Casting iron in ancient China

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ABSTRACT: Since at least the 5th century BC, cast iron was used widely in China in agriculture, warfare and craft production. Technological inovations in iron production led to societal developments such as increased food production, which in turn stimulated population growth. This paper presents the metallographic analyses performed on iron and steel artefacts from this period. The aim of this analysis was to understand the broader context and impact of iron casting technology, which ultimately helped to shape the development path of Chinese civilisation.

Introduction

The casting of iron in ancient China was a significant invention that occurred during the 5th century BC or earlier (Han 2000). Due to the absence of historical records regarding iron technology in this early period, scholarship concerning early iron production must rely on the archaeological record. Iron artefacts have been metallographically studied and the results of these investigations, including SEM-EDX analyses, are presented below.

According to current research, the earliest worked iron was meteoric iron, which was made into blades during the middle of the Shang Dynasty period, around the 14th century BC. The use of meteoric iron lasted more than 500 years, until the 9th to 8th century BC (Han, Jiang et al., 1999). The cooling and transformation of meteorites in space can take 4×10^9 years. The slow cooling rate (about 1-10°C per million years) creates a special Widmanstätten microstructure, in which nickel and cobalt are interspersed (Li, 1975). The iron-nickel alloy is easy to forge and quite tough, making it perfect for use as a sharp blade. Even within badly corroded iron artefacts, the meteoric microstructures can still be determined by metallographic analysis and electron microscopy. So far, seven meteoritic iron artefacts have been identified in China. The results indicate that ancient craftspeople were aware of the differences between iron and bronze, and familiar with the heat treatment of iron to enhance its performance (Han, Jiang et al. 1999). All seven meteoric iron objects were buried in high-status tombs, indicating that they had symbolic value for their owners.

Six iron weapons and tools excavated from the Guo State tombs dated to the 9th century BC in Sanmenxia, Henan Province, demand particular attention. Three of the objects are made from smelted iron, while the other three are made from meteoric iron, suggesting that the ancient craftspeople used both sources of iron simultaneously (Han, Jiang et al., 1999). Similar situations have been recorded in other parts of the world, such as in the ancient civilisations of Mesopotamia, Egypt, and Anatolia (Waldbaum 1980). These results have also pushed back the date of the earliest use of man-made iron in China to the 9th century BC or even earlier. (The earliest man-made bloomery iron objects dating to about the 14th century BC were unearthed from the Mogou site in Gansu Province in 2009; the results are forthcoming). The earliest smelted iron was made by the bloomery process, although archaeometallurgical remains of bloomery furnaces dating before the 2nd century BC are yet to be found in China. Shortly after the use of bloomery iron was established, cast iron was invented. The relationship between the use of meteoric iron and the invention of iron smelting technology is still not very clear.

Iron production before the 5th century BC

Iron artefacts dating to this early period have been excavated from various tombs. Prior to 1998, approximately 150 objects had been excavated, and 40 of these were studied using metallographic methods. From the analysis of these iron artefacts, the early iron production techniques can be summarised as follows.

Early iron artefacts were small and thin in size and simple in form and design. Many of the objects have handles of gold, jade, and bronze; some of them are inlaid with turquoise, gold, and jade, suggesting that they served as prestige items. Using such materials to decorate iron was one of the signature features of these early objects. The iron objects shared similar designs with the bronze wares found in the same tombs and dating to the same period. Agricultural tools such as shovels, hoes, sickles, and adzes also started to be produced in iron at this time.

The study of the 40 iron artefacts showed that 15 of them were produced from bloomery iron or bloomery steel and 25 were produced from cast iron or decarburised iron (Han 1998), as shown in Table 1.

Most of the early iron objects were badly corroded. Through careful identification and observation, however, smaller pieces of metallic iron with a cementite structure and minute inclusions could be found in the microstructure. In the

Table 1: Results obtained from 40 iron artefacts by metallographic examination.

Location	Object	Material
Changsha, Hunan	Sword 1	Bloomery steel, 0.5% C
Liuhe, Jiansu	Rod 1	Bloomery iron
Wuxian, Jiangsu	Shovel 1	Bloomery steel, 0.2% C
Linyi, Shandong	Knife 1	Bloomery iron
Changqing, Shandong	Dagger-axe 1	Bloomery iron
Sanmenxia, Henan	Sword 1, dagger-axe 1, spear 1	Bloomery steel or bloomery iron, weapons with bronze handles
Hancheng, Shaanxi	Dagger-axe 1, knife 1	Bloomery steel
Lingtai, Gansu	Sword with bronze handle 1	Bloomery steel
Guyan, Ningxia	Sword 2	Bloomery steel
Xiji, Ningxia	Sword 1	Bloomery steel
Pengyang, Ningxia	Sword 1	Bloomery steel
Tianma-Qucun, Shanxi	Iron fragment 2	White cast iron
Changzhi, Shanxi	Shovel I	Decarburised cast iron
Liuhe, Jiangsu	Bola 1	White cast iron
Changsha, Hunan	Ding 1	White cast iron
Jiangling, Hubei	Axe 1	Decarburised cast iron
Laohekou, Hubei	Shovel 1, adze 3, sickle 1, iron fragment 3	White iron 3, Decarburised cast iron 3, Solid state decarburising steel 2
Daye, Hubei	Axe 1	Decarburised cast iron
Dengfeng, Henan	Adze 5, hoe 1	Decarburised cast iron
Luoyang, Henan	Adze 1	Decarburised cast iron
	Shovel 1	Malleable iron
Xinzheng, Henan	Thin plate 1	White cast iron
Lixian, Gansu	Ding 1	White cast iron

bloomery iron very low levels of carbon (< 0.06%) were found, indicating a ferritic iron structure. Within the inclusions of ferrous oxide – an iron-olivine eutectic mixture – there were several areas of phosphorus, sulphur, manganese, silicon and other volatile elements from the original ore. During the forging of bloomery iron, the metal came into contact with charcoal. The carbon diffused into the iron, thereby changing it into steel, with increased strength and durability. Bloomery steel was used for sharp weapons and tools because of its higher hardness than bronze tools. The development of bloomery steel techniques played a critical role in the history of iron and steel technology.

From the data obtained so far, the earliest cast iron pieces were found in Tianma – Qucun of Shanxi Province, dating to around the 9th to 8th century BC. One sample's microstructure is shown in Fig. 1 (Han 2000). However, the original shape of these cast iron pieces was indistinguishable because they were too small. In addition, they were excavated together with one piece of bloomery iron. Therefore, it is not clear if these two cast pieces were intentionally made or rather produced accidentally during the iron smelting process. Cast iron and bloomery iron artefacts were also excavated from the tomb of Liuhe, Jiangsu Province, dating to the middle of the 8th century BC (Jiangsu 1965; Nanjing 1974). One excavated adze from Laohekou cemetery (Hubei Province) and one thin plate from Xinzheng (Henan Province) were identified as having been made during the Warring States Period, around the 5th century BC, and contained white iron micro-structures as shown in Figs. 2 and 3. Artefacts associated with the iron production

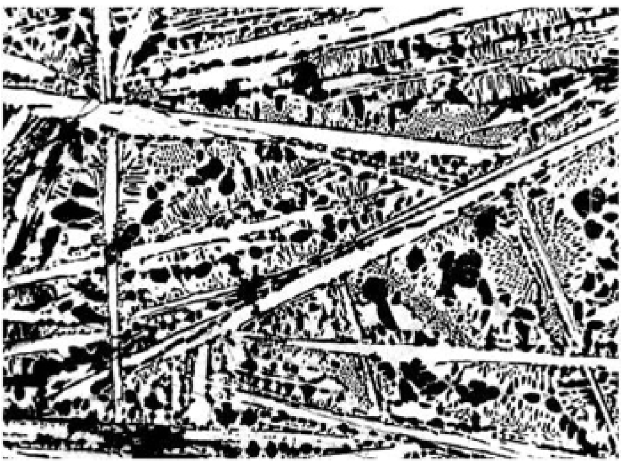

Figure 1: The microstructure of the earliest known cast iron fragment dating to the 9th-8th century BC and found at the Tian-ma Qucun sites in Shanxi Province.

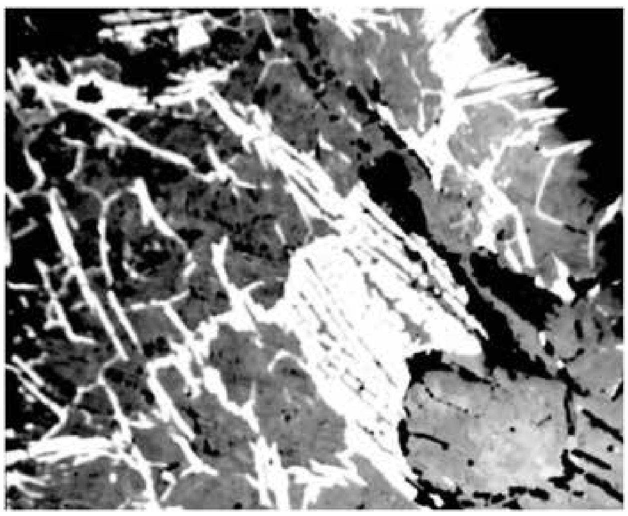

Figure 2: Microstructure of an iron artefact of Eastern Zhou period, excavated from Liuhe City in Jiangsu Province (mid-8th century BC).

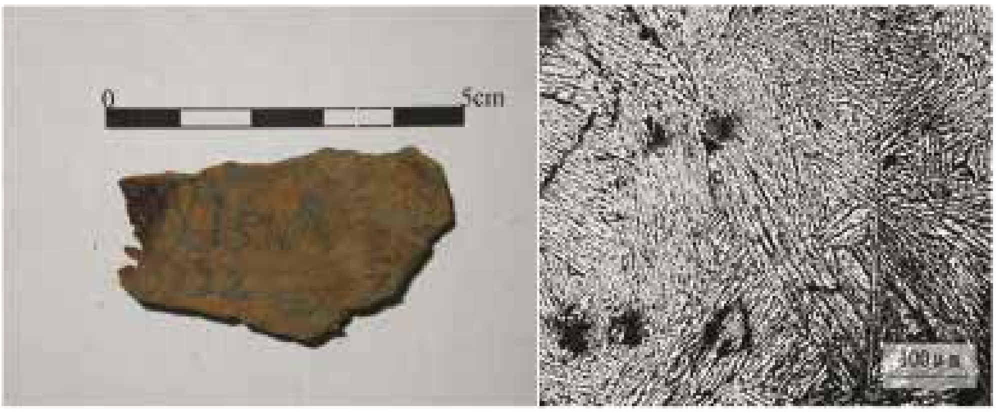

Figure 3: An adze unearthed from Laohekou, Hubei Province, and its microstructure (5th century BC).

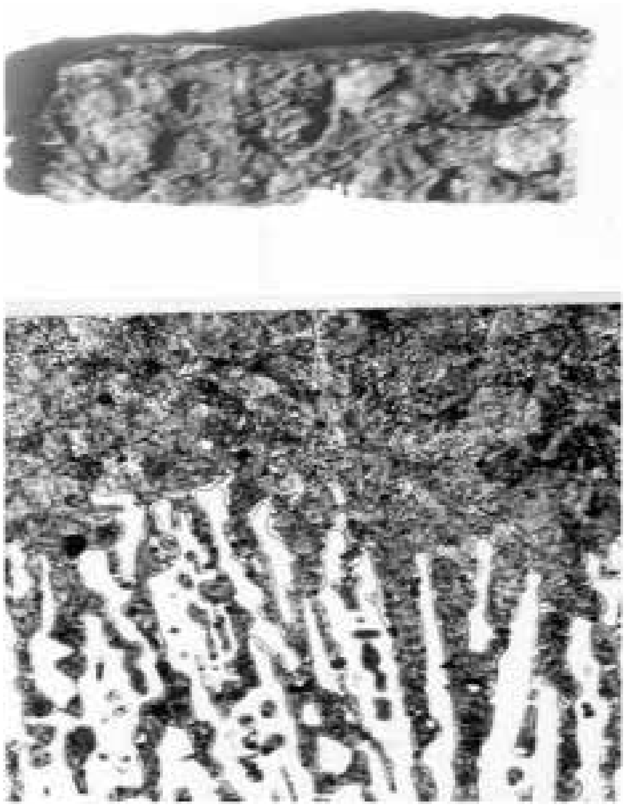

Figure 4: Adze unearthed from Luoyang, Henan Province, and its microstructure (5th century BC).

process were mainly found within the areas of the Jin and Chu states, where advanced iron-making technology had been known from an early time. The same raw materials and fuel were used to produce bloomery iron and cast iron; the only differences between the two technologies were the smelting temperature and the furnace style.

Ancient Chinese craftspeople invented the technique of cast iron and the use of the annealing process to decrease the brittleness of cast iron. Cast iron objects subsequently contributed significantly to the development of society. Decarburisation was used in many tools and weapons. For example, one of the excavated adzes found in Luoyang, Henan Province, was dated to around the 5th century BC, and comprised of white iron in the core of the object with a decarburised layer of steel on the surface, as shown in Fig. 4.

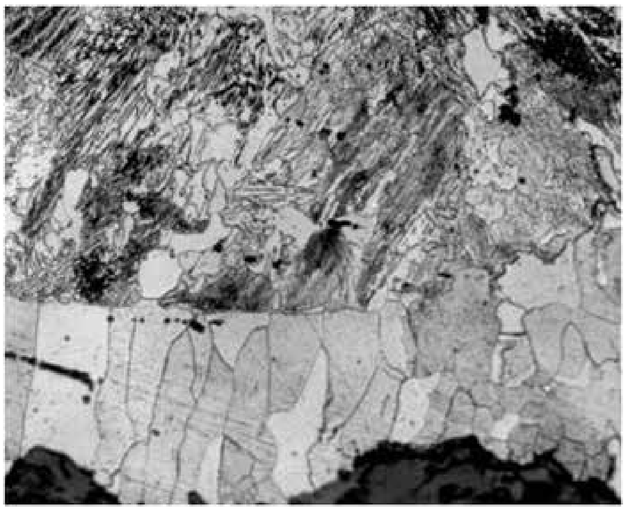

Figure 5: Microstructure of a hoe (T3H32:1) excavated from the Yangcheng smelting site, Henan Province (5th century BC).

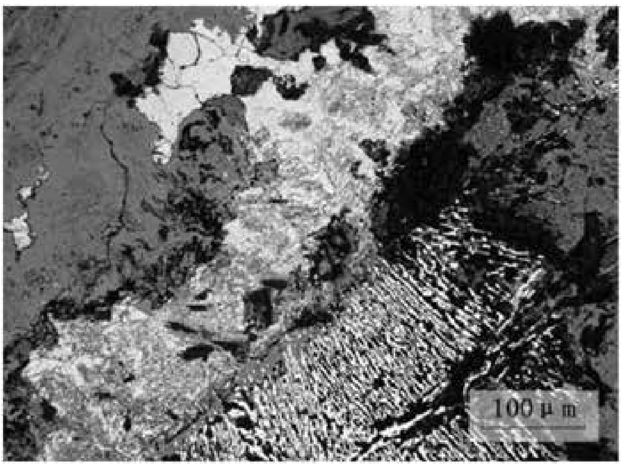

Figure 6: Microstructure of a sickle (43007) unearthed from Laohekou, Hubei Province (5th century BC).

A decarburised steel structure was formed by heat treatment at a temperature around 900°C and a short annealing time. Iron items including a hoe from Yangcheng, Henan Province and a spade from Laohekou of Hubei Province all displayed similarly characteristic indicators of decarburised cast iron, as shown in Figs. 5 and 6.

It is worth mentioning that three major factors were involved in the technological shift from bloomery to cast iron: furnace structure, the use of bellows to produce a forced air blast through the furnace and bronze casting technology. The same raw materials, e.g. ore and fuel, are used to obtain bloomery iron and cast iron; the main differences are structure of the furnace and smelting temperature. Higher temperatures can be reached in a blast furnace to produce cast iron. Furnace structure and blasting facility were well developed in the copper smelting and casting technologies of the Shang and Zhou dynasties as many very complicated bronze vessels were cast with molten bronze rather than shaping and forging solid metal. The Chinese metallurgical tradition favoured casting over deformation-based shaping techniques and it is thus not surprising that the Chinese invented iron casting technology. The blasting facility is the other important factor for obtaining appropriate thermal conditions inside a furnace. Smelting temperature can be calculated based on the compositions of iron objects and slag. The silica content is lower in early iron casting technology than in later periods, due to the limits of blast and the lower smelting temperature.

Iron production during the 5th-3rd century BC

Excavations of ten burial and smelting sites have yielded approximately 2,000 iron pieces, out of which 100 pieces have been systematically analysed. The results demonstrate that as early as the 4th century BC, cast iron and steel had already played an important role in the development of agriculture, craft industries and the production of weapons and tools. The materials used for the iron items include decarburised iron, white iron, grey iron, malleable iron and malleable iron with nodular graphite. During this period, ancient Chinese craftspeople used cast iron to produce farming tools and developed an annealing process to decrease the brittleness of cast iron.

The number of iron objects excavated from 20 provinces and dating to the 3rd century BC is 56 times that of the preceding period, as shown in Fig. 7 (Duan 2001).

The quantity and variety of iron farm tools increased rapidly during this period following the developments in agriculture during the Warring States period, as shown in Table 2.

The quantity and variety of iron farm tools increased rapidly during the Warring States period. Based on re-investigations of ten tombs and three iron smelting sites of the Warring States and Han periods in Shanxi Province, sixty iron artefacts have been examined by metallographic methods. The results are shown in Table 3. This investigation was the first study of the development of iron making process in the Jin state before the 3rd century BC. 90% of the sixty iron artefacts were made of cast iron that had been annealed. High quality weapons made of steel gradually replaced bronze tools.

In 1977, the Cultural Heritage and Archaeology Institute of Henan Province discovered an iron casting site dating to the 4th-2nd century BC in Yangcheng, Dengfeng City. Pieces of furnace wall, kiln remains, a large number of broken pieces of pottery, pieces of models, and a variety of iron items were found. 90% of the excavated iron items were farming tools and weapons including pickaxes, hoes, chisels, adzes, knives and arrowheads, as well as several plates of iron. The total number of iron objects was 1158, together weighing 110 kilograms (Henan and Zhongguo 1992). The metallurgical study of thirty-four iron items selected from this group indicated that thirty-three of them had gone through surface heat treatment (Han 1992). The microstructures indicated that craftsmen were able to choose heat treatment conditions in order to attain various desired levels of hardness on the iron surfaces.

Table 2: The number of iron farm tools dating before the 3rd century BC.

Location	Number of iron objects	Number of iron farm tools
Lianhuabao, Fushun, Liaoning	More than 80	68
Changzhi, Shanxi	36	21
Xinglong, Hebei	87	58
Huixian, Henan	93	58
Changsha Chu tombs, Hunan	More than 70	17
Yinshanling, Pingle, Guangxi	184	91

Table 3: Sampled iron objects excavated from several tombs in Shanxi Province.

Material	Houma (24)	Changzhi (27)	Yuci (7)	Yongji (2)	Total (60)
White cast iron	Adze 3, shovel 2, belt hook 9, container 1, ironware 1, jar 1	Belt hook 11	Adze 2, pickaxe 1	Container 1	32
Decarburised cast iron	Shovel 1, belt hook 1, knife with round hoop 1, ploughshare 1	Shovel 2, belt hook 3		Adze 1	10
Solid state decarburised steel	Sickle 1, belt hook 1	Knife with round hoop 3, sword 2, dagger 1, iron ring 1	Sword 2, knife with round hoop 1		12
Bloomery or steel		Knife 1, nail 1			2
Steel	Belt hook1	Belt hook 1, ironware 1 (quenched)	Belt hook 1		4

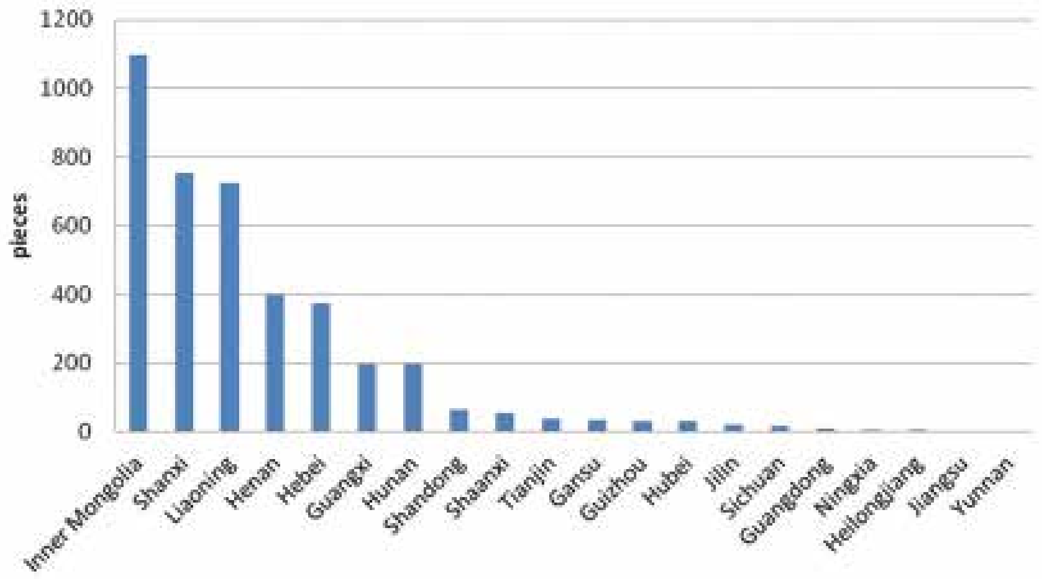

Figure 7: The number of iron objects excavated from 20 provinces.

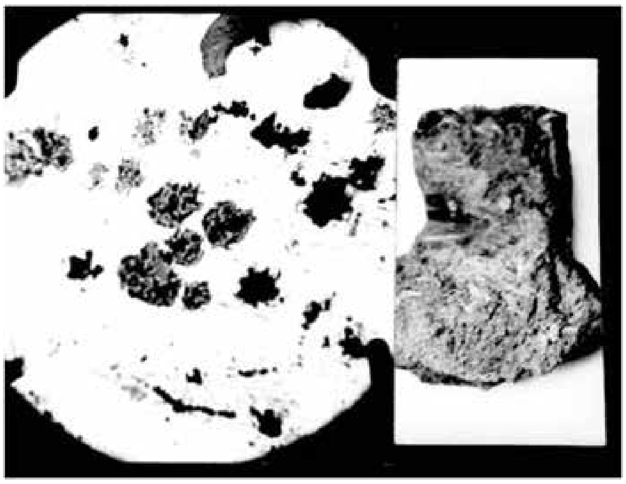

Figure 8: A shovel unearthed from Luoyang, Henan Province, and its microstructure.

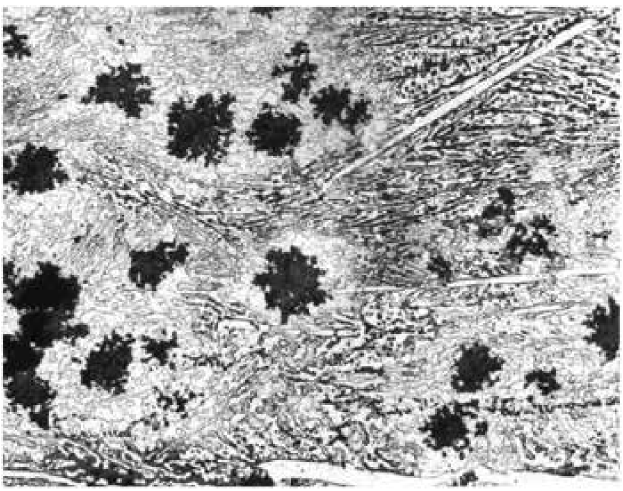

Figure 9: The microstructure of the Han shovel (16) 4109 excavated from the iron casting site at Yangcheng, in Dengfeng, Henan Province.

Although only a hundred objects dating to the period between the 5th and 3rd centuries BC have been metallographically analysed and subsequently published, and the sample size is thus limited, the results can be summarised as follows:

The materials are mainly white iron, decarburised cast iron, malleable iron, and solid state decarburised steel, but bloomery steel was still being used and the production techniques were continually being improved.

Craftspeople used annealing treatment to improve the performance of cast iron. Annealed cast iron with a structure corresponding to malleable iron was also found in a spade excavated from Luoyang, Henan Province (Zhongguo 1978), as shown in Fig. 8.

Several farming tools excavated from other smelting sites and tombs also demonstrated a decarburised layer on the surface, or a malleable structure, indicating the invention of a process used to render the iron malleable. When the annealing temperature of cast iron surpassed 900°C and the iron was subjected to a longer annealing time, the cementite structure in white iron would decompose into the graphite structure shown in Fig. 9. After the graphite gathered into floccus, the structure would enhance the performance of cast iron by improving its ductile strength. Depending on annealing temperature, atmosphere and the various annealing times, the properties of cast iron can differ significantly.

The microstructures of some farming tools showed matrices consisting of ferrite, ferrite and pearlite, pearlite and flocculation, or graphite blocks, as shown in Figs. 10, 11, and 12. Spherical graphite structures were also observed in excavated iron objects. The earliest known iron artefact with a spherical graphite structure is an iron hoe of the late Warring States period which was unearthed from the Yangcheng site in Dengfeng county, Henan Province (Fig. 13). More than ten iron objects excavated in Henan Province during the 1980s had spherical graphite structures and were dated to a period from the Warring States to the Han Dynasty, between the 4th century BC and the 1st century AD (Qiu 1981). Some examples of the finds from

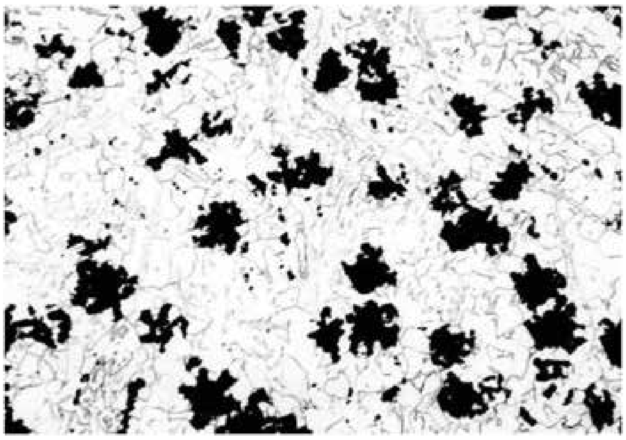

Figure 10: The microstructure of a Han shovel T12:8 (excavated from Tieshenggou, Henan Province, and dating to the Han Dynasty) consists of a ferrite matrix with graphite blocks.

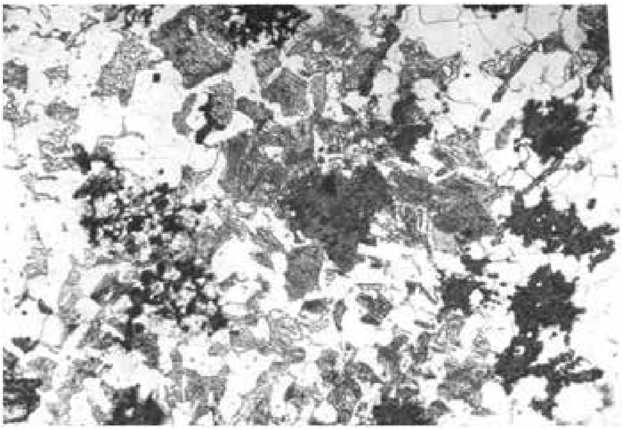

Figure 11: The microstructure of an iron shovel consists of a ferrite and pearlite matrix with graphite blocks.

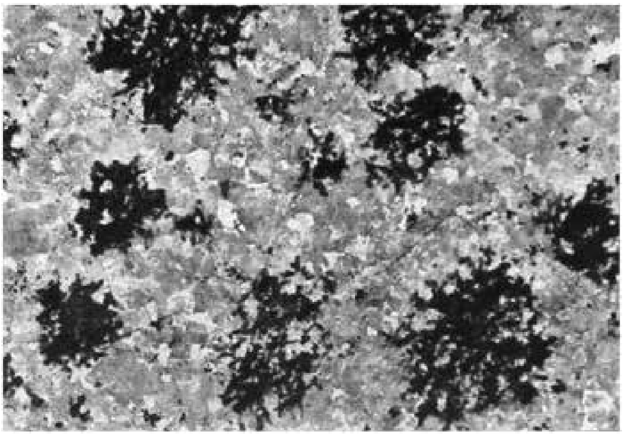

Figure 12: The microstructure of a Han iron object unearthed from a cellar at Mixian, Henan Province, consists of pearlite matrixes with graphite flocculation.

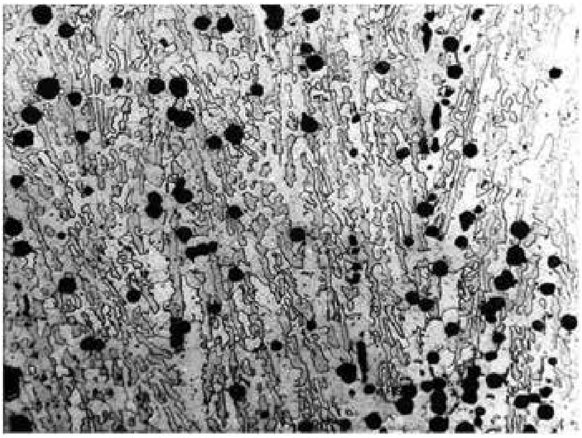

Figure 13: The spherical graphite structure of a hoe excavated from Yangcheng, at Dengfeng, Henan Province.

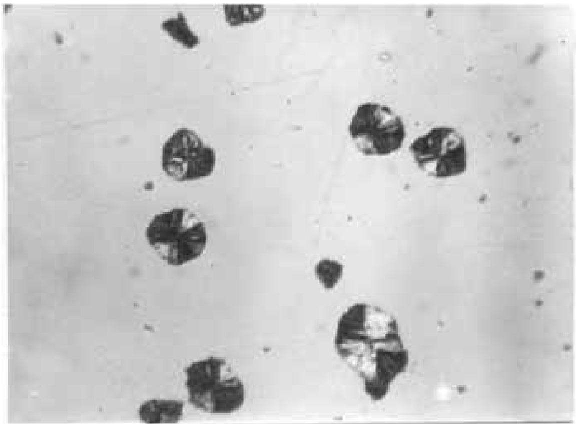

Figure14: An iron plate with spherical graphite in malleable iron unearthed from Xinzheng, Henan province and its polarised photograph.

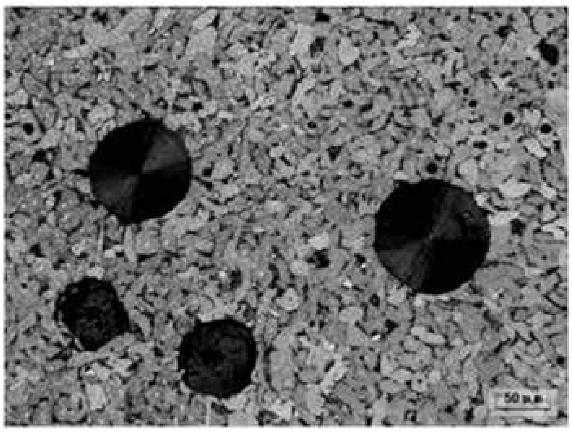

Figure 15: An iron plate with spherical graphite in steel unearthed from Xinzheng, Henan Province.

this group are shown below: an iron plate and strip from the Warring States Period unearthed in Xinzheng (Figs. 14 and 15) and iron tools from the Han Dynasty unearthed in Zhengzhou. By studying the microstructures of cast iron, it was concluded that the spherical graphite in the excavated iron artefacts was formed by annealing white iron. This study also concluded that the spherical graphite could have been formed during either the ancient charcoal smelting process or the modern coke smelting process for white iron, as long as the annealing temperature reached 920°C.

The invention and the earliest use of malleable iron in China took place no later than the 5th century BC. This discovery means that, based on the data currently available, China was the first country in the world to achieve this technique.

By studying the excavated iron tools it is clear that malleable iron was widely used in the late Warring States period and down through the Han, Wei (4th century BC to 4th century AD), and Northern and Southern Dynasties, and to the Tang Dynasty (5th-9th centuries AD). The use of malleable iron therefore has a history of 1300 years in China.

Another important contribution of ancient Chinese craftspeople was the invention of decarburisation of solid iron into steel during the Warring States period (ca. 4th century BC). The ancient craftspeople developed a unique decarburising method to change iron into steel through annealing treatments. Some pieces of broken casting moulds and strips of iron were found at the Yangcheng iron casting site at Dengfeng, Henan Province, which was dated to the 4th century BC; examples are shown in Fig. 16 (Qiu 1981). The microstructure of the excavated iron tools from this site consisted of a homogeneous ferritic structure with fewer inclusions, as shown in Fig. 17. In addition there was one iron object that still displayed surface adhesion traces, indicating a failed annealing process. After studying these items, the process used by the ancient Chinese craftspeople can be summarised as follows: first they made various iron tools using cast iron with 3-4% carbon. Then, after the iron pieces cooled down, they were decarburised via oxidation in an annealing furnace. When the cast iron became steel after decarburisation, it could be forged or heat-treated again, depending on the desired object. Observations of the iron objects show that flash lines are sometimes visible. The carbon concentration on the surface of iron objects was lower and there was very little to no graphite precipitation. It was found that overall the majority of the structure had become steel.

At the ancient cast iron production site excavated at Guxing Zhengzhou, Henan Province, dozens of kilograms of trapezoidal iron plates were found. These plates were about 19cm long, 7-10cm wide and 0.4cm thick. The analysis indicated that the iron plates had undergone decarburisation and had a steel composition of 0.1-0.2% carbon (Zhengzhou 1978). Other similar discoveries were made at Nanyang, Henan Province. As shown in Fig. 18, the iron items had various shapes, for example 74 pieces of flat iron, 44 pieces of cubic iron, and 36 pieces of round iron (Li and Chen 1995). A number of strips made of decarburised solid state steel and a bar-shaped iron object actually made from a rolled up iron sheet were also excavated.

Another important piece of evidence that China was the first country to discover steel making technologies was the finding of a decarburising furnace at the casting site of Gong Xian – T12 furnace 11, shown in Fig. 19 (Zhao, Li et al., 1985).

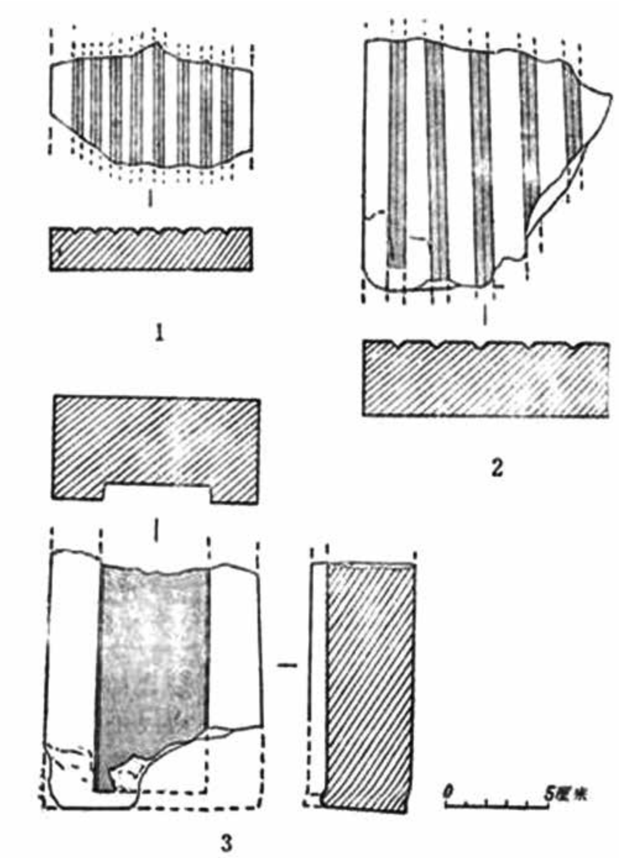

Figure 16: Clay moulds unearthed from the iron-casting site of Yangcheng, Henan Province, dating to the early Warring States period (Henan and China, 1992).

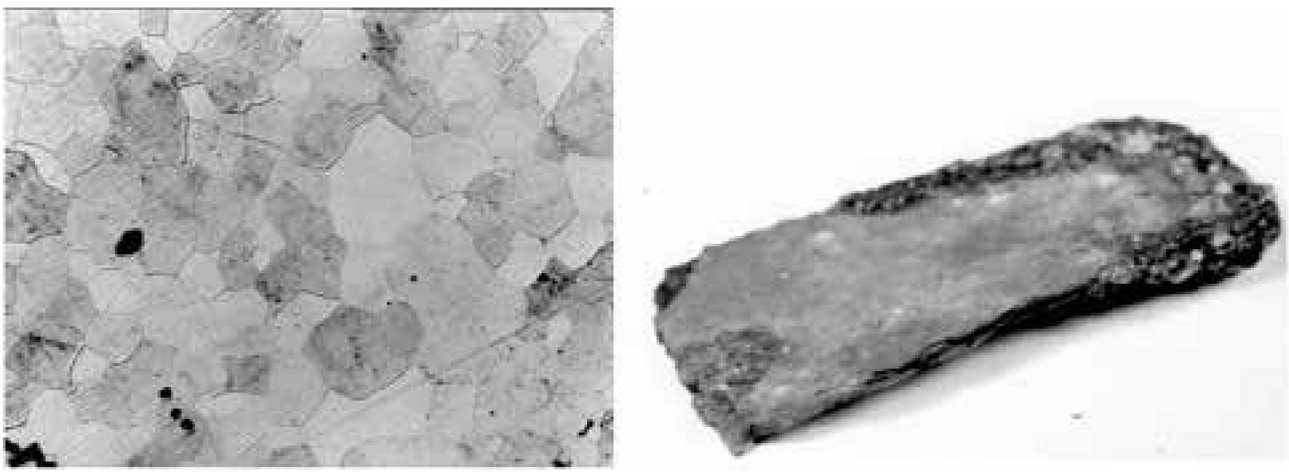

Figure 17: A decarburised iron plate excavated from the Guxing ironworks site in Zhengzhou, Henan Province.

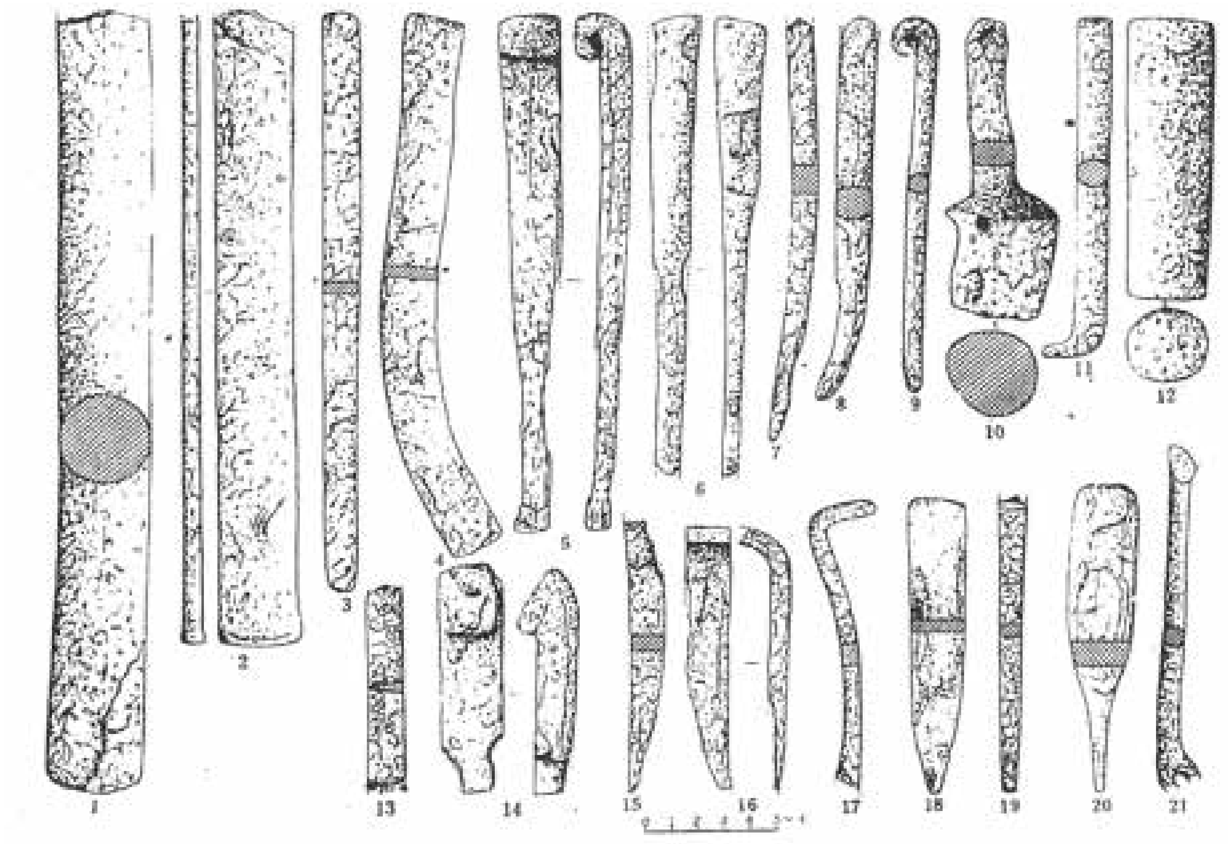

Figure 18: Iron strips unearthed from the Wafangzhuang iron-casting site, Nanyang City, Henan Province (Li and Chen, 1995).

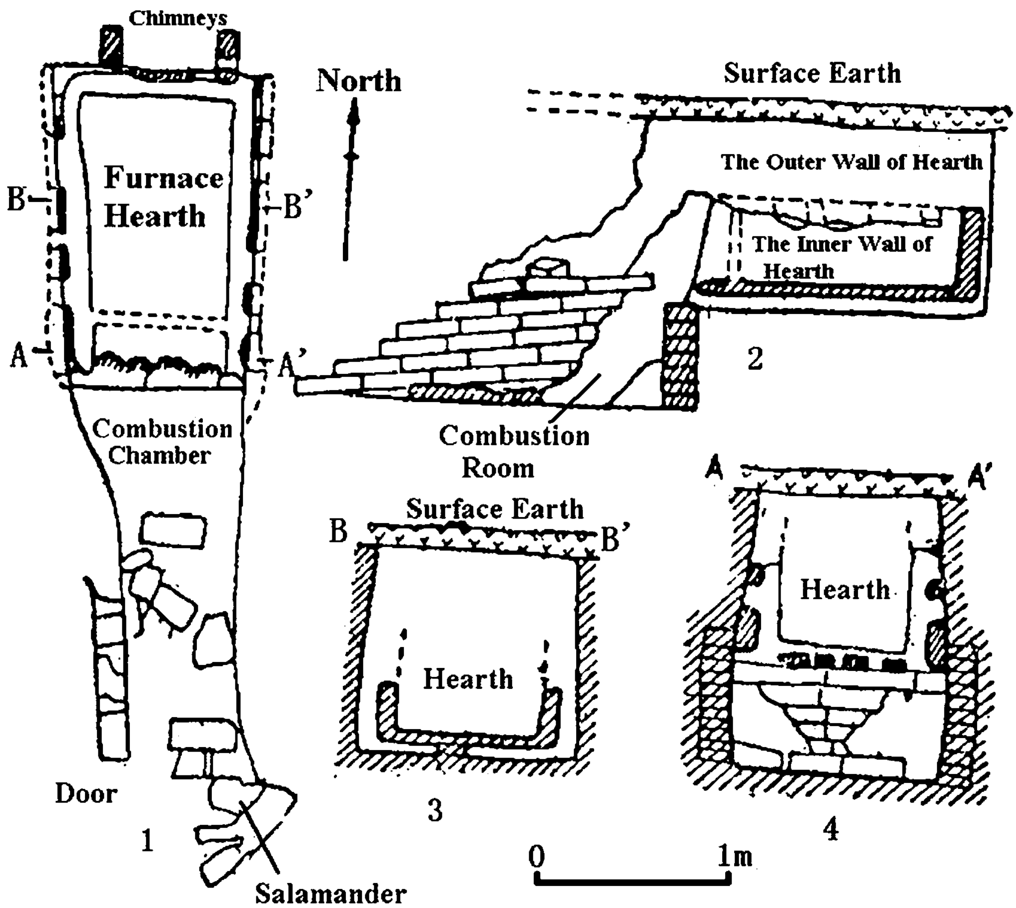

Figure 19: The plan and profile of decarburising furnace T12:11 at the casting site of Tieshenggou, in Gong Xian, Henan Province (Zhao, et al., 1985).

By the late 4th-3rd century BC, permanent moulds for casting iron items had been developed (Zheng 1956), greatly increasing productivity, the precision of casting and the capacity to replicate objects such as ploughshare tips. This can be considered a primitive model of mass production and standardisation. Standard mould for making casting moulds were issued by the Iron Official of the Han Dynasty to various foundries and the permanent moulds subsequently made were then used to cast iron and steel objects. This shows that cast iron and steel production played a very important part in the advancement of agriculture and water irrigation and was a significant technological development promoting the formation of a unified China.

It should be pointed out that although bloomery iron objects have not been found after the 3rd century AD in central China, this technology did not disappear. For example, one bloomery iron smelting site dated to the 2nd century BC – 2nd century AD was found in Pingnan County, Guangxi Zhuang Autonomous Region of Southern China (Huang and Li, 2011) and several bloomery objects dated to the 9th century AD were unearthed in Xinjiang (Chen, 2010), while many cast iron objects were also found in these areas. The social, economic and technical level of development may have been among the factors influencing the choice of bloomery or (decarburised) cast iron under certain circumstances. The production efficiency of cast iron is higher than that of bloomery iron, and this may be the real reason behind such choices.

Comparative studies of iron technologies between central China and outlying areas show that the earliest use of cast iron took place in central China. Cast iron objects found in northwest, northeast, south and southwest China, the Korean Peninsula, Japan and Vietnam indicate that cast iron objects or technologies had been adopted in these areas no later than the 2nd century BC, though the dates of the earliest use of iron and smelting technology in these outlying areas are not the same. It is very likely that the earliest iron objects excavated in these areas came from central China. The use of raw, iron-like ingots to make implements was then adopted by local people, before the eventual development of indigenous iron smelting (Chen and Han, 2007). Iron casting technology contributed to the progress of civilisation in these areas. Recently, more iron casting evidence dating from the Han Dynasty has been found in Xinjiang, Hainan, Yunnan and other frontier areas; we will discuss these materials further in future publications.

Conclusion

The invention of cast iron and the use of iron tools contributed significantly to the development of agriculture in ancient China. Archaeological excavations show that iron tools were widely used during the Warring States period. Evidence from the latter stages of this period indicates that iron agricultural tools occupied a dominant position, which led to an unprecedented veritable revolution in farming methods. The development of agriculture in turn promoted the progress of ancient culture, science, and technology and consequently led to changes in social structure, after which feudalist relations of production were established.

The extensive use of iron promoted the development of agriculture, handicrafts and the exchange of commodities, which enhanced economic vitality and allowed cities to prosper. In turn, the development of cities also generated demand for more iron objects, promoting the prosperity of iron smelters. Linzi, the capital of the Qi state during the Warring States period, was well-known for its iron industry and was described in several historical records as a crowded, busy, and bustling city with 70,000 households.

High-quality iron weapons were an important factor in the development of the Qin state into the first unified empire in Chinese history and the large-scale iron industry can be considered as one of the most important foundations of the political and economic might of the Han Dynasty, the powerful empire following that of Qin. Bloomery iron and carburised steel weapons of superior quality to bronze weapons, gradually replaced bronze weapons during the Warring States period. Iron weapons played an important role in warfare, especially in the wars among the Qin and other states, like Han and the Huns. At the beginning of the Western Han Dynasty, the empire established 49 local iron officials to manage iron casting works. To date, about 30 iron smelting and melting sites of the Han Dynasty have been identified in China, some of them occupying an area of 1,000,000 m^2 or more. Every iron workshop had one or more furnaces. For example, eight blast furnaces and one puddled steel furnace were found within the 'He San' (河三) site in Gongyi County, Henan Province. Iron working sites and unearthed iron objects dating to the Han Dynasty indicate that iron had become the main raw metal material that was used in agriculture, military, handicrafts, transportation etc.

In short, by the 5th century BC or even earlier, cast iron had been invented and was widely used in agriculture, warfare, production, etc., representing a discovery significant to the development in Chinese society for the next 2500 years. Cast iron and steel-making technologies made significant contributions to the progress of civilisation in China and the world.

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