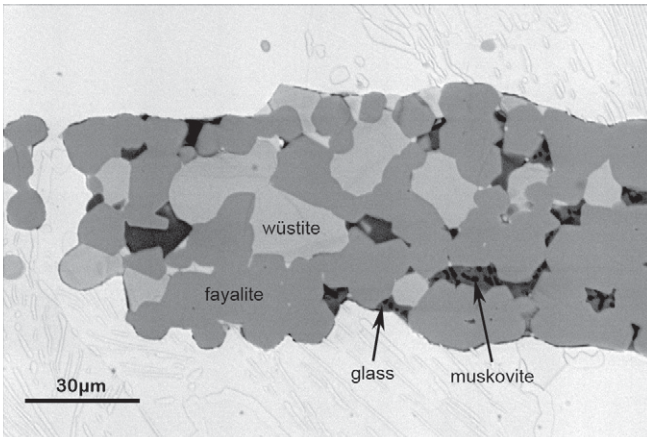

Figure 15: Example of slag inclusion in hypo-eutectoid blister steel (sample 18). Dark areas are glass/muskovite mixture.

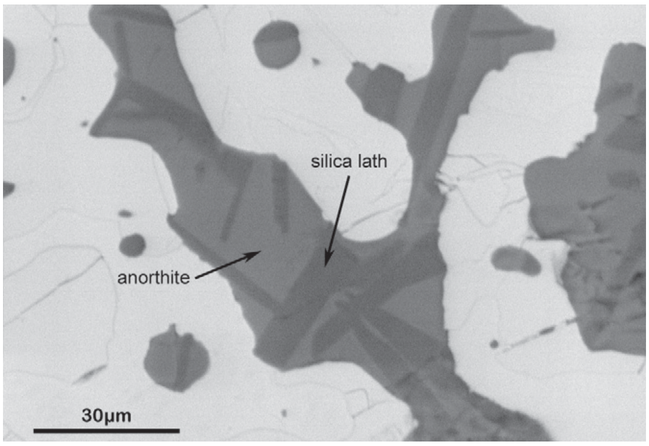

Figure 16: Example of slag inclusion in hyper-eutectoid blister steel (sample 6).

Composition of slag inclusions

At the typical operating temperature of a cementation furnace (1100°C), carbon is thermodynamically capable of reducing FeO in both wüstite and fayalite (Rostoker and Dvorak 1988, 177). The wüstite is reduced to metal, whilst fayalite is reduced to metallic iron, wüstite and silicate slag.

As wüstite is the most easily 'cleansed' phase within the slag inclusions, the higher proportion of wüstite in the WF irons meant that less slag was left in the blister steel after conversion. In theory, if two bars of iron containing the same volume of slag were converted for the same length of time, the bar with a higher proportion of wüstite would give a cleaner blister steel.

It is difficult to illustrate a 'typical' blister steel inclusion as the appearance varies widely. Figures 15 and 16 illustrate inclusions within hypo- and hyper-eutectoid blister steel. Thermodynamic calculations show that oxides of other elements such as Mn, Si, Al and Ca, cannot be significantly reduced at the operating temperature of the cementation furnace. As the FeO in the inclusions was reduced during cementation, these other elements became concentrated in the remaining slag, forming numerous complex silicate phases.

Blister-steel samples with the highest carbon content may be expected to have the lowest volumes of slag, because of the reduction effect of cementation. However, as the volume of slag in the steel also depends on the initial volume and type of slag in the wrought iron, this is not always true, as Figure 17 shows. Sample 6 contains 1.45% carbon and has 1.85% slag, while sample 7, manufactured from the same brand of SLH wrought iron, has approximately 1.00% carbon and 1.06% slag.

Conclusions

Despite the limited availability of material for sampling it has been possible to draw some general conclusions:

- The blister steel made from Walloon finery iron generally had a lower volume of slag inclusions than blister steel made from Swedish Lancashire Hearth iron. The lower volume of slag inclusions and the higher proportion of wüstite in the two-phase inclusions made Walloon Finery iron more suited to cementation steelmaking.
- Qualitative analysis highlighted the extremely variable nature of inclusions in both the wrought iron and blister steel bars and the results show how both the carbon content and abundance of inclusions can vary hugely across the width and thickness of the bars, especially in the wrought-iron samples. It has not been possible to say whether the degree of variability between samples 1, 2, 3 and 4 was only found in Swedish Lancashire Hearth iron. However, if Walloon finery iron was less variable, it may be another reason why the steelmakers preferred it.
- Sample 12 came closest to the ‘ideal wrought iron’ and it was taken from a ‘Double Bullet’ brand bar, perhaps unsurprisingly a brand that was regarded by steelmakers as one of the top three. Similar results were not seen for the equally highly regarded ‘Hoop L’ bars analysed, (samples 9, 13 and 15). It has not been possible in this research to confirm if the ‘Double Bullet’ and ‘Hoop L’ bars examined were typical of the brands.
- The wrought iron contained numerous randomly distributed patches of high carbon content. The results of this research show that these variations in carbon content along the length of the wrought-iron bar survived the cementation process. As suggested by Doncaster (1967), the need for consistent hardness may have been one of the reasons why Huntsman developed crucible steel for his clock and watch springs. Sheffield steelmakers developed strategies to deal with the variability along the bar, breaking the material into short lengths and using the fracture surface to assess carbon content. The steel was classified into different tempers according to its potential use, but a consistent product could never have been guaranteed.

The results of this study suggest that Sheffield steelmakers did have a valid reason for paying more for WF iron. Although the differences in quality between SLH and WF were relatively small, they would have shown in the finished steel. As the steelmakers could only fully assess the quality of the bar iron after it had been cemented, it seems likely that the Sheffield steelmakers’ preference for particular brands of wrought iron was the result of pragmatism rather than conservatism, with a preference towards bars from forges where previous experience showed a consistent output of high quality iron.

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