'Not even if we had offered him £50': Early crucible steel production and the history of the Huntsman process

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ABSTRACT: The early records of the Huntsman crucible steel process are sparse and unsatisfactory. Until recently information on the early process had to rely on the often ill-informed speculations of the various visitors or the cryptic comments of the Sheffield crucible steel makers themselves. Excavations at Riverside Exchange in central Sheffield have recovered quantities of crucible debris from contexts dating before the 1790s. The crucibles are of refractory clays in the form of mullite, tempered with graphite. The slag on the interior of the crucibles contains appreciable quantities of manganese suggesting that manganese dioxide was already being added as a flux. The role of manganese through the ages in the production of steel is discussed. In the light of this new information the paper reviews the likely origins of the Huntsman process and of its successors, with especial reference to the central and south Asian processes.

Introduction

The second volume of Ken Barraclough's *Steelmaking before Bessemer* (1984a) is a magisterial survey of the history of the crucible steel industry, with especial reference to Sheffield. Perforce, in the absence of excavated remains of early sites, Barraclough had to rely mainly on documentary evidence, which meant that there was continuing uncertainty about the process, especially for the earlier phases of the industry when ill-informed speculation and secrecy were rife. In particular there were considerable doubts and contradictions over the crucibles themselves. When the Swedish industrialist, Ludwig Robsahm, visited Benjamin Huntsman he was willingly shown all over his works, but was not allowed to see where the crucibles were made '… not even if we had offered him £50'(Barraclough 1984a, 9). An additional problem was the nature of the fluxes added to the crucible charge that foreign steel makers believed were the secret of the English success. There are no good contemporary accounts of the process in Sheffield, the earliest being that of the Swede, Benct Andersson in 1769, who had visited Huntsman in 1767, prior to establishing his own works in Sweden (Pipping and Barraclough 1988). Perhaps the most useful local description is that of Harry Brearley (1933), over a century later, describing the traditional process as he observed it early in the 20th century. Trying to make sense of the 18th-century statements and speculations is made difficult by their frequently contradictory nature, often misinformed, sometimes probably deliberately so. The task is further hampered by the prevalent contemporary misunderstanding of the real chemical and metallurgical processes that were taking place. The Sheffield steel makers knew how to make a superior product, but almost certainly did not fully understand the reasons why their processes worked.[1] This situation has recently been transformed by archaeological excavations in Sheffield and its environs which have uncovered remains of the early cementation and crucible steel industry. These include crucibles dating from late in the 18th century from John Marshall's Millsands works at Riverside Exchange in the centre of the city (Andrews 2015) that are the subject of this report (Figs 1 and

Figure 1: Fragment of crucible 5377-1. Note the internal coating of manganese silicate slag.

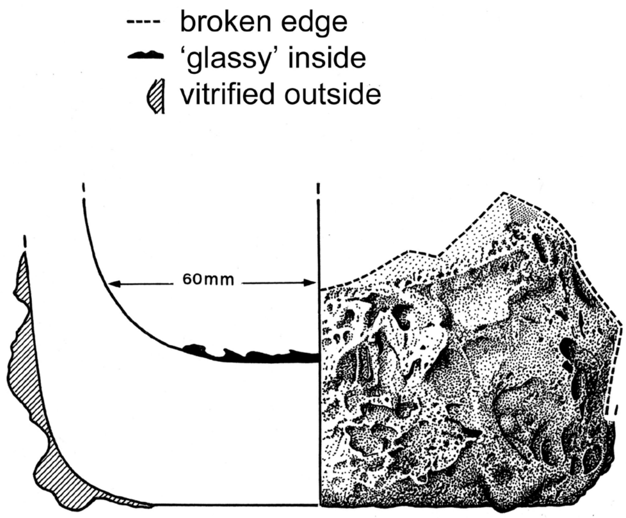

Figure 2: Drawing of crucible 5377-1.

2). Before discussing these discoveries further, it will be useful to outline the history and technology of the Huntsman process in the light of modern scientific understanding.

The early Huntsman crucible steel process

Benjamin Huntsman (1704-1776) was a watch and clock maker from Doncaster who, like many in his profession, was dissatisfied with the steel available for making springs. These often tiny components underwent considerable stress and strains almost continuously through their working life until, inevitably, they broke (Wayman 2000). This was because cementation steel from which they had been made had never been molten and thus the carbon content varied considerably through the metal which still contained slag stringers (Barraclough 1984b). Huntsman may not have fully understood this but would have been aware of hard or weak points in the steel as he worked it, and thus reasoned that if the cementation steel could be melted then it could be made homogenous and impurities removed.[2] The problems were twofold, generating temperatures in excess of 1400°C necessary to melt the steel, and creating a ceramic for the crucibles that could withstand these temperatures. The first problem was relatively easily solved. Updraught furnaces, based on those used by the brassmakers, fuelled with coke, the fuel that was becoming increasingly widespread to smelt iron through the 18th century, could attain and sustain the necessary temperatures. The problem was with the crucible ceramic. A French report of 1793 (quoted in Barraclough 1984a, 33) succinctly listed the requirements:

- To be highly infusible.
- To have sufficient thickness to resist the weight of the metal.
- To withstand the initial firing without breaking.
- To be able to be returned to the fire after pouring the steel so as to serve for several consecutive heats.

To these may be added the requirement that the carbon content of the molten steel must be preserved within a narrow range, typically between 0.5–1.5%. If the conditions were too oxidising then the steel becomes solid wrought iron, if too reducing it becomes cast iron.

The solution was to use the high-purity refractory clays already used by the glassmakers for their crucibles (Angerstein 2001, 176; Douglas and Frank 1972, 96-9). These were mainly of silica and alumina, with relatively little of other metal oxides forming silicates that could promote the vitrification and potential collapse of the ceramic (Searle 1940). As the clays were quite plastic the body would need a more rigid temper. This was made by pre-firing a portion of the refractory clay, crushing, and adding it as a grog temper, sometimes with clean sand, to counteract shrinkage during firing (Douglas and Frank 1972, 99). The steelmakers also added tempers of either graphite or, more usually from early in the 19th century, coke dust (breeze).

Several of the early foreign reports state unequivocally that secret fluxes were added to the crucible charge which, in the absence of direct evidence, was latterly regarded with some scepticism. However the discovery of manganese silicate on the inner surface of Marshall's crucible confirms that fluxes were indeed being added (see below).

One of the real reasons behind the great success of the English steel makers was their reliance on Swedish bar iron as the feedstock for the cementation furnaces. Critically the Swedish iron ores were of a high purity, being especially low in phosphorus which if present inhibited the absorption of carbon into the iron. In addition the Swedish ores were always charcoal smelted, and thus their iron had a low sulphur content compared with English irons which by the late 18th century were usually coke smelted.

Huntsman moved from Doncaster to Sheffield in 1742, and after many years of experimentation, about which nothing is known, finally produced metallurgically satisfactory and commercially viable crucible steel at his Attecliffe works early in the 1750s. Huntsman never wrote or communicated anything about his process, and being a Quaker would not swear an oath, and thus could not patent his process. He seems, anyway, to have believed that secrecy was a better protection than the law. The early technical and commercial history of crucible steel in Sheffield is similarly uncertain. Local potential customers such as the cutlers were initially rather unenthusiastic, but Huntsman was soon processing orders from far afield, such as from Matthew Boulton, of Handsworth, Staffordshire for rolls, dies and buttons (Barraclough 1984a, 4-5; Craddock and Lang 2004), and Henry Milward of Redditch, Worcestershire, for wire for needles (Rollins 1981, 17), as well as from foreign cutlers who did appreciate the superior properties of crucible steel. Despite Huntsman's secrecy others such as John Marshall commenced crucible steel production in Sheffield.

Marshall's Millsands steelworks

In 1999 the opportunity arose to excavate a large, former industrial site at Millsands in the centre of Sheffield (Figs 3-5), in advance of the Riverside Exchange development (Andrews 2015). This had been the location of two steelworks, the larger comprising the early site of Naylor Vickers, the name still famous today, and also Marshall's (later taken over by Naylor Vickers) which is much less well known and is poorly documented. However, in its heyday, Marshall's was respected throughout Europe as a large producer, with a reputation for high quality steel. Marshall's also holds an important place in the history of steelmaking, being the earliest example of an integrated works, having cementation furnaces to convert wrought iron to blister steel, and crucible steel furnaces to refine the blister steel and produce crucible steel (Andrews 2015).

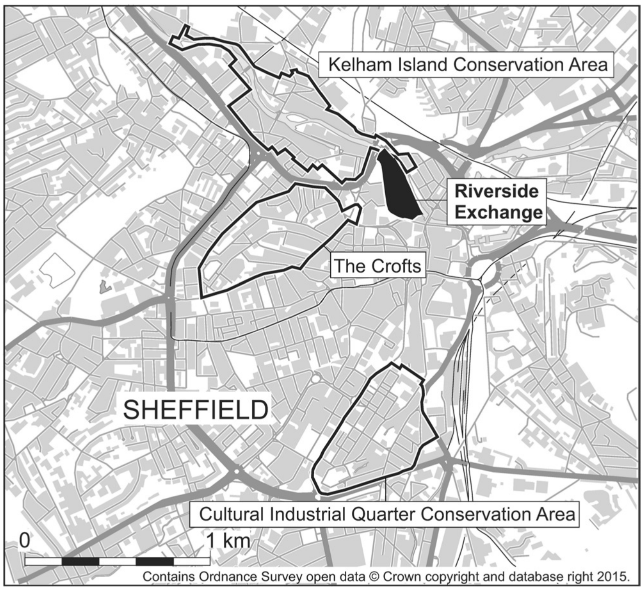

Figure 3: Central Sheffield showing the location of the Riverside Exchange site.

In 1759–60 John Marshall was steelmaker for the Cutlers' Company, and worked a cementation furnace in Scotland Street under the control of Joseph Ibberson, a former Master Cutler (Barraclough 1984b, 79). The Cutlers' Company was worried at that time by an apparent shortage of steel for the cutlery trades, and began a steelmaking experiment in the summer of 1759. Records show that on 17 August 1763 John Morton, the mason of the Cutlers' Company, did work at 'Millsands Furnace', and it appears that steelmaking had begun in the Millsands area around this time (Barraclough 1984b, 85). This is the first reference to steelmaking at Millsands and the only one apparently connecting it with the Cutlers' Company. The Company also had a 'new steel furnace', assumed to be a crucible furnace, which began operations on 6 July 1764; Leader (1901, 174) suggests it was in the Furnace Hill area, but it could have been at Millsands (Barraclough 1984b, 85). This operation closed in 1769.

The first mention of John Marshall as a steelmaker in his own right comes in the 1765/6 Sheffield (Sheffield Lower) Rate Book no 6 which notes Marshall's steel house under 'Water Lane', at the southern end of the Riverside Exchange site. In 1769 John Marshall is recorded as sub-tenant of Sarah Broadbent for a messuage, furnaces etc at Millsands (Lease Book, Arundel Castle Manuscripts (ACM) (Norfolk Estate collection in Sheffield Archives), S379 f.232), and it appears that John Marshall worked both a cementation and a crucible furnace (probably one of each) at Millsands by the late 1760s. The crucible furnace could have been that used by the Cutlers' Company until 1768–9, when the premises

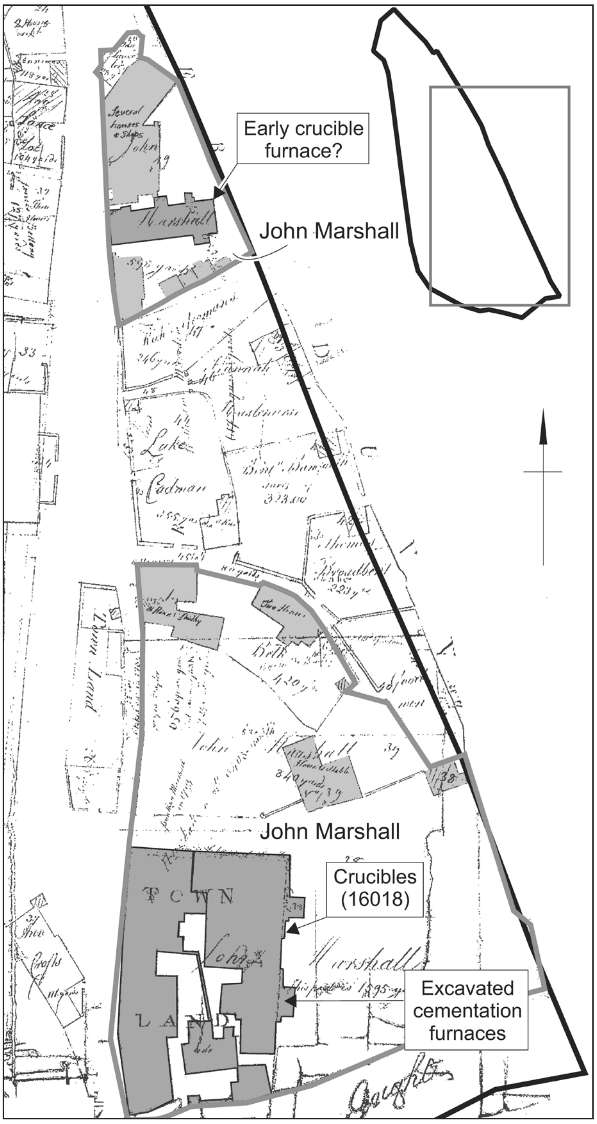

Figure 4: Extract from the 1781 Fairbank Survey map. The black outlines delimit the area of the Riverside Exchange site with the River Don to the east. The thick grey outlines added to the map indicate properties owned by John Marshall.

may have been taken over by Marshall (Barraclough 1984b, 85). However, Marshall's steelworks is not mentioned in the rate books until 1772/3 when a 'Steelhouse [apparently still singular] & Tents etc' are recorded, and the rate paid has risen from 1s to 4s 6d per annum. Further confirmation of his presence and occupation is provided in directories of 1774 (Sketchley's Directory) and 1787 (Gales and Martin's Directory) where John Marshall is listed as a producer of cast steel. Between 1770 and 1774 he was supplying cast steel ingots to the filemaker Mattias Spencer, each ingot weighing between 19 and 22lb (8.6–10 kg) (Day and Tylecote 1991, 287).

The earliest relevant map, dating to *c*1770 (ACM SheS 1494S), shows fewer buildings than are present by 1780, by which time John Marshall owned 'eight houses, part of the Steel Furnice, Workshops and vacant ground' (Bagshaw Collection C297). These works are shown on maps of 1781 (Fairbank Collection [FC] SheS 716L) and 1787 (FC SheS 717L) as an agglomeration of at least four structures around a yard with an entrance to the south, occupying a large property at the southern end of Millsands (Fig 4). The use of individual buildings, or indeed the entire complex, is not indicated on either of the maps.

However, an illustration of *c*1830 (provenance unknown, but reproduced in Scott 1962, frontispiece; Fig 5), somewhat idealised in the setting and layout of the buildings depicted, shows three steelworks, of which two have been identified as at Millsands (Marshall's and Naylor Vickers). Marshall's steelworks is shown as a building complex associated with four cementation furnaces (indicated by conical stacks) and four crucible furnaces (with rectangular stacks), the latter on the side closest to the river, together with a forge building, around a central courtyard with an imposing archway entrance and the administrative block flanking it. The arrangement depicted only very broadly matches that shown on the earlier, late-18th-century maps, even allowing that some rebuilding may have taken place during the intervening period, and perhaps some artistic licence.

In addition to the large property at the southern end of Millsands, the 1781 Fairbanks Survey map (FC SheS 716L) shows that John Marshall also occupied two smaller properties a short distance to the north. The more extensive of these, adjacent to the River Don, appears

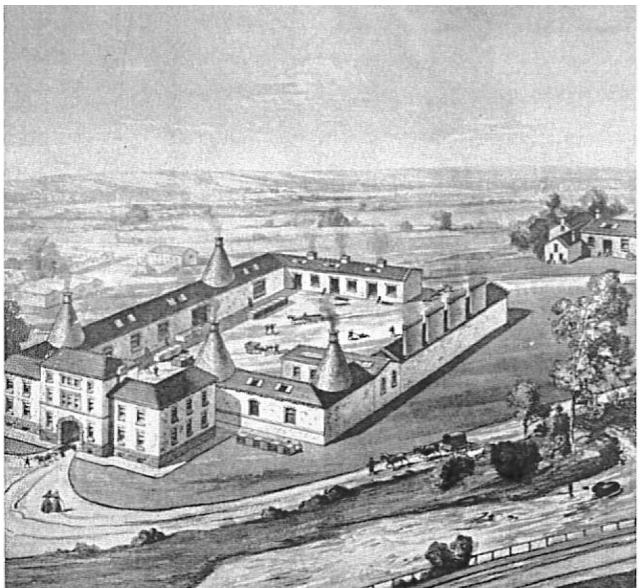

Figure 5: Extract from idealised depiction (c1830) of three steelworks shown next to the River Don, looking northwest, with Marshall's works to the left (reproduced from Scott 1962).

to have contained at least one relatively substantial building likely to have been associated with steelmaking, though this is not indicated on the map (Fig 4). However, excavations in this area in 2002 revealed the damaged remains of a crucible furnace of probable late 18th-century date, comprising at least one ash pit and part of the associated cellar (Andrews 2015, fig 7). Could this have been the site of the crucible furnace established by the Cutlers' Company in 1764 and perhaps subsequently taken over by John Marshall in 1769?

During the late 18th century, John Marshall (died 1793) and Jonathan Marshall, his nephew and successor at Millsands until 1830, were the only proprietors consistently described in Sheffield directories as 'convertors and refiners' (that is, having both cementation and crucible furnaces), and the Cutlers' Company records for 1774 confirm this (Barraclough 1972, 28; 1984b, 90).

Excavations on the Marshall's site in 1999–2003 uncovered the remains of three cementation furnaces, including one early, and unique, single-chest example dating to the second half of the 18th century (Fig 6), preserved *in situ* and now partly visible beneath a glass panel in the forecourt of one of the new buildings at Riverside Exchange. The other two cementation furnaces were of probable late 18th- or early 19th-century date.

In addition to the cementation furnaces and probable late 18th-century crucible furnace, parts of several 19th- and 20th-century crucible furnaces were also recorded at Riverside Exchange and approximately 1000 fragments of used metallurgical crucibles were recovered. The majority of the fragments, which comprise lids, rims, walls, bases and pedestals, relate to 19th-century steel-

Figure 6: Remains of earliest cementation furnace found in Marshall's works in the southern part of the Riverside Exchange site, prior to preservation in situ, with steps and ash pit/flue in centre. It dates to the second half of the 18th century.

making, although a few appear to have been used for the production of brass, bronze or copper objects. Note that traces of bronze were found on the crucibles examined here (see below).

Post-excavation assessment identified a small but important group of early steelmaking crucible fragments from the larger, southern property associated with Marshall's. The 13 base and 27 wall fragments were found in a context (16018) assigned to late in the 18th century and interpreted as a dump of fragments against what would have been the outside, eastern wall of the group of buildings forming Marshall's steelworks during this period (Fig 4), and probably close to the crucible furnaces (Fig 5).

The petrographic and elemental analysis of the crucible fragments

The scientific examination is reported in greater detail in Spataro and Craddock (2015) which also includes colour photomicrographs and elemental maps.

Methods

Samples were cut with a diamond saw from the fragments of two crucibles (sample 5377-1 from the most complete base and 5377-2 from a representative wall fragment), cutting through the thickness of the crucible from inside to outside thereby showing the complete structure. The polished thin sections were examined using a Leica DMRX polarised light optical microscope and a Hitachi S-3700N variable pressure (VP) scanning electron microscope with energy dispersive X-ray spectrometry (SEM-EDX), Oxford Instruments Inca Xact, SN 43781, for the study of the samples' microstructure and chemical composition.

Three bulk SEM-EDX analyses were carried out on each sample at x100 (*c*1.4x1.0mm), and spot analyses in different regions, using the default manufacturer's standardisation (Table 1). The SEM was used at a vacuum of 30Pa with a 20kV accelerating voltage; the samples were analysed uncoated at a 10mm working distance. Thirteen elements (Fe, Al, Mn, Mg, Ti, Na, Si, K, Ca, P, S, Cu and Co) were quantified and the results were converted into oxide percentages. These percentages were normalised (oxygen by stoichiometry) to take into account the fact that oxygen and carbon are not measured (for more detail about the methods used see Spataro 2014).

Crucible 5377-1 was also analysed by X-ray diffraction with a STOE STADI MP; the diffractogram confirmed the presence of mullite.

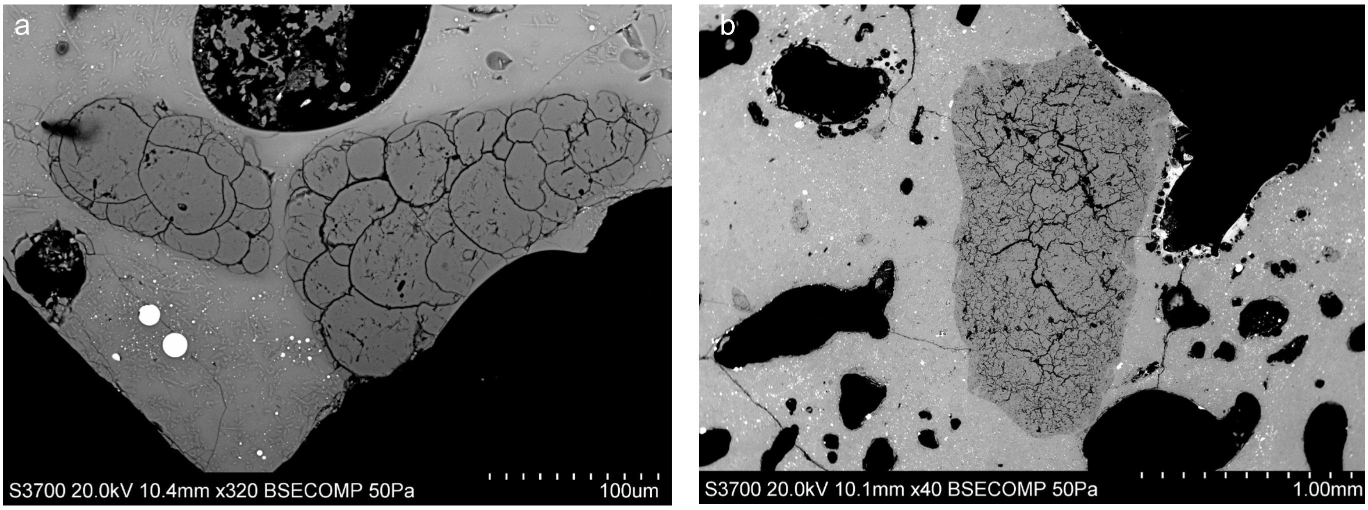

Figure 7: Backscattered SEM images of sample 5377-1 showing quartz grains shattered by the thermal stress; a) small size; b) very coarse inclusion.

Thin section petrographic analysis

The two polished thin sections were analysed by optical microscopy. Both samples have a dark grey highly vitrified fabric, with abundant rounded voids left by the bloating pores. The matrix is fine with some inclusions. Sample 5377-1 includes abundant iron oxides and opaques, including some iron particles in the voids which originate from iron-rich minerals in the original clay which were reduced to iron metal during the process, and small amounts of shattered quartz grains (Fig 7). Crystals of mullite ($Al_6Si_2O_{13}$) are visible throughout the fabric (Fig 8a). There are also some scattered graphite flakes and a spherical metal inclusion surrounded by corrosion products. Sample 5377-2 is similar to the first fragment, but it is surrounded by a secondary deposit of iron-rich corrosion products, very likely coming from the burial surroundings.

SEM-EDX microscopy and analysis

The two polished thin sections were analysed by SEM-EDX to identify the different areas, such as the surface slag, crucible paste and metallic features. SEM images show the highly-vitrified fabrics of mullite crystals with metallic iron globules scattered through the fabric (Fig 8a), added graphite (Fig 8b) and shattered quartz (Fig 7).

Both crucible fabrics contain mainly alumina and silica (glassy phase and mullite), with some potassium, titanium and iron oxides. Most of the oxide concentrations are similar, except for alumina and silica, which have slightly different concentrations in the two crucibles.

The fabric of 5377-1 includes localised traces of copper and tin, one of which is visible in optical microscopy. Tin was detected but not quantified, zinc and lead were

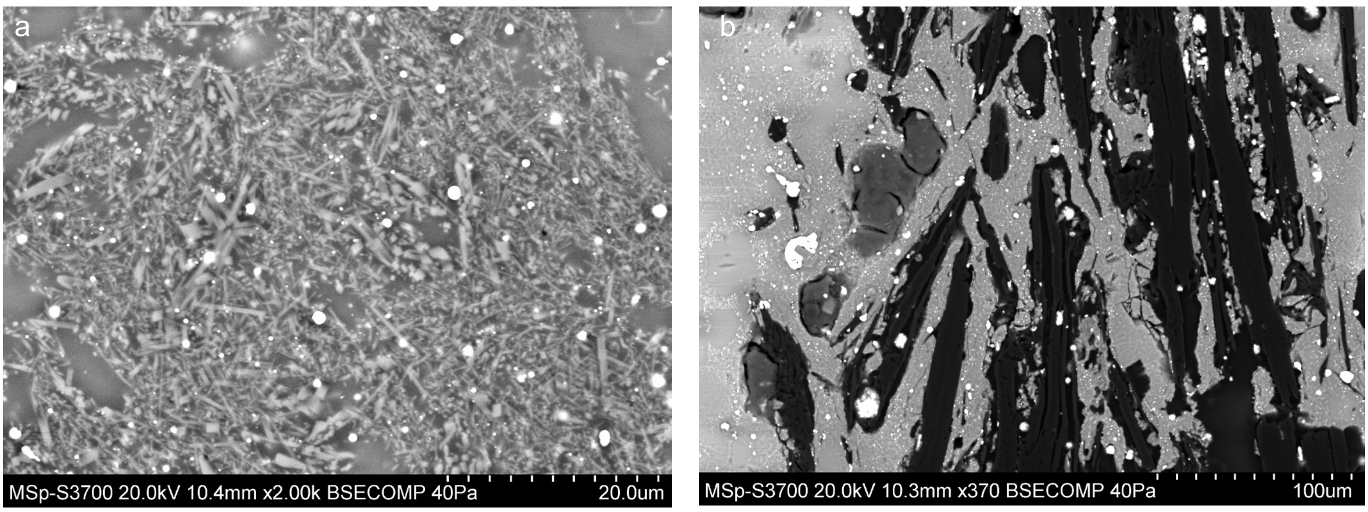

Figure 8: Backscattered SEM images of the fine fabric of sample 5377-1, showing a) mullite crystals and metallic iron (white spots) and b) graphite (black flakes) in the paste. More detailed colour photomicrographs and elemental maps are given in Spataro and Craddock 2015..

Table 1: Compositional data from SEM-EDX analysis of the two crucible sherds (normalised wt%).

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	FeO	CoO	CuO
Crucible 5377-1													
ceramic fabric	0.4	0.4	22.6	72.5	bdl	0.1	1.2	0.4	1.2	bdl	1.0	bdl	bdl
sd	*0.1*	*0.2*	*7.3*	*8.6*		*0.1*	*0.3*	*0.2*	*0.1*		*0.4*		
Crucible 5377-2													
ceramic fabric	0.4	0.6	28.1	66.5	bdl	0.1	1.4	0.5	1.1	bdl	1.1	bdl	bdl
sd	*0.1*	*0.1*	*2.8*	*2.1*		*0.1*	*0.1*	*0.1*	*0.2*		*0.5*		
inner glassy layer spot 4	1.0	1.6	22.6	53.2	-	-	4.0	3.1	1.0	7.6	5.4	bdl	-
inner glassy layer spot 5	0.4	1.1	17.9	40.3	-	-	1.6	2.2	1.0	7.6	27.4	0.2	-

Notes: Data for the ceramic fabrics are the means of three area analyses at x100.
The standard deviations are shown in italics.
Individual spot analyses were made at two points on inner glassy layer.
bdl = below detection limit. - = no data.

sought but not detected showing that the copper alloy involved was bronze rather than brass or gunmetal. Elemental analysis of 5377-2 also detected a small blob of bronze. This suggests that actual fragments of bronze had become incorporated rather than bronze-melting crucibles being reused as grog. Other crucibles in the assemblage in which these crucibles were found had held copper alloys (see above).

Sample 5377-2 has a glassy phase on the inner surface, probably related to its use, which was also analysed (Fig 9). The glassy region is very rich in manganese and iron oxides, richer in magnesia and calcium oxide, and poorer in silica than the paste of the crucible (see Table 1).

Elemental composition maps

Three compositional maps of both samples were produced over about fifteen hours each to identify the elemental distribution. These are reported in full by Spataro and Craddock (2015, 57 and plates 30-32). They show the fabric of 5377-1 is rich in aluminium and silicon (mullite and glassy phase or vitrified paste) and some graphite (cf Fig 8). In 5377-2 the surface glassy phase (Fig 9, to the left) is rich in calcium, manganese and potassium, and lower in aluminium and silicon than the ceramic body which contains quartz grains and scattered tiny iron and titanium-rich particles which are usually not associated.

Scientific examination shows that the crucibles are refractory ceramics containing high proportions of mullite fibres in a vitrified matrix, as found in previous investigations of later crucibles, but tempered with graphite instead of the coke temper used in the later crucibles (Freestone and Tite 1986). This refractory clay, possibly the original Stourbridge clay, favoured by the glassmakers, or similar clays from one of the local sources such as Bolsterstone or Stannington, was tempered with 10-20% of graphite by volume. No evidence for grog was found in the fragments examined here. The presence of manganese in the slagged layer in one of the crucibles suggests the addition of a manganese dioxide flux to the charge.

Early descriptions of the crucibles

The Huntsman process attracted a great deal of foreign attention, not least from the French, who purchased Sheffield crucible steel in quantity, and the Swedes who were keen to find out what the English were doing with their bar iron, purchased in ever increasing quantities.

There is considerable confusion over the exact nature of the early crucibles from the often-conflicting con-

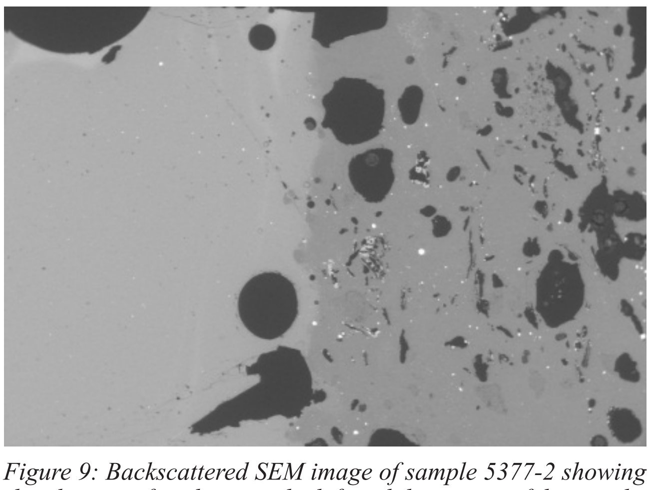

Figure 9: Backscattered SEM image of sample 5377-2 showing the glassy surface layer to the left and the ceramic fabric to the right. The large black areas are voids/bubbles and the small bright specks either iron- or titanium-rich particles. Image width 350µm.

temporary statements. It is likely that almost from the inception of the process there were two basic crucible ceramics, those made of refractory clays tempered with pre-fired clay and/or clean sand and others, including the Marshalls' crucibles analysed here, tempered with carbonaceous material. Although no one early source specifically mentions two types, there are separate early references to both white crucibles[3] and to blue crucibles; the latter are likely to have contained carbonaceous material.

Descriptions of the crucibles being of clay alone include the paper written by Andersson in 1769 (Pipping and Barraclough 1988). His manuscript gives a detailed description of the whole process, very likely based on the Huntsman works although he does not specifically state this. He unequivocally stated that the crucibles were to be made from Stourbridge clay, half of which was to be pre-fired to form the necessary grog temper. The Swedish engineer, Erik Geisler, who visited Sheffield in 1772-3 (Barraclough 1984a, 14-5) stated that the crucibles were made from the same clay as came from Staffordshire (presumably Stourbridge is meant, which is actually in Worcestershire). The technically well-informed French report of 1793 on the production of crucible steel, referred to above, stated that 'the crucibles themselves are made from specially selected clays, which are pure mixtures of silica and alumina, free from lime and magnesia, to which was added a temper of the same clay previously fired and crushed' (quoted in Barraclough 1984a, 33), once again with no mention of any other materials. Yet another Swede, Gustav Broling, who visited the Huntsman works during 1797-1799, made a detailed description, published in 1816 (Barraclough 1984a, Appendix 3), and described the crucibles as being made of refractory clay to which was added a temper of fired clay grog.

However, other Swedish visitors believed that graphite was added as a temper. Although Robsahm was told by Huntsman that his crucibles were just made of refractory clays, and at another Sheffield crucible works Robsahm visited he reported that the crucibles were made 'entirely of Stourbridge clay' (Barraclough 1984a,12), he remained unconvinced. Instead he believed that goldsmiths' graphite crucibles were being imported from Holland, crushed and used as a temper mixed with the refractory clays.[4] In support of Robsahm's suspicions Barraclough (1984a, 11) noted that the Austrian town of Ypse (Ybbs), where crucibles were made from the local graphitic clays, was supplying crucibles to Sheffield. Other production centres such as Obernzell in Bavaria are also possibilities.

There are other plausible interpretations. Barraclough (1984a) assumed that these crucibles were intended for the steel makers, but they could also have been used by the precious metal refiners who were very active in Sheffield, especially working with the manufacturers of silver plated wares, the well-known Sheffield Plate (Wilson 1960). Huntsman's son, William, who was involved in his father's business, also denied that that goldsmiths' crucibles were being imported from Holland, but did express a wish for a few tons of the clay from which the Dutch crucibles were made. This has been interpreted as a clue that they were really importing crucibles after all. However, could he instead have been referring to the graphite-rich clays mined in Austria and Bavaria, used to make crucibles which were traded very widely, including to Britain from Dutch ports? The export of these graphite-rich clays themselves was forbidden; hence it really would have been something for which the Huntsmans could only wish.

Fluxes and nostrums

The early visitors believed the success of English crucible steel production lay in the mysterious fluxes that formed part of the charge. Jars (1774, 257-8, reproduced in Barraclough 1984a, 13), who had visited in 1765, stated that 'the steel was placed in a crucible with a flux that is kept secret.' Geisler, who had visited Sheffield in 1772-3, reported that:

> 'According to the workers at the crucible furnaces some flux was added to the charge but this is kept a secret. It was possible to see that a used crucible which had broken had a whitish to yellow and rough glass coating, bottom and sides' (cf the Marshall's crucibles described here; Fig 1).

Great emphasis was laid on discovering the nature of the fluxes, though J H Hassenfratz, reporting on the production of crucible steel in France in 1793, complained with some justification, that 'everyone has focussed his researches on the proper flux for fusion and has neglected to investigate the crucibles.' (Barraclough 1984a, 272).

Broling, reporting in 1816 on his visits between 1797 and 1799 (Barraclough 1984a 253), described the function of the fluxes in some detail:

> 'in large smelting plants various types of material are used as flux and these can rapidly produce a thin glass-like slag in which the metal particles sink without any difficulty and are prevented from burning [decarburising?]. However, in order to judge the most suitable flux for a certain type of ore, it is necessary to know well those rock types accompanying this ore with regard to their condition in smelting heat and,

> furthermore, to know with what kind of additives they may be brought to melt or their all too rapid cutting nature may be reduced to that degree necessary for the keeping up and condition of the smelting furnaces [that is, the propensity of the flux to erode the crucible or furnace walls]. The only flux in question should have the one property common to all glass, namely that of floating on top of the steel during melting and furthermore, it should be composed of such materials which do not attack the crucible too much.
>
> It is of this type of flux that the English steel manufacturers make such a big secret, especially as they suggest that the various compositions thereof contribute to a greater or lesser degree towards the quality of the molten steel. All such materials which, in conjunction with each other, can be melted together into a fairly slow melting glass, without incurring any damaging side effects may be used. It seems, however, that the best composition of flux is that which, in addition, comprises those materials of which the crucible is made.
>
> The flux I have used consisted of two parts of crushed crucible well mixed with one part burnt lime or chalk, to which I have sometimes added one part of crushed bottle glass in order to make it flow more easily.'

Broling believed the addition of a flux was not essential, but that without a flux layer there was 'naturally a greater loss by oxidation', and concluded his section on fluxes by stating 'I am convinced that there is no other secret in the art of cast steel manufacture than to obtain the best iron, convert it twice in the cementation furnace and, with due care and attention, melt it to cast steel.'

Analysis of one of the Marshall's crucibles shows that fluxes were indeed being added, including manganese dioxide (Table 1). This new evidence provides an important link between the use of manganese salts from antiquity and the use of manganese metal and salts in the modern world.

The role of manganese in iron and steel production

Manganese dioxide (pyrolusite, MnO_2) has been associated with the production of iron and steel for millennia, sometimes already present in the ore, sometimes as deliberate additions. Pyrolusite was added as a flux in Chinese iron smelting in the Song Period of the 12th–13th centuries AD (Huang 2015). As with so many aspects of steelmaking, the actual function of the manganese oxides in the process was often not understood, but the fact that it produced a better product was appreciated and acted upon. The earlier significance of manganese salts has been overshadowed and thereby confused by Josiah Heath's 'carburet of manganese', patented in 1839 (Percy 1864, 840), which although not stated, was a tarry mixture of manganese oxides together with some metallic manganese. The presence of metallic manganese was a new development which was to have profound effects on the iron industry generally,[5] but the addition of manganese oxides themselves also came to be seen as an innovation in steelmaking, dating from the mid-19th century, which is incorrect.

Stable manganese oxides preserved the carbon in the iron during the smelting of the so-called natural steels. Most of these such as the Roman Noricum iron, mentioned by Pliny (*Natural History* 34.145, *eg* Rackham 1952, 232-3), and the later medieval and post-medieval natural steels, variously from Austria, Sweden and Catalonia, were smelted from manganese-rich 'spathic' iron ores (Craddock and Wayman 2000). On smelting ordinary iron ores by the direct or bloomery process the product was an intimate mixture of metallic iron, initially containing some carbon, and an iron silicate slag. The iron oxide component of the slag could react with the adjacent carbon in the iron to form carbon monoxide, effectively decarburising it. If, however, the iron ore also contained significant amounts of manganese, then manganese oxide tended to be the major component of the slag, which being more stable, did not decarburise the surrounding iron, and the intrinsic carbon content of the metal produced by the smelting process was preserved. The presence of manganese minerals in the smelting process was well understood throughout Europe wherever such direct steel processes were practised. Where the ores did not contain sufficient manganese then in the post-medieval period, manganese-rich ores such as braunite, di- and trivalent manganese silicate, were added to the molten cast iron to better control and preserve the carbon content during the fining or puddling processes (Barraclough 1990 10-11; Craddock 2003). Thus there was some knowledge and appreciation already by the post-medieval period that the presence of manganese oxides was beneficial in the steel-making process, long before Heath's patents.

Manganese oxides were a common addition as fluxes in the early Asian crucible steel processes (Craddock and Lang 2004). Indeed the earliest known recipe for the production of crucible steel by the carburisation of wrought iron in India, that of Zosimos of Panopolis written in the second century AD, specifies the addition of *magnesia*, which is to be understood as manganese dioxide (Berthelot 1888, II V.v, 347-8; III V.v, 332). This is not an isolated mention, several of the medieval Islamic texts also specify the addition of *magnesia* as a flux in the carburising crucible steel process, as exemplified by those of al Kindi in the 9th century AD (Gilmour 2015) and al Tarusi written in the 12th century AD (Cahen 1947-8 106; Craddock and Lang 2004). Analysis of slags adhering to the steel-making crucibles from the broadly contemporary medieval Islamic Central Asian steel-making centres were found to be manganese-rich, confirming the reality of the textual evidence. The crucible slags from Merv in Turkmenistan divided into two groups, those with about 2% of manganese silicates and those with about 10% (Feuerbach 2000, 76-7, table 4 and appx E). The crucible slags from Achsiket, in the Ferghana Valley of Uzbekistan, contain about 15% of manganese (Rehren and Papakhristu 2000). These figures are far higher than the manganese content in the ordinary iron-smelting slags from these sites. Yet another advantage of the great affinity of manganese dioxide for silicon would be the almost total removal of silicon dissolved in the iron.

In contrast the 19th century descriptions of the Central Asian crucible steel-making processes make no mention of manganese (Wulf 1966, 8-9; Anasov 1841), neither do any of the 19th century descriptions of the Indian processes (Bronson 1986). Also, slags inside the post-medieval steel-making crucibles from India (Anantharamu *et al* 1999) and Sri Lanka (Wayman and Juleff 1999) only contain traces of manganese. This suggests that the addition of manganese fluxes in the Huntsman process was derived from the European natural steel-making traditions rather than suggesting any contact with the contemporary Central and South Asian crucible steel traditions.

The function of the manganese oxides in these early Asian carburising crucible steel processes is problematic. Adding an oxide would not have directly aided the reduction process chemically. The most likely reason for the addition of the manganese oxide was to form a slag to protect the molten steel from oxidation (see Broling's comments above).

The role of the manganese dioxide in the very different Huntsman process has been thoroughly discussed by Barraclough (1984a, 56-60). The feedstock for the Huntsman process was cementation steel that would still have contained some residual iron silicate (fayalitic) slag. During the crucible melting process the majority of this would have been reduced to iron, generating carbon monoxide.

$$FeO.SiO_2 \text{ (fayalite)} + C \text{ (from the steel)} = Fe + CO + SiO_2$$

This was no problem whilst the steel was still molten but if there were still some iron oxides or silicates present at the end of the process, then after casting the ingot there was a very real danger that the reduction would continue but now the forming gas bubbles would be trapped in the solidifying metal, a phenomenon known as honeycombing, which ruined the ingot. To ensure against this the steel was kept molten for a considerable time after the melting stage was complete, adding significant costs to the operation. If a manganese flux was present then this could attack the walls, eroding away the silica and exposing the carbon material to the molten steel, thereby significantly accelerating the reduction of any oxides present thus reducing the risk of honeycombing. In addition, as with the early Islamic processes, the manganese silicates would form a liquid slag over the steel preventing oxidation.

Origins of crucible steel in Europe

Crucible steel was in extensive use from the end of the first millennium BC over much of Central and South Asia and the Middle East (Craddock 1998; 2003; Allan and Gilmour 2000) but there is currently little evidence or appreciation of its availability in Europe (Bronson 1986). Williams (2009) has shown that crucible steel was likely to have been imported from Central Asia in the 10th–11th centuries AD by the Vikings and used for prestige blades, although that ended with the cessation of the Volga trade route. However, knowledge of crucible steel must have been current across the Mediterranean through contacts with the Islamic world, many crusaders, for example, must have had a very direct, sometimes fatal, contact with this superior steel. Williams (2015) has listed some of the medieval European references to crucible steel.

Moving forward to the Renaissance and post medieval world, there is rather more evidence of Europeans actually forging the metal (Schubert 1957, 325; Craddock and Wayman 2000). Thus Giovanni della Porta (1589) related that crucible steel could only be worked with difficulty. In 1677 Joseph Moxon compared locally made crucible steel with Damascus steel (Moxon 1703). The writer and biographer Thomas Fuller (1662) also referred to Damascus steel when comparing English steel used for razors etc unfavourably with that from Flanders, Spain or Damascus. He also noted that 'Indian *Symeters* are by many workmen thought to be cast steel'(Smith 1960, 24). Thus already in the 17th century Asian crucible steel was familiar and being discussed in contexts where high quality steel was required, and in the early 18th century Réaumur investigated its properties

(Birembaut 1958, 140-1). However, this knowledge was clearly in the context of an intellectual curiosity rather than as an industrial commodity (Evans 2008; Evans and Withey 2012). This commercial reticence is again surprising as both the English East India Company and the Dutch equivalent, the VOC (Verenigde Oostindische Compagnie), were engaged in country trade in the Indian Ocean on a considerable scale with ingots of Indian crucible steel forming part of their cargoes (Craddock 2013). It seems inconceivable that steel ingots were not also being sent on to Europe along with other commodities.

Production of crucible steel

Robert Hooke recorded in the 1670s that:

> '… steel was made by being calcined or baked with dust of charcoal, and that brings it up soe as to melt it made the best steel after it had been wrought over againe, that it would be at first porous but upon working over to be as fine as glasse' (Robinson and Adams 1935, 193).

This would seem to describe carburisation followed by melting with the evolution of carbon monoxide whilst the metal solidified, the phenomenon latterly known as honeycombing and encountered during the Huntsman process (see above).

There is some evidence that crucible steel was being produced in London some decades before Huntsman began production. The German traveller, Count Zacharias von Uffenbach, in 1710 visited the Pingo family in London (Quarrell and Mare 1934) who were engaged in clock and medal manufacture (Eimer 1998; Norman 1971; Craddock and Wayman 2000). They were apparently casting small decorative items from steel. It was explained that because they were of steel they were exceptionally hard, clean and bright, which of course were the factors appreciated at the end of the 18th century for crucible steel buttons, free from slag inclusions (Rawlings 1978; Craddock and Lang 2004). Uffenbach questioned Pingo as to how they were made but could get little beyond that 'The metal or steel that he uses is nothing but old sword blades which he melts down'. It has been suggested that the castings were no more than white cast iron but it is surely significant that Pingo's feedstock was old swords which would have been made of cementation steel, which would have been most unlikely to have melted to form cast iron. Cementation steel was the very feedstock that Huntsman was to use, except that he could obtain supplies directly instead of having to rely on scrap.

Henry Horne (1773) also made a rather convoluted claim that crucible steelmaking had been taking place in London in the early 18th century, and that moreover one of the steelmakers, named John Waller, had attempted to sell the process, first in Birmingham and then in Sheffield (Evans 2008; Evans and Withey 2012). Apparently the secrets of the process were extracted from him before adequate payment was made and poor Waller returned home cheated and forgotten. This story has been refuted many times, especially in Sheffield (Barraclough 1984a, 21), and it does seem highly unlikely that this was the true origin of the Huntsman process. However, both Uffenbach's and Horne's separate accounts do suggest a familiarity with crucible steel and very possibly its manufacture, albeit on a very limited scale, already taking place in London in the early 18th century. It is against this background that Huntsman's achievement should be understood.

The Huntsman process in the 18th century

Huntsman's requirements were to obtain a good (high carbon) steel that was of uniform quality, and to be able to produce it in quantity and at a reasonable price if it was to be commercially viable. Although Huntsman was apparently of a mechanical bent he was not a practising metallurgist, much less a smelter. This was perhaps an advantage, for in the makeup of his crucibles he turned to Sheffield's other industries, the glassmakers (Ashurst nd) and the precious metal refiners (Wilson 1960). Huntsman's works at Attecliffe, near Sheffield were not only close to his cementation steel feedstock, but were, after all, next to the Attecliffe glass works (Ashurst nd, 50-1).

Preparation of the crucibles

Following the practice of the glass makers (Douglas and Frank 1972, 99; Ashurst nd, 33-4), the tempered clay would be spread over a floor and very thoroughly kneaded to squeeze out any air pockets, treaded with bare feet so that any hard impurities could be located and removed. The crucibles were formed in cast iron moulds, as were Marshall's crucibles, studied here. After forming, the crucibles were dried and then stacked on shelves above the furnaces and allowed to slowly dry over several weeks before being fired to a good red heat in a kiln. Thus the crucible as loaded into the furnace with its charge of cementation steel was a high quality stoneware ceramic. As the temperature rose above about 1300°C, the aluminium silicate mineral mullite ($Al_6Si_2O_{13}$) would begin to form and has been found in 19th century crucibles previously examined (Freestone and Tite 1986; Figs 7b and 8a).[6] Mullite has excellent refractory properties, combining a melting point in excess of 1800°C and good resistance both to thermal shock and to high temperature chemical erosion (Martinón-Torres *et al* 2006; Martinón-Torres *et al* 2008; Duval *et al* 2008).

It seems likely that already by the 1760s, soon after the process was commercially established, two types of crucible were in use: those made according to the glassmaker's methods, of refractory clay, with a grog temper of pre-fired clay, and those of refractory clay tempered with graphite, either in the form of reused graphitic crucibles or as separate additions of graphite alone, very likely inspired by those used by the local precious metal refiners. It is probable that Huntsman, and maybe others, initially used the graphite-tempered goldsmith's crucibles as the only graphite-tempered ceramic with which they were familiar. However, this would have been a very expensive way of introducing graphite. Marshall's crucibles suggest that relatively soon it was realised that the important ingredient in the goldsmith's crucibles was the graphite and that this could added directly.[7] By the early 19th century coke breeze began to be substituted for graphite. Thus Rees in the 5th volume of his *Cyclopaedia* (the parts issued in 1819-1820, Cossons 1972, 158) could state that the crucibles were made of Stourbridge clay and coke dust, with no mention of graphite. It is somewhat surprising that the changeover took so long, especially as the furnaces were fired with coke; possibly the steelmakers were worried by the harmful effects of coke on iron generally, arising from the sulphur content. However, graphite-tempered crucibles continued to be made and used on a very limited scale, thus Brearley (1933, 31-5) had experience with them as late as the early 20th century, and there were certain advantages.

The graphite-tempered crucibles lasted considerably longer (approximately ten re-uses, compared to only two or three re-uses for the coke-tempered crucibles), and heat transfer through the crucible was much quicker (Brearley 1933, 32). However, this could be a problem for although the melting process proceeded a little faster, on removing the crucible from the furnace it cooled down more quickly. Brearley noted that if the molten steel was not to be poured immediately from a graphite-tempered crucible it would be transferred to an ordinary crucible to conserve the heat. Searle (1940) stated that carbon

> '… improves the heat resistance, reduces the tendency of the contents to oxidise, enables heat to pass more readily into the interior of the crucible, improves resistance to sudden changes in temperature so much that plumbago (graphite) crucibles may be subjected to very sudden changes without cracking and may be used repeatedly'.

In the wall of the crucible the graphite flakes, if added as a mineral rather than as grog, tended to orientate parallel with the faces of the crucible during moulding and thus any heat cracks developing in the clay from the face would be likely to run into a flake and stop. As graphite is much more resistant to oxidation than the alternatives, coke or charcoal, it would be present in the crucible for much longer (contributing to their greater life). The slow oxidation at high temperature extended the overall reducing conditions in the crucible and thus preserved and even increased the carbon content of the steel (Barraclough 1984a, table 1, 54).

Fluxes were added from the early days of the process as recorded in Sheffield from the 1770s by Geisle. The Marshall's crucible indicates that the flux contained manganese dioxide. Such fluxes were not actually necessary, but the steel makers clearly believed that the very mobile liquid manganese slags formed an essential protection for the molten steel as stated by Broling (see above). These additions of manganese dioxide continued to be made to the crucible charge through the 19th century, often confused with Josiah Heath's very different 'carburet of manganese',[5] but it can now be appreciated their addition long pre-dated the carburet in Sheffield.

Later developments and Indian inspirations

Descriptions of how the Asian steel was made based on direct observation, in particular details of the *in situ* carburisation and co-fusion methods, were not published until the 19th century and thus are most unlikely to have played any part in the in the early technical development of crucible steel processes in Europe (Bronson 1986), and Huntsman's process was fundamentally different from either of the Asian processes.[2] In 1795 George Pearson published his work on the working of Indian crucible steel, which he believed was made by an *in situ* carburisation process (although erroneously stating that the feedstock was iron ore rather than wrought iron). Francis Buchanan published the first detailed and illustrated eye witness account of the *in situ* process in 1807, followed by that of Benjamin Heyne in 1814. Buchanan's description was based on his travels in India in 1802-3, but Heyne's account was based on travels in the early and mid 1790s, and from the late 1790s he had been in London corresponding freely about his travels. Thus there was an awareness of the *in situ* method at about the time that David Mushet took out his patent on it in 1800 (Mushet 1805), and interestingly Mushet also believed that iron ore could be used directly as the feedstock as well as metal (Barraclough 1984a, 63; 1990, 22). Percy (1864, 778) drily remarked:

> 'It is curious that Mushet's process so far as it relates to the use of malleable iron in the production of cast steel should in principle, and I may add even in practice too, be identical with that by which the Hindoos have from ancient times prepared their wootz. I cannot discover any essential difference between the two.'

The process with either ore or metal was not a success as the temperatures necessary to melt the wrought iron could not be satisfactorily maintained.[8]

The Indian co-fusion process was first published by H W Voysey in 1832, eight years before it was patented in England by William Vickers in 1839 (Percy 1864, 776; Barraclough 1984a, 64). Interestingly, in Vickers' patent the wrought and cast iron were to be melted with both charcoal and manganese dioxide, once again showing the continuity of the use of manganese minerals in English steel production.

By the 1830s the potential of Indian iron and steel was at last being realised. Indeed, in the 1830s John Heath established blast furnaces fired with charcoal at Porto Novo (modern Parangipetta in the South Arcot District of Tamil Nadu) with the intention of producing good quality charcoal-smelted bar iron as an alternative feedstock to Swedish iron for the Sheffield steel makers (Ball 1881, 34-50; Heath 1832). To publicise their product the company supplied much of the iron for the Menai and Britannia Tubular railway bridges in Britain.

Up to the middle of the 19th century the Huntsman process was the sole commercial method of producing liquid steel. The 1850s brought the Bessemer process (Barraclough 1990) and the era of cheap steel, but crucible steel was still very much in demand for top quality high carbon steels (Carnegie and Gladwyn 1918). Thus, other cheaper crucible methods began to be explored, including both co-fusion and *in situ* carburisation, utilising new furnace technologies, notably Frederick and William Siemens' regenerative gas-fired crucible furnaces (Barraclough 1990, 23). Thus although the traditional Asian processes did not inspire the original Huntsman process, they could well have spurred research and experimentation, especially into the *in situ* and co-fusion methods. By the end of the 19th century, these methods had all but replaced the original Huntsman process, except in Sheffield, where production continued on a very minor scale into the 20th century.

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Notes

1 It must be borne in mind that until the early 19th century most English steel makers did not even fully understand that the crucial factor differentiating steel from iron was the carbon content.

2 This is a fundamentally different approach from the Asian crucible steel makers who actually made the steel from iron in their crucibles (see note 8).

3 There is a patent of 1762 for a white crucible of refractory clays, tempered with high purity Woolwich sand (Barraclough 1984a, 34).

4 Although often called graphite crucibles, they were in fact of refractory clay which either contained graphite or was tempered with additions of graphite. Such a crucible could contain between 20 and 70% by volume of graphite (typically around 40%), although considerably less by weight (Martinón-Torres *et al* 2008; Martinón-Torres and Rehren 2009).

5 Metallic manganese serves to render the presence of sulphides in the iron harmless. Even traces of iron sulphides are extremely deleterious as they concentrate on the grain boundaries and at the relatively low temperatures required to hot work iron are molten and thus act as centres from which cracks can propagate during working, rendering the iron what is known as hot short. If metallic manganese is added to the molten iron it will preferentially unite with any sulphides present and the resulting manganese sulphide has a much higher melting temperature and is relatively harmless. Thus Heath's carburet enabled coal and coke, which contain sulphur, to be used to smelt iron, greatly reducing the cost of smelting, and from the mid 19th century it has been common practice to add small amounts of manganese to iron and steel for this purpose. From the 1880s, manganese was a component in some of the more important early alloy steels, being especially useful where heavy wear was likely such as on railway points (Hadfield 1888; 1926; Anon 1956).

6 The central European crucibles were fired to 1300–1400°C sufficient to form mullite (Martinón-Torres and Rehren 2009). Thus any steel-making crucible that incorporated these crucibles, either new or used, ground up as a grog temper, would already have contained some mullite. The Bavarian crucibles, used by the gold refiners etc, were made from refractory clays containing graphite and were fired to temperatures in excess of 1300°C.

7 The obvious source of graphite for Sheffield was the deposits at Borrowdale in Cumbria which were being worked through the 18th and early 19th centuries. However, apparently none of the Sheffield sources mention Borrowdale and none of the Borrowdale sources mention Sheffield or crucible steel as the destination of their graphite (Lax and Maxwell 1998-9).

8 This lack of success seems surprising as the *in situ* method had been used successfully for millennia in Asia using much simpler installations. However, the Asian processes were very different,

seemingly more primitive, but in practice chemically much more sophisticated. The Sheffield steel masters attempted to carburise wrought iron with charcoal, that is by reacting two solid materials. In practice the carburisation can only really take place if there is a gas or liquid phase to ensure intimate contact, hence the necessity of melting the wrought iron, but even so contact was poor as the charcoal floated on the surface of the molten iron. By contrast the Asian processes always used plant material, including leaves, nuts etc along with charcoal and the wrought iron. On heating the initial reaction would be to char the plant material, generating carbon monoxide. This gas could be reduced and carburise the hot iron surface (identical to the European case hardening process, but carried out at higher temperatures and under more controlled reducing conditions). The carburised face would begin to melt at the temperatures of 1200-1400°C attained in the crucibles, allowing further carburisation of the iron directly by carbon, leading to the carburisation and melting of the whole mass of the remaining iron.

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