The metallurgy of early Chinese wrought-iron and steel objects from the British Museum

M L Wayman and C Michaelson

ABSTRACT: The collections of the Department of Asia, British Museum contain a number of early Chinese objects made of iron or steel. A selection of these, including crossbow bolts, stirrups, edge tools and miscellaneous objects, have been analysed metallographically. The results illustrate various ferrous metallurgical technologies in use between the late 1st millennium BC and the mid 2nd millennium AD. A number of the objects are conventional wrought irons made by the bloomery process or the fining of blast furnace iron; some of these had been carburised to produce steel with a wide range of carbon contents. Other objects had been produced as cast iron, and then subjected to solid-state decarburisation to produce low-carbon iron or steel. Piled, forge-welded structures were common. Composite crossbow bolts had been made by the casting-on of bronze heads onto iron shafts.

Introduction

Despite much recent work (as discussed by Needham 1958; Rostoker and Bronson 1990; Rawson 1993; Han Rubin 1998; Bronson 1999; Wagner 1993; 1999; forthcoming; Chen Jianli *et al* 2003), our understanding of the history of iron and steelmaking in China is still evolving. At present there seems to be general agreement that smelted wrought iron first appeared in China at some time during the first half of the 1st millennium BC, *ie* significantly later than in Western Asia, from whence the knowledge of its use if not the relevant production technologies (likely the bloomery process) presumably spread. Furthermore, it appears likely that around the middle of the 1st millennium BC, liquid iron was being produced in Chinese blast furnaces, and being used both for castings and for conversion to wrought iron by decarburisation employing a fining or puddling process. This is in contrast to the situation in Europe, where such technologies did not appear until after 1000AD. The many remaining deficiencies in our understanding are partly a result of the difficulty of identifying production processes by analysis of iron artefacts, and partly a result of excavation and dating uncertainties. But it does seem clear that at least for the latter part of the 1st millennium BC in China both cast iron and wrought iron were being produced and used for weapons, tools, agricultural implements, vessels, ornaments, horse trappings and a host of other purposes (see *eg* Wagner 1993).

Wrought iron is a material that was widely used because of its tensile properties, including good toughness, and the ability to be readily shaped by forging and forge welding. Cast iron has a lower melting temperature and good casting properties but it is much more brittle than wrought iron, having both poor ductility and poor resistance to crack growth. Neither wrought iron nor cast iron is capable of the combination of strength and toughness that can be obtained from steel.

Recognizing the limitations of cast iron, the Chinese applied a number of processes to improve its deleterious properties. The products of these various processes include a range of materials that we would now call wrought iron, malleable cast iron, and steel, all of which have properties that are in some respects improved over those of the basic cast iron. Some of these processes involved melting the cast iron while others were heat treatments applied at temperatures below the melting point, so that the advantages associated with the ready creation of desired shapes by casting were not lost. These products and processes will now be discussed individually.

Processing of white cast iron

Most of the early Chinese cast iron that has been analysed has been found to be the type known as white cast iron (also referred to as white iron), and hence it is the processing of this material that is considered here.

Solid state decarburisation processes

If white cast iron is annealed for many hours at a temperature that is high but still well below its melting temperature, the distribution of the carbon (which in white cast iron exists predominantly as cementite) can change in ways that depend on the annealing time and temperature, and the furnace atmosphere. The result lies somewhere on a continuum between fully malleablised cast iron at one extreme, and fully decarburised iron at the other, with steel as an intermediate state.

During annealing in a reducing atmosphere the carbon dissolves in the (austenite) matrix and, during several days at, typically, 900–1000°C in a furnace or kiln, gradually reprecipitates as irregularly shaped clusters or agglomerations of graphite. During subsequent cooling, the matrix transforms to a mixture of ferrite and pearlite depending on the amount of carbon remaining in solution. This product is ‘malleable cast iron’ which exhibits some of the desirable properties of grey cast iron but without the brittleness caused by its thin and sharply-pointed graphite flakes. No such processes are known in the West prior to experiments in England by gun founders in the 17th century AD.

If the annealing is carried out in an oxidising atmosphere, iron oxide forms on the surface and reacts with the carbon creating a CO/CO_2 gas mixture that escapes into the furnace atmosphere leaving a carbon-depleted austenite layer at the iron surface. With increasing annealing time the process continues, with carbon diffusing from deeper in the bulk of the casting out to the surface where it is removed by the oxidation reaction. Thus during this process the microstructure consists of a decarburised surface layer with a high-carbon core in the centre of the casting. During subsequent cooling, the austenite transforms to ferrite and/or pearlite, depending on the amount of carbon remaining in solution. Longer annealing times give a deeper decarburised surface layer and under the right conditions the casting can be fully decarburised, leaving a completely ferritic microstructure after cooling. Alternatively, before all of the carbon has a chance to diffuse out to the surface some of it may have sufficient time to precipitate as graphite clusters in the central regions of the casting. This is the case, for example, for an early Chinese sword in the British Museum collections (Wayman and Michaelson in press).

Full decarburisation would create a material equivalent to a wrought iron but without the slag inclusions that are trapped in normal wrought iron. However, if the decarburisation process is not carried to completion, it is possible to produce steel. For example in regions where the carbon content is lowered to 0.8% carbon, then the slow cooling would create a fully pearlitic microstructure, *ie* a eutectoid steel. Carbon contents below 0.8% would yield hypoeutectoid (ferrite-pearlite) steels, providing that they were cooled relatively slowly. Furthermore, in principle these steels could be quenched from the austenite range to form martensite that could then be tempered to obtain a wide range of strength/ductility properties. In reality, a uniform carbon content would not be anticipated, so a heterogeneous microstructure would be likely; however, the concept of creating a steel by solid-state decarburisation of a cast iron is a feasible one, albeit not economically feasible by modern standards. One problem is that since it relies on carbon diffusion from the centre to the surface of the object, the necessary annealing times for thick objects would be excessively long, and a carbon gradient decreasing from the centre of the object towards the surface would normally be expected. This might in some cases be an advantage, but more often it would be deleterious to the service performance of the steel.

Solid-state decarburisation processes, including malleablisation, were utilised in 1st millennium BC China, leaving their evidence in the microstructures of artefacts (see *eg* Wagner 1989; 1993; forthcoming). Archaeological excavations at several early iron-smelting sites have exposed kilns in which such heat treatments could have been carried out. Furthermore, there is archaeological evidence for cast iron having been cast into thin sheets that could subsequently be decarburised in a reasonably short annealing time. This is suggested by the existence of appropriate moulds along with large numbers of thin cast-iron sheets having carbon contents as low as 0.1% at a Han dynasty (206BC–AD220) site (Bronson 1999, 189). After decarburisation, the thin sheets could have been stacked and then forge-welded together to create thicker objects.

Formation of wrought iron (or steel) by fining

By melting cast iron in the presence of excess oxygen, *eg* an air blast, the carbon is progressively oxidised and removed from the liquid iron. As its carbon content decreases, its melting temperature rises and the liquid becomes a pasty semi-solid mass. This process is called fining; a variant is called puddling (terms used in the West), and the Chinese term is translated as 'stir frying' (Wagner 1993, 290 fn37) or 'steel frying' (Bronson 1999, 186). During the process the liquid iron reacts with the furnace walls to form a slag that protects the solid steel against excessive oxidation. Eventually the pasty lump is removed from the hearth and smithed to consolidate the mass and remove as much of the trapped slag as possible. The process therefore creates solid low-carbon iron containing slag inclusions, in other words it creates wrought iron that is comparable to the product of a bloomery furnace. If all the carbon is removed the matrix will be ferritic. However, by arresting the operation before all the carbon is removed the solid product could be left with a carbon content in the range appropriate for it to be called a steel. Although control of this process must have been difficult, it is not impossible. On the other hand steel was more readily produced by the carburisation of low-carbon iron that had been produced by the fining or puddling of cast iron.

Because of the inability to confidently distinguish fined iron from bloomery iron, it is not possible to be sure when each process was first used in China but it is known from archaeological evidence that fined/puddled wrought iron was produced at least as early as the 2nd century BC (Bronson 1999).

Other processes

Several other processes were used in China to produce iron and steel objects. Included among these is the carburisation of wrought iron by exposing it to liquid cast iron. Various techniques were used (Needham 1958, 26; Wagner forthcoming, 55–7 and 205–16), the most widely known being immersion of the wrought iron in a bath of liquid cast iron, a process referred to by Han Rubin (1998) as 'infusion carburisation'. The steel produced in China in this manner was known as 'irrigated' steel. A similar process appeared much later in Europe where it was used for carburisation of a surface layer and is sometimes known as the Brescian process.

A considerable number of other Chinese ferrous metallurgical processes appear to be unique or at least to have preceded the development of similar processes in the West (Han Rubin 1998), including stack moulding for the high volume production of castings and, at least by the beginning of the 2nd millennium AD, the successful replacement of charcoal by coal and/or coke as the fuel and reductant in blast furnaces.

Still there remains a great need to improve and consolidate our understanding of the history of Chinese ferrous metallurgy. With this in mind an integrated programme of metallurgical characterisation has been carried out on a selection of early Chinese ferrous artefacts from the collections of the British Museum, from both the Department of Asia and the Department of Coins and Medals. Parts of this programme have been reported elsewhere, specifically cast irons in the form of coins and statuary (Wayman and Wang 2003, Craddock *et al* 2003, Wayman *et al* 2004), as well as iron and steel swords (Wayman and Michaelson in press). The present work deals with other objects made of wrought iron and steel.

Experimental procedures

Samples of the order of a few cubic millimeters in size were cut from each of the objects using a jewellers' saw or a low-speed diamond wheel and the microstructures characterised using optical and scanning electron metallography. Elemental compositions (notably Si, Mn, S and P contents), both bulk analysis of objects and microanalysis of microstructural constituents such as inclusions, were obtained by energy dispersive X-ray analysis (EDX) in the scanning electron microscope (SEM). Analysis of standard reference materials confirmed that the lower limits of detection of these elements were approximately 0.1–0.15%. The SEM-EDX results can be considered to have a precision and accuracy of ±10–20% relative to the values obtained. Carbon contents were estimated from the microstructures. Details of the procedures have been previously reported (Wayman and Wang 2003).

Results and discussion

A selection of early Chinese wrought iron and steel objects in the British Museum's collections was analysed, including four crossbow bolts, four stirrups and seven miscellaneous objects (a knife, a dagger, two skewers, an axehead, a spear point and part of an opium pipe). The dimensions and attributions of these objects are shown in Table 1, and their compositions and microstructural characteristics in Table 2.

Crossbow bolts

Crossbow bolts are known from at least as far back as the 4th century BC, examples having been excavated from graves dating to the late Warring States period (5th–3rd century BC), about the time when crossbows are believed to have been developed (Wagner 1993, 157). The bolts are typically 150–200mm long and have a straight

Table 1: Details of objects analysed

Code	Museum Reg No	Object	Findspot	Date (century)	Dimensions (mm)
CB1	1917 MAS 762, 2 pc.	crossbow bolt, iron shaft, bronze head	Dunhuang wall station	late 2nd BC–mid 2nd AD	244 long
CB2	1917 MAS 814	crossbow bolt, iron shaft, bronze head	Dunhuang wall station	late 2nd BC–mid 2nd AD	124 long
CB3	1945.4-18.1	crossbow bolt		5–4th BC (Eastern Zhou)	156 long
CB4	1907.11-11.149	iron crossbow bolt	Kara-dong	3rd–4th AD	79 long
S1	1939.3-11.3	stirrup		14–17th AD	167 high, 147 wide
S2	1939.3-11.4	stirrup		14–17th AD	167 high, 147 wide
S3	1939.3-11.5	stirrup with silver inlay		17th AD	145 high, 130 wide
S4	1939.3-11.6	stirrup with silver inlay		17th AD	145 high, 130 wide
M1	1917 MAS 807	spear point	Dunhuang wall station	late 2nd BC–mid 2nd AD	152
M2	1917 MAS 777	axe head	Dunhuang wall station	late 2nd BC–mid 2nd AD	167
M3	1917 MAS 839	skewer	Dunhuang wall station	late 2nd BC–mid 2nd AD	108
M4	1917 MAS 512	dagger with wood handle	Kara-dong	3rd–4th AD	202 long
M5	1917 MAS 603	knife	Miran Fort	mid 8th–mid 9th (750–860) AD	152 long
M6	1917 MAS 734	skewer	Dunhuang wall station	late 2nd BC–mid 2nd AD	127 long
M7	1917 MAS 959	part of an opium pipe	So-yang-cheng	7–13th AD	51

Note: The seven miscellaneous objects, as well as CB1, CB2 and CB4 are part of the collections made by Sir Aurel Stein in far western China (Chinese Turkestan, now Xinjiang Province) in the early 20th century. One of the crossbow bolts (CB4) was excavated during Stein's first expedition (Stein 1907), while all the other Stein material reported here was excavated during his second expedition (Stein 1921).

shaft 3–5mm in diameter with a pointed head that has a triangular or winged cross-section. Many crossbow bolts are composite objects consisting of bronze heads on iron shafts, but all-bronze bolts and all-iron bolts were also produced. Wagner quotes Chinese work that concludes that the composite bronze-iron bolts were widely used from the 3rd century BC to the 2nd century AD. Hundreds of crossbow bolts are known to exist and it is likely that enormous numbers of them were manufactured.

In the present work, the iron shafts of four crossbow bolts (Fig 1) were analysed. Three of these are composite bolts with bronze heads on iron shafts while the fourth (CB4) is all iron. Bolt CB3 is believed to predate the

Table 2: Sample microstructures and approximate compositions

Code	Object	%Si	%P	%S	%C	Inclusions (abundance)	Microstructure
CB1	crossbow bolt shaft	nd	nd	nd	0–0.1	silicates (moderate)	ferrite-cementite
CB2	crossbow bolt shaft	nd	0.25–0.3	nd	0–0.1	sulphides (low)	ferrite-cementite
CB3	crossbow bolt shaft	0.5	0.5 (0.2 Mn)	0.1	0	sulphides (low), some localized silica	ferrite with solidification pores in central region
CB4	crossbow bolt shaft	nd	nd	nd	0	various (moderate)	ferrite
S1	stirrup	nd	0.2	nd	0	silicates (high)	ferrite
S2	stirrup	nd	0.3	nd	0	silicates (high)	ferrite
S3	stirrup	nd	nd	nd	0	silicates (high)	ferrite
S4	stirrup	nd	nd	nd	0	silicates (high)	ferrite
M1	spear point	nd	0.15	nd	0–0.1	silicates (moderate)	ferrite-cementite
M2	axe head	nd	0.25 (patchy)	nd	0–0.1	silicates (high)	ferrite-cementite
M3	skewer	nd	0.2 (patchy)	nd	0.1–0.2	silicates (high)	ferrite-pearlite
M4	dagger	nd	0.1–0.4 (patchy)	nd	0.1–0.7	silicates (high)	ferrite-pearlite
M5	knife	nd	nd	nd	1	silicates (high)	ferrite-cementite
M6	skewer	0.3	0.1–0.2	nd	0.6–0.7	sulphides (low)	pearlite-ferrite
M7	opium pipe	nd	0.25	nd	0.1	sulphides (moderate)	ferrite-cementite

Note: nd = not detected

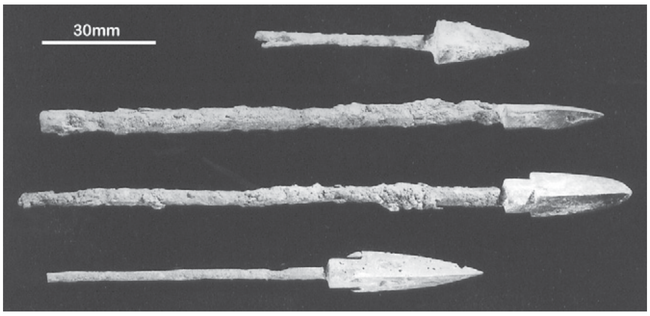

Figure 1: Crossbow bolts. From the top: CB4 (the all-iron bolt); CB3; CB1; CB2. (photo: T Milton/British Museum).

other bolts (Table 1). Qualitative XRF analysis of the head of CB3 showed it to be a leaded bronze, and the other bronze bolt heads appeared to be similar.

Metallographic analysis showed that all four of the bolt shafts are low-carbon iron with ferritic microstructures, some of which also contain small amounts of grain boundary cementite and/or pearlite. In all four cases, the carbon contents are well below 0.1%, however they exhibited noticeably different microstructures. One (CB1) is a classic wrought iron, with a ferrite matrix and abundant slag inclusions. The microstructure exhibits alternating elongated bands of higher and lower inclusion content, with the small amount of iron carbide localized in the high-inclusion bands. These characteristics suggest that the shaft had been fabricated by folding or forge-welding together (piling) several different pieces of iron with different carbon and inclusion contents. A void resulting from incomplete welding during the piling operation confirms that this is a piled structure.

In contrast, the shafts of the other two bronze-iron bolts (CB2 and CB3) are quite different in that both have very low abundances of non-metallic inclusions, *ie* they are strikingly clean microstructures, the only inclusions being sub-micrometre sized sulphide particles. In CB2 a small amount of phosphorus occurs in the ferrite (as evidenced by EDX and by the observation of ghosting in the etched microstructure) and a small amount of iron carbide is present in the approximate centre of the cross-section. In CB3 the ferritic microstructure was found to have high silicon and phosphorus levels and, importantly, a considerable amount of solidification porosity in the central regions of the shaft (Fig 2). These characteristics are indicative of iron that has been cast into the rod shape and then subjected to solid-state decarburisation to create a low-carbon iron shaft. The presence of casting porosity in CB3 shows that the shaft is a monolithic piece, not a piled or forged structure; liquid cast iron must have been cast into this rod shape and the cast rods were then subjected to solid-state decarburisation in a kiln. Although casting porosity was not observed in CB2 the carbon distribution, showing some cementite in the centre of the cross-section, is also suggestive of a monolithic structure rather than a piled structure. These shafts are sufficiently thin that they would have been readily decarburised in a reasonable time (*eg* a few days), so it would have been feasible, and economically advantageous, to cast them directly to final size and shape and then decarburise them, rather than forging them to shape after decarburisation. This interpretation is supported not only by the presence of the solidification porosity but also by the observation of an internally oxidised layer just below the surface of the shaft CB3; within this layer all of the silicon was in the form of silica inclusions, unlike the remainder of the cross-section where the silicon was in solution in the ferrite. Such an internally-oxidised layer could be expected to form during the decarburisation anneal in material with the observed level of silicon in solution in the austenite. The occurrence of the sulphide inclusions may be interpreted as evidence for the use of (sulphur-bearing) coal (or coke) in the kiln used for the decarburisation anneal.

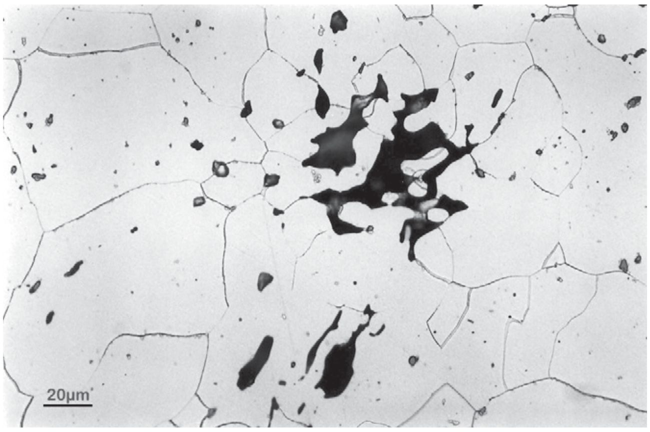

Figure 2: Transverse cross-section of crossbow bolt shaft CB3, showing distribution of shrinkage porosity in the centre of the cross-section. Optical micrograph, nital etch.

Of relevance here are the studies of Hua Jue-ming *et al* (1960), who have reported the results of metallographic analysis of another iron crossbow bolt shaft from a Western Han period (220BC–AD9) site. Here the iron exhibited a decrease of carbon content near the surface of the shaft, again consistent with the iron shaft having been cast and then decarburised. A similar casting-and-decarburisation process has been suggested to explain the microstructure (including the presence of sulphide inclusions) of one of the Han swords in the British Museum collections as reported elsewhere (Wayman and Michaelson in press).

The shaft of the all-iron crossbow bolt CB4 has a microstructure characteristic of a conventional wrought iron, rather than one made by solid-state decarburisation. The ferrite microstructure contains several types of unusual inclusions, mainly oxides with incorporated sulphur- and phosphorus-bearing phases. Minor amounts of silicate are also present. The inclusions are present in bands of high and low abundance. This is a heterogeneous wrought iron or a piled wrought-iron structure. Visual examination was unable to determine whether this is a one-piece wrought-iron bolt or alternatively whether a cast-iron head was cast-on to the iron shaft; the latter possibility will be discussed further below.

In summary, two of the four crossbow bolt shafts appear to be iron that has been cast directly to the shape of the shafts, and then subjected to solid-state decarburisation to create low-carbon iron. The other two bolt shafts are conventional wrought iron.

The overall appearance of the composite bolts suggests that the incorporation of an iron shaft into a bronze head was carried out by the 'casting-on' process, whereby the pre-formed iron shaft would be embedded in a shaped clay mould so that liquid bronze could be poured into the mould and allowed to solidify in contact with the iron shaft. Similar casting-on of bronze attachments onto bronze objects was a common technique in traditional Chinese bronze casting, both for joining components and for repairing defective castings (see *eg* Gettens 1965; Chase 1991). Alternatively the iron shaft could have been combined with a wax bolt head and the two coated with clay to build up a mould for the lost-wax casting of the bolt head.

It may not appear obvious why an object such as a crossbow bolt would have been made in such a seemingly complex manner as are these composite bronze-iron objects. However, since crossbow bolts were made in very large numbers, high-volume production operations would be necessary. Making of individual bolts or even the simpler bolt shafts by hand-forging iron blooms or fined iron lumps would have involved significant amounts of labour, and the dimensional irregularity of a hand-forged object could have detracted from its service performance. High-volume stack moulding casting operations are known to have been used for cast iron in China at least as early as the Han period (206BC–AD220) (Rostoker *et al* 1983; Hua Jue-ming 1983). Rods of the appropriate dimensions could have been cast in large numbers for service as bolt shafts (and perhaps other purposes), decarburised in large batches and then incorporated into moulds for the casting-on of the bronze heads. The fact that leaded bronze was used for the bolt heads, as well as the observation of file markings on the surfaces of the bronze (possibly related to the removal of the casting gating systems) support this suggestion.

As Wagner has suggested, as-cast cast iron would have had adequate properties to serve as a crossbow bolt shaft, however applying the solid-state decarburisation process provided a better shaft in several respects. First of all, decarburising the iron raises its melting point so that 'casting-on' bronze to a low carbon iron shaft would be easier than to a cast-iron shaft (the melting temperature of typical bronze is not far below that of cast iron). Furthermore, decarburisation removes the brittleness that is inherent in cast iron, hence any warping in the casting or casting-on processes could be rectified by judicious deformation of the iron shaft. It would be expected therefore that crossbow bolt shafts would have been made of low-carbon iron, either normal wrought iron or solid-state decarburised cast iron as shown above.

The casting-on process could also have been used for the manufacture of all-iron crossbow bolts. Because cast iron has a much lower melting temperature than low-carbon iron, a cast-iron head could have been cast onto a low-carbon iron shaft as readily as bronze heads. In the case of CB4 further analysis of the head of this bolt would be necessary to confirm this.

Wagner (1993, 157) speculates that the use of a bronze head on a crossbow bolt was desirable for both technical and economic reasons. According to these arguments, the aerodynamics of a bronze-headed bolt would be superior, since bronze is capable of being cast to more precise shapes than is iron. Furthermore, the higher density of leaded bronze as compared with iron may have contributed to performance. The use of iron rather than bronze for the shaft is likely to be a result of economics, with vast numbers of bolts being produced and iron being cheaper and more readily available than bronze. In fact at times economics must have completely dominated performance requirements, hence the occurrence of all-iron crossbow bolts.

Stirrups

Two pairs of 17th century AD iron stirrups, pair A (stirrups S1 and S2) and pair B (S3 and S4), were also analysed. Each stirrup consists of a suspension yoke in the shape of an inverted U-shaped strip to which a two-piece flat base is attached, most likely by welding. S3 and S4 are inlaid with silver. Samples for analysis were taken from the suspension yoke of each stirrup.

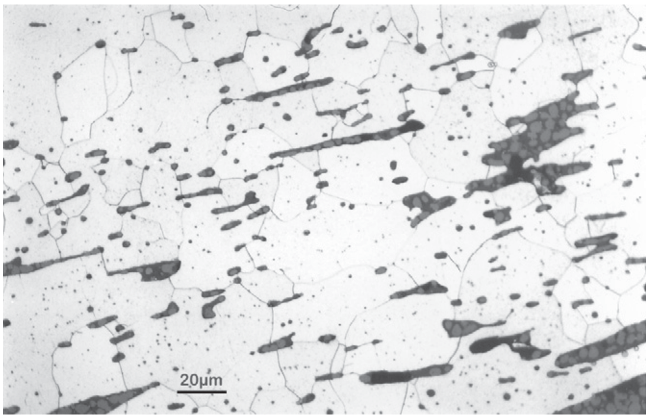

Figure 3: Microstructure of stirrup S1 showing ferrite with slag inclusions. Optical micrograph, nital etch.

The yokes of all four stirrups were found to be wrought iron, with the characteristics of each pair being similar to each other and somewhat different from those of the other pair. All of the microstructures consist of equiaxed ferrite grains with a high abundance of non-metallic inclusions (Fig 3). Typical ferrite grain sizes range around 50μm, although some regions of significantly larger grains are present in both stirrups of pair A. Both stirrups of pair A showed detectable levels of phosphorus in the matrix, and this is manifest as a ghost network present in the etched microstructure, as is normal in phosphoric iron (Stewart *et al* 2000). The iron of pair B does not contain detectable levels of phosphorus in the areas analysed, although some phosphorus was noted in the inclusions. No other elements were detected in the matrices of any of the stirrups and little or no cementite was observed, showing that the carbon contents of all of them are very low.

The non-metallic inclusion abundance in all four of the stirrups is extremely high (Fig 3). These inclusions are distributed heterogeneously but there is no sign of the banding that is sometimes associated with forge-welded iron. The inclusions are typically rounded and many are elongated, forming patterns which must reflect the pattern of deformation to which the iron had been subjected. Most of the inclusions consist of two or three phases, typically a globular dendritic iron oxide phase in a glassy iron silicate matrix, although in some cases iron silicate crystals are also present in the glassy matrix. These are slag inclusions typical of the type found normally in wrought iron, although their abundance here is noticeably high. In many regions the ferrite grain boundaries could be seen to be pinned by inclusions, and as a consequence those regions with higher inclusion abundance have finer ferrite grain sizes. This is expected when ferrite recrystallizes in a ‘dirty’ iron like this one, and results from the heat used in forging. A few Neumann bands (deformation twins), a characteristic consequence of hammering at low temperatures, were noted in localised near-surface regions of two of the stirrups (one from each pair).

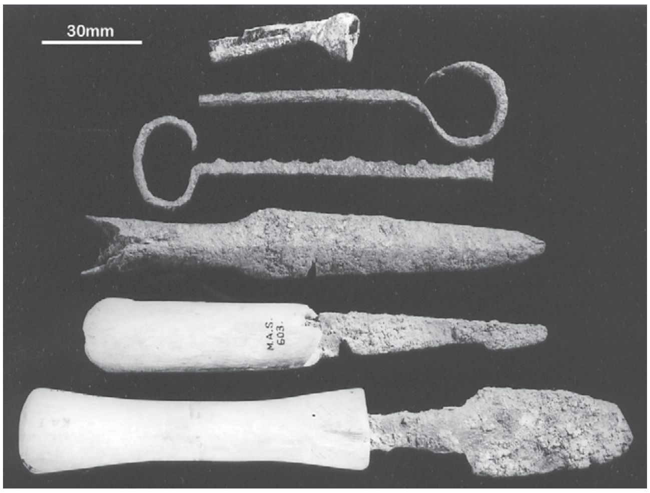

Figure 4: Six of the seven miscellaneous objects analysed. From the top: opium pipe M7; skewer M3; skewer M6; spearpoint M1; knife M5; dagger M4. (photo: T Milton/British Museum).

The differences in the characteristics of the wrought iron of the two pairs are sufficient to allow them to be distinguished. The phosphorus level is clearly higher in pair A, while sulphur-rich particles are present only in the inclusions of pair B. The shapes of some inclusions of pair B are highly irregular giving the impression that these two stirrups had not been forged as heavily as those of pair A.

In summary, the suspension yokes of these stirrups are made from wrought iron of poor quality, having negligible carbon content and a high abundance of slag inclusions. The iron of the two pairs differs slightly. In all cases the iron had been forged to shape at high temperature but in two of the stirrups there are indications of local hammering at room temperature. There is no evidence that any of these stirrup bars had been made by forge-welding several pieces of iron together. Nothing was revealed by these analyses that would allow this wrought iron to be distinguished from typical wrought irons originating in many parts of the world over many time periods, or to associate them with a particular ironmaking process.

Miscellaneous material

Of the seven objects described here (Fig 4), six are categorised as edge tools (see Table 1). The seventh object is the remains of an opium pipe, consisting of a metal tube widened at one end to form a bowl. For each of the edge tools, with the exception of M6, a cross-section was cut through the object transverse to its axis and including the cutting edge of the blade (a longitudinal section was cut through the shaft of skewer M6). The stem of the opium pipe was also sampled. Irons and steels with a full range of carbon contents are represented amongst these objects (Table 2).

Five of the objects have microstructures typical of early irons, with low carbon content, heterogeneously distributed, and significant amounts of silicate slag inclusions. The spear point M1 and the axehead M2 were both found to be low-carbon wrought irons with carbon contents no greater than 0.1%. The microstructure of the spear point is heterogeneous, having a central region that is coarser in grain size and cleaner in terms of slag inclusions as compared to the outer regions, which are similar to each other. This is consistent with the object having been made from a piece of wrought iron that was wrapped around to enclose a different piece of iron and the whole forged together to produce an object with three layers, the outer two of which are the same material. The axehead is also heterogeneous, being in general coarse-grained with patches of fine-grained material having cementite particles on the ferrite grain boundaries. Slag inclusions are abundant in the microstructure, and the presence of phosphorus is signalled by a ghosting effect. Along the centre-line of the axehead is a narrow band of fine equiaxed grains and a high density of non-metallic inclusions. This is interpreted as the result of the folding of a plate of material to double its thickness, followed by forging to consolidate. Near the cutting edge the grains are more elongated, the phosphorus ghosting is distorted and the inclusions are narrower and somewhat fragmented, all signs that the latter stages of shaping were carried out by forging at moderate temperatures. The orientations of the inclusions relative to the surface showed also that the cutting edges of both the spear point and the axehead had been sharpened by abrasion (*eg* filing or grinding), the former abraded from one surface and the latter from both.

The skewer M3 was found to be a low-carbon steel, with heterogeneous carbon content ranging up to about 0.2%. The dagger M4 is a similar material but with a much wider spread of carbon contents, ranging from about 0.1–0.7%. In this case the lowest carbon content was found at the cutting edge, where a high carbon content would have been desirable. Both of these objects were found to have a high abundance of slag inclusions, elongated by the forging and in some cases cracked, suggesting that some of the forging was done at low temperatures. The microstructures of both are consistent with their being monolithic pieces of material, forged to shape.

The microstructure of the knife blade M5 showed it to be a relatively homogeneous hypereutectoid steel consisting of spheroidised pearlite and proeutectoid cementite. The cementite morphology suggests that the blade has been hot worked preferentially at the blade edge. A high abundance of silicate slag inclusions was observed, somewhat banded, but there are no clear indications of the presence of a forge weld. This type of steel would make a good sharp knife blade, although a quenching heat treatment would have much improved its cutting abilities. It is notably homogeneous for a steel of this time period, but the high density of slag inclusions shows that it was made by a traditional smelting process, either the bloomery process or the fining/puddling of blast-furnace iron.

The microstructures of the other two objects, the skewer M6 and the opium pipe M7, are significantly different from those described above. One striking difference is the abundance and type of non-metallic inclusions. While all of the five objects described above contain silicate slag particles from smelting or fining/puddling operations, these two are notably clean in terms of silicate slag, although they do contain submicrometre iron sulphide or, in the case of the skewer, manganese-iron sulphide particles. The microstructure of M6 was found to be homogeneous, consisting primarily of pearlite with some proeutectoid ferrite, characteristic of a carbon content in the range 0.6–0.7%. There is no indication that the carbon content increases or decreases close to the surface. A large interdendritic shrinkage void was observed in the thick part of the blade cross-section. The homogeneity, cleanliness and porosity are consistent with a steel that has passed through the liquid state, and the presence of shrinkage porosity confirms that this is a cast-iron object that has been subjected to solid-state decarburisation. It is not obvious how this object ended up with a relatively homogeneous and relatively high carbon content. Either the solid-state decarburisation process was arrested, leaving a high carbon content, or it was fully decarburised and then re-carburised. In either case, a gradient between the carbon content near the surface and in the centre of the section might have been expected, but such a gradient was not observed. Perhaps a homogenising anneal had been carried out following the carburisation/decarburisation step. It must be noted that the pin of this skewer has a wedge-shaped cross section, and it is not impossible that, contrary to the excavator's impression, this is in fact a knife, the desired properties of which would justify a carburisation step.

The stem of the opium pipe is a thin sheet having a homogeneous coarse-grained equiaxed ferrite microstruc-

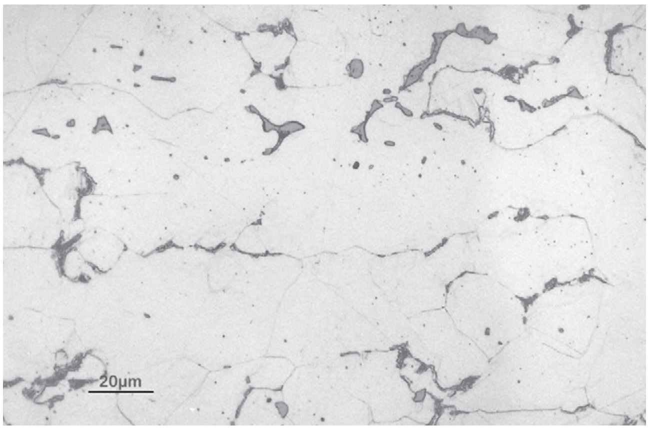

Figure 5: Section through the stem of the opium pipe M7, with the plane of the sheet horizontal, showing distribution of sulphide inclusions. Optical micrograph, nital etch.

ture with about 0.1% carbon present as grain boundary cementite. Like M5, it contains very few silicate slag inclusions but does display a moderate abundance of sulphide inclusions (Fig 5). The shapes of these inclusions suggest that they had been the last phase to solidify and had not changed their shapes since that time; all have rounded corners, giving them a globular appearance, but some are elongated and appear to have formed along grain boundaries. The elongations of the inclusions are in all orientations including perpendicular to the surface, a highly unusual orientation for inclusions in sheet.

In many respects this sheet appears microstructurally more like a casting than mechanically-worked sheet. Many of its characteristics, including its low carbon content, its sulphide inclusions and its thinness, are consistent with those expected of a piece of solid-state decarburised cast iron. The unexpected orientations of the sulphide inclusions can be explained if solid-state decarburised iron was hot worked to thin sheet, and/or to the final tubular shape, at a temperature high enough that the sulphides melted and agglomerated on austenite grain boundaries. The transformation to recrystallised ferrite with cementite would then have occurred as the sheet cooled following the hot working.

All of these seven objects would have had properties suitable for their intended purposes, although in some cases, not the optimum. This was particularly true of the knives which would have been much more functional if the same material had been given quenching treatments.

Conclusions

The objects examined here illustrate a number of the techniques employed by early Chinese ferrous metallurgists to produce iron and steel. Some of the objects, including two of the crossbow bolt shafts, all four stirrups and five of the miscellaneous objects were made of ferrous material produced either by the bloomery process or by the fining of cast iron. The spear point and the axe head had been fabricated by piling and/or folding and forge welding. The material in two of the crossbow bolt shafts, one of the skewers and the stem of the opium pipe had been cast into the final desired shape and then subjected to a solid-state decarburisation process in a coal- or coke-fired kiln. The properties of some of the objects would have benefited from quenching, but they did not appear to have been so treated. The analyses of these objects and others that have been studied elsewhere confirm that iron production and processing in early China must have been a true industry, with factories rather than workshops, that did not become characteristic of iron-working in other parts of the world until much later times.

The variety of processing treatments illustrated by these few objects is striking. It is likely that as more metallurgical studies are carried out the full spectrum of ferrous technologies used in early China will be revealed.

Acknowledgements

The authors are indebted to Jessica Rawson, who while keeper of the Department of Oriental Antiquities (now Department of Asia), greatly expanded the collection of Chinese iron material, encouraged our scientific study and has retained her active interest in the project. They are grateful to colleagues at the British Museum, especially Paul Craddock and Janet Lang, for advice and support. They also wish to express their appreciation to Donald Wagner for helpful comments and for supplying a draft of the manuscript of his forthcoming volume of *Science and Civilization in China*.

References

Bronson B 1999, 'The transition to iron in ancient China', in V C Pigott (ed), *The archaeometallurgy of the Asian Old World* (Philadelphia: MASCA Research Papers in Science and Archaeology 16), 177–193.

Chase W T 1991, *Ancient Chinese bronze art: casting the precious sacral vessel* (New York).

Chen Jianli, Han Rubin and Wan Xin 2003, 'The manufacturing technique of ferrous artefacts excavated from Xianbei gravesite at Lamadong village of Liaoning province', in P Jett (ed), *Scientific Research in the field of Asian Art: Proceedings of the First Forbes Symposium at the Freer Gallery of Art* (London), 70–78.

Craddock P T, Wayman M L, Wang H and Michaelson C 2003, 'Chinese cast iron through twenty-five hundred years', in P Jett (ed), *Scientific research in the field of Asian art: Proceedings of the first Forbes Symposium at the Freer Gallery of Art* (London) 36–46.

Gettens R J 1965, 'Joining methods in the fabrication of ancient bronze ceremonial vessels', in P Rathbone and W J Young (eds), *Application of science in examination of works of art* (Boston).

Han Rubin 1998, 'Iron and steel making and its features in ancient China', *Bulletin of the Metals Museum* 30, 23–37.

Hua Jue-ming, Yang Geng and Liu Enzhu 1960, 'Preliminary report on metallographic examination of some Warring States and Han period iron artifacts', *Kaogu xuebai* [*Acta Archaeological Sinica*] 1960.1, 73-88 (in Chinese); trans Wagner 1993, Translation 6.18, Fig 6.47.

Hua Jue-ming 1983, 'The mass production of iron castings in ancient China', *Scientific American* 248, 107–114.

Needham J 1958, *The development of iron and steel technology in China* (London).

Rawson J 1993, 'Chinese iron technology: the workshop and the factory', paper presented at the annual meeting of the Association for Asian Studies, Los Angeles, March 1993.

Rostoker W and Bronson B 1990, *Pre-industrial iron: its technology and ethnology* (Philadelphia: Archeomaterials Monograph 1).

Rostoker W, Bronson B, Dvorak J and Shen G 1983, 'Casting farm implements, comparable tools and hardware in ancient China', *World Archaeology* 15(2), 196–210.

Stein M A 1907, *Ancient Khotan: detailed report of archaeological excavations in Chinese Turkestan* (Oxford, reprinted New Delhi 1981).

Stein M A 1921, *Serindia: detailed report of explorations in central Asia and westernmost China carried out and described under the orders of HM Indian Government* (Oxford, reprinted Delhi 1980).

Stewart J W, Charles J A and Wallach E R 2000, 'Iron-phosphorus-carbon system: Part 3 – Metallography of low carbon iron-phosphorus alloys', *Materials Science and Technology* 16, 291–303.

Wagner D B 1989, *Toward the reconstruction of ancient Chinese techniques for the production of malleable cast iron* (Copenhagen: East Asian Institute Occasional Papers 4).

Wagner D B 1993, *Iron and steel in ancient China* (Leiden).

Wagner D B 1999, 'The earliest use of iron in China', in S M M Young, A M Pollard, P Budd and R A Ixer (eds), *Metals in antiquity* (Oxford: British Archaeological Reports Int Ser 792), 1–9.

Wagner D B forthcoming, *Science and civilization in China, 36 (c): Ferrous metallurgy*, unpublished draft dated 30 March 2005.

Wayman M L, Lang J and Michaelson C 2004, 'The metallurgy of Chinese cast iron statuary', *Historical Metallurgy* 38, 10–23.

Wayman M and Michaelson C, in press, 'Early Chinese ferrous swords from the British Museum collections', in Proceedings of the conference *Metallurgy- a touchstone for cross-cultural interaction*, British Museum, London, April 2005.

Wayman M and Wang H 2003, 'Cast iron coins of Song Dynasty China: a metallurgical study', *Historical Metallurgy* 37, 6–24.

The authors

Michael Wayman is a Professor Emeritus of Metallurgy at the University of Alberta in Edmonton. His research interests lie in archaeometallurgy and materials characterisation with recent emphasis on early ferrous materials.
Address: Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6.
e-mail: mwayman@ualberta.ca

Carol Michaelson is an Assistant Keeper in the British Museum. Her research interests focus on early Chinese material in general and the Qin and Han dynasty periods and jade in particular. She is currently writing a book on Chinese Jade and Chinese Art in Detail. In 2002 she opened a new gallery of Chinese jade in the Museum and is collaborating on a research project, conducted by the Museum's scientific research department, into establishing a chronology of jade tool working in China. Carol is also in charge of the digitization of the Museum's Central Asian material.
Address: Department of Asia, British Museum, London WC1B 3DG.
e-mail: cmichaelson@thebritishmuseum.ac.uk