Journal of Archaeological Science: Reports 18 (2018) 447–462

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

Reevaluating early iron-working skills in the Southern Levant through microstructure analysis

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A R T I C L E I N F O

Keywords:
Iron objects
Iron Age
Bronze/Iron transition
Southern Levant
Iron working
Microstructure analysis
Steeling
Quenching

A B S T R A C T

The question of whether improved technological skills of Iron Age smiths, such as carburization and quenching, were behind the significant transition to utilitarian use of iron in the eastern Mediterranean has been long debated, with the answer relying on the analyses of a few exceptionally well-preserved objects from Israel and Cyprus. In order to systematically examine this question, 59 iron objects from several major Iron Age settlements in Israel were sampled for metallographic analysis. First and foremost, it is shown that none of the analyzed objects were preserved in metallic form and that only in rare cases, small islands of metallic iron were preserved. Objects with full preservation of metal, heavily relied upon in past discussions, are therefore the exception and not the rule.

Using relics ("ghost structures") of the original metallic microstructure, pearlite and cementite were observed in an overwhelming majority of the samples, indicating that almost all of the objects were made of steel. A wide variety of carbon concentrations was estimated, reflecting a range of compositions from low-carbon hypoeutectoid to high-carbon and hypereutectoid steels. Since no clear correlation between object type and steel quality was observed, we conclude that steeling was, in fact, a spontaneous and non-deliberate result of the smelting process, rather than a deliberate systematic act of carburization. In addition, martensitic structures, indicative of quenching, were not identified, suggesting that quenching was not routinely performed and that iron was unlikely to have been superior to bronze at this time. It thus appears that the iron-working skills of the Iron Age smiths cannot be used as a factor that can explain the advent of iron in the Southern Levant nor as a reason for the dramatic increase in iron production during the 10th–9th centuries BCE.

1. Introduction

The advent of iron in the eastern Mediterranean has been a debated subject since the 1970's (e.g. Pleiner, 1979; Tholander, 1971; Waldbaum, 1978; Wertime and Muhly, 1980). Many suggestions were put forth as to why this significant transition from the use of bronze to iron for utilitarian purposes occurred (see for e.g. summaries in Bunimovitz and Lederman, 2012; Yahalom-Mack and Eliyahu-Behar, 2015), one being the alleged technological superiority of iron over bronze (recently, Muhly, 2006, p. 21). With the lack of evidence for iron production that prevailed until recently, the research focused mainly on the finished products; their relative numbers with regards to bronze and their physical properties. Based on the analysis of several iron objects from the Levant and Cyprus, it had been concluded that carburization and heat treatments, including quenching and tempering aimed at improving the quality of the steel, were practiced as early as the 12th century BCE. Among these objects were the pick from Mount Adir (Davis et al., 1985), several objects from Taanach and Kinneret (Muhly et al., 1990; Stech-Wheeler et al., 1981) and three iron objects from Idalion (Maddin, 1982; Tholander, 1971).

The diffusion of carbon into iron is known as carburization. When this is identified as being the spontaneous result of the smelting process, it is known as 'primary carburization' to distinguish it from the deliberate, 'secondary carburization', that is undertaken during the manufacturing process or finishing treatments of an object (Scott and Eggert, 2009). The more reducing the conditions, at temperatures within the austenitic region of the phase diagram (between ca. 800–1100 °C), the greater is the degree of penetration of carbon. Deliberate carburization (such as case hardening), is a lengthy process, which would result in a gradient of carbon content in the surface layers of the treated object. The depth, to which the carbon would penetrate, increases with time to a maximum value determined by the temperature and gaseous

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https://doi.org/10.1016/j.jasrep.2018.01.040
Received 17 October 2017; Received in revised form 22 January 2018; Accepted 24 January 2018

atmosphere. For example, at 950 °C it takes 30 min to achieve a penetration depth of ca. 70 µm, or 4 h to reach a depth of 1.5 mm (McConchie, 2004, p. 61 and ref. within). In order to produce high-quality steel, which would be considerably harder than bronze, carburized iron from a temperature exceeding 723 °C was quenched, by immersing the red-hot tool in water or oil for extremely rapid cooling. This action generates a rearrangement of atoms to form martensite, resulting in a much harder, though brittle metal. Reheating (tempering) was required in order to relieve the brittleness caused by quenching (Maddin, 1982; Notis et al., 1986). These practices, if indeed performed during the Iron Age, would have resulted in a metal generally superior to bronze.

Since the above-mentioned metallographic studies, no new microstructural analyses of iron/steel objects from the Southern Levant or Cyprus, dating to the Iron Age, have been published. Muhly (2006, p. 26) wrote: "*The sad thing is that no other research team has followed up the pioneering work done by Maddin, Muhly and Stech, and our last report was published in 1990*". Notably, several studies of iron artifacts from Anatolia were conducted (e.g. Masubuchi, 2008; McConchie, 2004).

In light of the extensive archaeological excavations in modern-day Israel in the past few decades, yielding numerous stratified iron objects, it was the purpose of this study to reassess previous conclusions regarding the technological capabilities of the Iron Age smith in a systematic study. To this aim we subjected fifty nine iron objects from well-dated contexts to microstructure analyses. The objects originated in major Iron Age sites, from contexts dated from Iron I to Iron IIB (ca. 11th–8th centuries BCE), including Hazor (Upper Galilee), Megiddo and Rehov (Northern valleys), Tell es-Safi/Gath (Shephela) and Khirbet Qeiyafa (Ella Valley) (Fig. 1).

2. Materials and methods

Artifacts for analyses were chosen from well stratified archaeological contexts and derive from three main categories: tools, weapons and jewelry. Blades, which could have been used as both tools and weapons were particularly prevalent, and included three bi-metallic knives (see e.g. Sherratt, 1994; Waldbaum, 1982, for such knives in Cyprus). Table 1 lists all the objects included in the study, their registration numbers (according to the excavation system from which they originated), their typology (when possible), stratigraphic context, relative dating and a summary of the results of the analysis. Selected objects are illustrated in Fig. 2.

In order to reveal maximum information regarding their microstructure and technological history, objects were cross-sectioned using a diamond saw, with minimal damage to the outline; Fragmented objects were chosen over complete ones, where possible. The samples were mounted in a cold setting epoxy resin, and subsequently ground and polished using standard procedures to produce metallographic sections. Etching was performed on island of preserved metal (where applicable), using 2% Nital solution (100:2 ethanol: HNO_3). After preparation, the sections were examined using an optical microscope with reflected light (Nikon Eclipse E-600 Pol) and a scanning electron microscope (Ultra-LEO-55VP) equipped with an Oxford Instruments Energy Dispersive Spectrometer (SEM-EDS).

Identification of the microstructure and estimation of the carbon content are primarily based on the relative volume of pearlite and cementite (and/or their relics), identified in the matrix, and in comparison to microstructure with known amounts of carbon (modern samples). These estimations do not take into account the effects that cooling rates has on the formation of pearlite, and are therefore, by all means neither quantitative nor accurate. Depending on the current preservation state of the items, pearlite formations were mostly identified as relics (occasionally with the cementite phase preserved) and were mainly used to differentiate between low and high carbon steels. EDS analysis performed on a few cementite (Fe_3C) remains for confirmation, proved helpful in their identification (unpublished results).

3. Results

3.1. Preservation

State of preservation is a major component in the study of early iron objects. All of the objects under study, although carefully assembled based on their relative preserved appearance, were badly corroded and almost completely oxidized. It was readily apparent that objects have undergone considerable swelling due to oxidation. It was therefore often difficult to determine an object's profile prior to sectioning.

Following sectioning and polishing, three main zones were usually visible (Fig. 3); Zone 1 comprised of secondary corrosion layers, in which foreign materials, such as quartz and calcite grains, and occasionally pseudomorphs of vegetal material, were observed. Zone 2 was usually better preserved, and was therefore the zone of interest. This area appeared black and shiny after polishing and in most cases revealed relics (pseudomorphs, also known as 'ghost' structures) that serve as indication for the original metallic structure. Microscopic islands of non-corroded metal were often observed in this area. Their size, ranging from several tens of microns to a few millimeters, was estimated in the best preserved samples, as comprising no > 1% of the overall volume of the sample. Zone 3 represents the core of the artifacts. Here, in almost all objects, no structure could be recognized, and in many of the objects, a hole surrounded by secondary corrosion products was actually formed.

This poor state of preservation was of course a major obstacle in the analyses, and limited the information that could be retrieved. Carbon content could be estimated based on the relative volume of pearlite relics, however often, different areas with varying carbon content were observed in the same sample. Whether the observed inhomogeneity reflected the original iron composition or was affected by corrosion is hard to tell; Does the lack of pearlite relics in certain areas, for example, suggests very low- to no-carbon content in the iron or rather reflects the preservation state? Evidence for deliberate carburization, appearing as a gradient of higher carbon content from the surface inwards, even if originally existed, was lost to corrosion together with the outer most layers (see Summary and discussion), as was our ability to identify welding lines. The latter indicating the act of joining steels, possibly of varying quality (carbon content). Moreover, out of the fifty-nine sampled objects only few had enough preserved metallic iron to enable etching, and micro-hardness measurements could not be performed (even under small loads) due to the very limited size of the preserved metallic islands. This is somewhat in contrast to some earlier publication of studied objects from Israel, and raises the question whether some of these objects were erroneously dated to the Iron Age or whether their unique preservation state is in itself a reason to regard them as the exception rather than the rule.

Non-metallic inclusions, mainly slags, were observed in all of the samples. These were mostly two-phased inclusions; comprising a wüstite (FeO) egg-shaped structure and a glassy matrix associated with fayalite (occasionally crystalline). As most of the samples were cut along the width of the object, it was difficult to see deformations of slag inclusions along the longitudinal axis. However, in many samples the slag inclusions appeared fragmented due to forging. The chemical composition of slag inclusions is often compared to potential iron ores (and/or smelting slags) for provenance (Blakelock et al., 2009; Buchwald, 2005; Charlton et al., 2012; Coustures et al., 2003; Desaulty et al., 2009; Dillmann and L'Héritier, 2007; Hedges and Salter, 1979; Leroy et al., 2012). As it was not the aim of the present study, slag inclusions were not analyzed in the framework of this research.

In the following sections the major results obtained in this study will be summarized according to site assemblages. Only representative samples or those of special interest will be presented and discussed.