Iron through the ages

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Abstract

A range of iron artifacts, covering an approximate time period from 1000 BCE to 1000 CE, have been metallographically examined. It is concluded that there was little change in iron manufacturing over this time span of 2000 years. It is also concluded that some artifacts, specifically tool and weapon blades, showed that knowledge existed, by at least 500 BCE, to increase hardness both by increasing carbon content and by rapid cooling from the austenite range. The study indicates that there was a considerable degree of sophistication on the part of these early ironworkers, although the processing is thought to have been empirical. © 2001 Elsevier Science Inc. All rights reserved.

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1. Introduction

The early history of mankind has been divided by scholars into “ages,” some of which are characterized by the nature of the materials used for the manufacture of tools and structures. That this scheme is not very sophisticated is widely understood by most historians, and certainly by those interested in historical metallurgy, but it has long endured. The “Chalcolithic,” “Bronze,” and “Iron” Ages were not distinct periods of time but rather overlapping periods during which new materials technology evolved slowly and the previously employed materials technology continued to be developed and improved. Thus iron-making technology was actually developed during the “Bronze” Age and bronze technology continued to be developed in the “Iron” Age.

It was curiosity about the development of metallurgical knowledge of iron making and processing over the centuries of the “Iron Age” that was the impetus for the study described in this paper. It is known that small iron lumps have been found in contexts that suggest that they were produced, probably accidentally, during the smelting of copper ores in the Sinai desert as early as 3000 BCE [1]. It appears that they had no practical usefulness and the concept of making something useful of them, for example a tool or knife, had to wait many years. By 2500 BCE, iron in the form of a knife blade was reported to have been found in a Hattic tomb on the Anatolian Plateau [2] and somewhat later in an Egyptian tomb, for example an iron-bladed knife found in the tomb of Tutankhamun (around 1300 BCE) [3]. It is not known whether these were made of smelted or meteoritic iron, but the suggestion is that they were manufactured from smelted iron.

What is known is that ancient smelters in the Western world could not generate high enough temperatures in their furnaces to produce liquid iron. Rather, the end product of the smelting process was sponge iron mixed with slag that gathered in the bottom of the furnace. The iron was produced by
direct reduction from iron ore in contact with hot charcoal in the presence of a silicate slag. The slag-rich sponge had to be subsequently hot forged to squeeze the slag out and to consolidate the iron, producing wrought iron.

Because this process could produce only small bars of iron, objects of any appreciable size required the forging together of a number of these wrought iron “blooms.” Remarkably, all of the iron used in the Western world was produced by this process, with some improvements, for at least 2000 years; it was not until after 1000 CE that molten (cast) iron was produced in the West.

There were important improvements along the way, however, some of them coming quite early. An interesting letter (cuneiform tablet) from a Hittite ruler to an Assyrian prince dated about 1300 BCE discusses the shipment to him of “good iron,” and as a show of good faith (or good business), indicates he is sending him a sample knife as a gift [4]. This would suggest that iron was being manufactured and fabricated into trade goods at least by this time, and some sophistication in iron making and processing had been developed in the Hittite Empire. This was at least the reputation that the Hittites had in the ancient world, a reputation that passed down to the Philistines after their conquest of the Hittite Empire in about 1200 BCE. The Philistine reputation for knowledge of iron working appears to be confirmed in a portion of the Bible describing events taking place probably about 1100 BCE, thus reinforcing the Hittites place in the development of iron technology [5].

Some of the intriguing questions about this and subsequent periods during this 3000-year period are “what did they know and when did they know it?” Some historians have suggested that the Hittites in the late second millennium had not only made iron regularly, but also knew how to carburize it to increase its strength [6]. This would make it “good” iron, i.e., strong iron — strong enough to be effective against bronze weapons. If this is true, even in this early period at least an empirical knowledge of how to heat iron in a carburizing atmosphere (probably in a hot charcoal bed) must have existed. Another ancient reference suggests that an early knowledge of the effects of quenching to increase strength also existed. This is based on one translation of the Odyssey (about 800 BCE) in which the quenching of hot iron in cold water to make it strong is referenced [7].

2. The present study

The investigation reported here is an attempt, in a limited way, to explore answers to these questions through metallographic examination and microhardness testing of iron artifacts made in the time frame described as the Early Iron Age through the Crusader Period, 1000 BCE to 1000 CE. The artifacts are all tools or weapons. All have been purchased commercially. As a result, the location in which they were found is not easily documented and their dating is not securely known. In some cases, they can be located in a particular cultural context and era based

Fig. 1. Artifact No. 7, the Roman Legionary dagger.
on their distinctive size, shape, and style in comparison with more securely dated similar artifacts in museums. For example, the Roman Legionary dagger (Fig. 1), even when well rusted, can be identified easily on this basis, although placing a date on this artifact to better than a 200-year period is not possible. However, for the purposes of this investigation, locating this artifact within this context and time period may be sufficient.

Much more problematic is the secure identification of iron arrow or spear blades that do not have such a distinct shape to their reported time and date, e.g., Early Iron Age Palestine. Other artifacts used in the investigation fall somewhere within these certainty/uncertainty boundaries of identification. The wide range of artifacts reported here covers the time period from about 1000 BCE to 1000 CE. However, their source reports are considered by the author to be reasonably accurate, and therefore, it is believed they can provide insight into the iron-making metallurgy in this 2000-year period.

3. The artifacts used

The artifacts that were used in the investigation are listed below.

- Early Iron Age artifacts
  1. Arrow point from Israel dated to about 1000 BCE
  2. Spear point from Israel dated to about 1000 BCE
  3. Razor blade from Israel dated to about 700 BCE

- Roman Era artifacts
  4. Leather knife dated to about 200 CE
5. Draw knife (scorp) dated to about 200 CE
6. Food (?) cleaver dated to about 200 CE
7. Legionary dagger blade dated to about 100 CE
8. Legionary spear blade dated to about 100 CE

- Late Roman and Crusader artifacts
  9. Javelin point dated to about 300 CE
  10. Arrow point dated to about 500 CE
  11. Hammer axe blade dated to about 300 CE
  12. Crusader arrow point dated to about 1100 CE.

4. Experimental techniques

4.1. Metallographic examination

The artifacts were sectioned to remove metallographic samples that were subsequently mounted in phenol–formaldehyde compound for metallographic preparation. Standard silicon carbide coarse polishing techniques followed by 6 µm diamond, 3 µm alumina, and colloidal silica in the final stages were used. The specimens were etched with 2% nital, picral, or Marshall’s reagent, depending on the microstructure of the sample.

4.2. Microhardness tests

The polished metallographic samples were employed for microhardness testing using a Leco M-400-G HV microhardness tester with 500-g load. At least five hardness tests were performed on each sample. In the cases where substantially different microstructural constituents were present, multiple hardness readings were taken on each constituent.

5. Results of the investigation

5.1. Microstructural results and discussion

Regardless of the other microstructural constituents present, all of the samples showed the long
stringers of slag separated by banded ferrite characteristic of wrought iron. The structures also show regions where the ferrite and inclusions have been folded over in the fabrication process. In some cases, the presence of slag pockets or oxidation prevented full consolidation of the metal and the artifact contains voids and seams from processing. A good example of this type of microstructure is seen in Fig. 2. The field shown is a cross-section through a portion of the Late Roman javelin head (Artifact No. 9), an artifact with a roughly square cross-section at its center tapering to a point on both ends (shown in Fig. 3). In addition to a very mixed grain size and the apparent presence of some cold work, the folded microstructure with slag stringers and unconsolidated (now oxidized) regions is evident. Most of the artifacts had this type of structure to some degree. Only the artifacts that had been worked to thin cross-sections (about 1–2 mm), such as the razor and knife blades, were relatively free of slag and oxidation along the surfaces of internal seams.

Another characteristic microstructural feature that appears in many of the artifacts is the presence of iron–iron carbide regions apparently isolated in the interior of the product. An example of one such region is seen in Fig. 4, from the interior of Artifact No. 1, an Iron Age arrow point like that seen in Fig. 5. This structure may be the result of the heating, folding, and hammering process used to consolidate the iron prior to or during the production of the arrow point. In this process, the exterior surfaces of the iron may have received light carburization from the forge charcoal bed and were subsequently folded onto themselves during further manufacturing. Another area of folding marked by a line of oxide stringers and evident microstructural change across the fold boundary is seen in Fig. 6, a section through Artifact No. 12, the Crusader arrow.
point. In both of these cases the carbide does not appear to be in the form of normal pearlite but rather fine irregular carbide regions. The same nonpearlitic ferrite-carbide regions are found in the Iron Age spear (Artifact No. 2) and the Roman era spear (Artifact No. 8). The Roman era spear blade is seen in Fig. 7 and its microstructure is shown in Fig. 8.

These microstructural features suggest that the temperature during the manufacturing process was erratic, sometimes subcritical, sometimes above the critical, and rarely high or long enough to allow transformations to approach equilibrium. These micrographs also indicate another characteristic of many of the artifacts, especially the early ones. They were evidently produced by consolidating many small pieces of iron together to make the raw material for production. This must have been a very labor-intensive process.

In terms of the advance of technology, the spear, arrow, and javelin points do not seem to show any significant difference from the earliest (Iron Age, Artifact No. 1) period to the latest (Crusader, Artifact No. 12). The Early Iron Age spear point (Artifact No. 2), the legionary spear point (Artifact No. 8), the Late Roman javelin point (Artifact No. 9), and the Late Roman arrow point (Artifact No. 10) are also not significantly different from Artifact Nos. 1 and 12. The Late Roman arrow point is shown in Fig. 9. Similar to the others, it consists

Fig. 12. Artifact No. 4, the Roman leather knife.

Fig. 13. Artifact No. 5, the Roman draw knife.
mostly of ferrite with mixed grain sizes indicating nonequilibrium conditions of manufacture. As will be seen later, many of the sharp-edged knives and tools made during the same time period show a more sophisticated approach to their processing and heat treatment but this was not applied to the spears and arrows.

One possible reason for this, at least in the later periods, is that arrow points were a commodity item and the knives and tools were more of a specialty item. Because many spear and arrow points had to be made and many were lost in battle, there was no particular incentive to improve their quality unless it greatly improved their effectiveness. As a result, if the common arrow or spear point worked well enough, and they apparently did, no more care was given to their manufacture than necessary.

When the razor, knives, and tools are examined, as indicated above, a different pattern is evident. For most of these artifacts, there seems to have been a more deliberate effort to increase hardness. The methods used appear to have been to carburize the iron and, in a few cases, to apply heat treatments. An example of the first method is seen in the microstructure of the cleaver (Artifact No. 6). The microstructure of the heel of the cleaver, which is about 3 mm in thickness, is seen in Fig. 10 while the microstructure of the sharpened blade is seen in Fig. 11. The microstructure of the cleaver heel consists of ferrite, slag stringers, and bands with fine pearlite colonies. The microstructure of the blade region indicates a higher level of carbon, bands of apparently coarser prior austenite grain size, and relatively fine pearlite spacing. The slag and oxide stringers typical of the other products are also present. The blade area was apparently intended to be harder than the heel.

Fig. 14. Microstructure of Artifact No. 4, the Roman leather knife (2% nital etch).

The observation that there is an increased carbon content in the blade area as compared to the heel raises the question whether or not this was deliberate or merely a result of random carburization from uncontrolled processing. Based on this single specimen, there would be no way to answer this question. However, after looking at the microstructures of all of the sharp-edged blades and tools, a pattern develops that is hard to rationalize except on the assumption that the increase in carbon in the sharp edges of these artifacts, and in at least some cases, attempts at heat treatment, were intentional.

Confirmation of this pattern is supported by the microstructures of the leather knife, the draw knife, and the Legionary dagger (Artifact Nos. 4, 5, and 7, respectively). These artifacts are seen in (Figs. 12, 13, and 1). Their microstructures are shown in Figs. 14, 15, and 16, respectively. In each of these cases, the microstructure consists of ferrite and substantial...
amounts of pearlite with the proportion of pearlite varying up to 100% in many areas. The microstructure of the draw knife (Fig. 15) is mostly pearlite with some scattered ferrite. In the leather knife and the Legionary dagger, as shown in Figs. 14 and 16, the amount of pearlite approaches 100%. This suggests a deliberate effort to carburize these tools by some means.

Equally important, none of these microstructures suggests a cooling process from austenitizing that is anywhere near equilibrium. Figs. 14 and 16 show fine acicular ferrite. The ferrite in Fig. 15 is also largely acicular. Moreover, there is an area in the center of Fig. 14 that appears to be ferrite partially transformed to austenite that has then been subsequently cooled and retransformed nucleating additional ferrite regions around a preexisting ferrite core. These characteristics suggest short-time nonequilibrium heating and cooling cycles rather than long cycles with slow cooling. Although some areas of these artifacts are only a few millimeters in thickness, for the most part, they are too thick for these microstructural characteristics to have been produced by air-cooling.

Not all tools were, or perhaps could be, given special treatment. The final tool on the list, the hammer axe (Artifact No. 11), is seen in Fig. 17. In this case, the microstructure of the blade edge, seen in Fig. 18, has a very shallow layer of possible carburization at its surface although much of the surface is well rusted. Perhaps this tool was too large or too mundane to merit any special treatment.
Additional clues to the nature of the attempted heat treatments applied to these artifacts may be derived from these microstructures. For example, it is possible to learn something about the cooling cycle from austenitizing used for the leather knife from its microstructure, which is seen at higher magnification in Fig. 19. This micrograph shows that the pearlite colonies have very fine carbide platelet spacing and that, in between some of the pearlite colonies, there is martensite. These two features suggest that the cooling process from austenitizing was by a liquid-quench.

The strongest evidence for the use of a liquid-quench from austenitizing is found in the microstructure of the Late Iron Age razor (Artifact No. 3) seen in Fig. 20. The microstructure of the razor is shown in Figs. 21 and 22. These figures show that the microstructure the of razor is mostly martensite (somewhat overetched to make it evident), with some very fine pearlite colonies present along prior austenite grain boundaries. This structure could not have been produced in a wrought iron without a liquid, probably water, quench being used even though the razor is only about 1 mm thick. The quench apparently caused the iron of the razor to just pass through the “nose” of the CCT diagram.

6. Microhardness results and discussion

The microstructural findings are substantially supported by the microhardness test results seen in Table 1 but the microhardness data provide some

<table>
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<th>ID number</th>
<th>Description</th>
<th>HV (500 g)</th>
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<tr>
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<td>194</td>
</tr>
<tr>
<td>2</td>
<td>spear point</td>
<td>149</td>
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<tr>
<td>3</td>
<td>razor</td>
<td>618</td>
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<td>leather knife</td>
<td>430</td>
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<td>draw knife</td>
<td>257</td>
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<td>6</td>
<td>food cleaver blade</td>
<td>213</td>
</tr>
<tr>
<td></td>
<td>heel</td>
<td>155</td>
</tr>
<tr>
<td>7</td>
<td>Legionary dagger</td>
<td>354</td>
</tr>
<tr>
<td>8</td>
<td>Legionary spear</td>
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<tr>
<td>12</td>
<td>Crusader arrow point</td>
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Fig. 20. Microstructure of Artifact No. 3, the Early Iron Age razor blade.

Fig. 21. Microstructure of Artifact No. 3, the Early Iron Age razor blade (2% nital etch).

Fig. 22. Microstructure of Artifact No. 3, the Early Iron Age razor blade (2% nital etch).
additional insights. The hardness data of the arrow and spear points all fall within the range of 140–194 HV, typically about 165, which is equivalent to a normalized 1030 steel. This is stronger than expected for their primarily ferritic microstructure, although some also have scattered carbides present. The javelin point hardness is somewhat higher, 239 HV, equivalent to a normalized 1060 steel. All of these values are higher than expected for 19th century wrought irons for which the HV is about 120. One possible explanation for this higher hardness is that these artifacts retain some cold work from processing. The javelin point, which appears to show some evidence of cold work in Fig. 2, shows even more in other areas. To varying degrees, this may be true for the other artifacts as well.

The microhardness results are especially useful in evaluating the significance of the microstructures observed in the knives and tools. For example, as might be expected, the hammer axe (Artifact No. 11) is only marginally harder than the typical arrow or spear with an average HV of 200. This is in agreement with the fact that it is mostly ferrite. The cleaver heel has an average hardness of only 155 HV and a maximum of 174 HV, while the blade has an average hardness of 213 HV with a maximum of 271 HV. This is also in agreement with its microstructural appearance (i.e., Figs. 10 and 11). The draw knife, with a microstructure of mostly pearlite but with some regions of ferrite (Fig. 14), has an average hardness of 257 HV with a maximum of 283 HV. This is harder than the cleaver blade on average but the maximum hardness is not much greater. The maximum hardness is found in the fine pearlite regions and should be about the same for the two artifacts. The Legionary dagger (Artifact No. 7), with virtually 100% fine pearlite (Fig. 16), has an even higher average hardness, 354 HV, with a maximum of 395 HV. This is somewhat higher than the hardness for a normalized eutectoid steel.

It is in the artifacts that have regions appearing to have martensite present that the microhardness readings are especially useful. The leather knife (Artifact No. 4), which appeared to have small martensite regions within a matrix of fine pearlite (Fig. 19), has a maximum hardness in these martensitic areas of 612 HV, corresponding to that in an as-quenched 0.45% C to 0.50% C steel. The average hardness in this artifact is 430 HV, which is reasonable because the martensitic regions are small and well distributed. The microhardness readings also confirm that the microstructure of the razor is largely hard martensite (Fig. 22) with an average microhardness in the range of 618 HV and a maximum of 645 HV.

Neither the metallographic nor microhardness results provide a definitive answer to the question about whether or not these artifacts were tempered after quenching. The structure of the martensite regions suggests it was transformed from high carbon rather than low carbon austenite. However, their hardness of these regions is in the 612- to 645-HV range rather than close to 800 HV. It is, therefore, tempting to propose that tempering after quenching was used to lower the martensite hardness and provide the ductility level required for service. However, without knowing the carbon content of the austenite, the anticipated hardness of the fresh martensite cannot be estimated. The structures seen in Figs. 19, 21, and 22 were etched to bring out the martensite platelets, otherwise the martensite areas appear relatively unetched. An alternate argument can be made that blades only partially converted to martensite could have been hard and ductile enough to have served as tools and weapons without tempering. This investigation does not appear to answer this question.

There is no assumption in this analysis that the producers of these artifacts had any theoretical understanding of the effects of their metallurgical processing efforts but it reveals a substantial degree of sophistication in their empirical efforts to produce the properties they deemed useful for service.

7. Summary

The examination of a broad range of iron artifacts covering an approximate time period of 2000 years, from 1000 BCE to 1000 CE, indicates that for some products, for example arrow and spear blades, there was little change in iron manufacturing technology. These products had varying but generally low carbon contents and the occasional slag stringers typical of wrought iron. Average hardnesses were also low for these artifacts, typically less than 200 HV. Based on the microstructures and hardness levels achieved in other artifacts, it is assumed that ways to improve their hardness were known, but deemed to be either too labor intensive or incapable of providing sufficient benefit in performance to merit employing them.

In contrast, certain of the artifacts, specifically some tool and weapon blades, showed that knowledge existed by at least 500 BCE to increase the hardness levels of the artifacts by both increasing their carbon content and by rapid cooling from austenitizing. These artifacts, which typically had blades no more than a few millimeters thick, had regions containing high proportions of pearlite and higher hardnesses, typically 250 to 400 HV. The
hardest artifacts, with hardnesses in some areas over 600 HV, had regions of martensite in their microstructure, indicating that a rapid quench was used in their thermal processing. The artifact with the highest overall hardness and largest proportion of martensite was a razor less than 1 mm in thickness dating to about 500 BCE. It is presumed that the metallurgical processing of the iron artifacts was empirical, but it reveals a fair degree of sophistication on the part of these early ironworkers.

Acknowledgments

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References