STUDY OF VARIOUS STEEL WORKING TOOLS EXCAVATED IN SHKODRA DISTRICT (FROM III-II B.C. TO THE MEDIEVAL PERIOD) WITH DIFFERENT PHYSICAL ANALYTICAL METHODS

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Abstract

Shkodra is a northwestern city in Albania, established during V-IV century B.C., while Melgushë is a village with few residents located 10km in south of Shkodra. Agriculture in Albania dates from the Neolithic era, followed by major social developments. Many iron objects have been brought into light during archaeological excavations. A spade, a pickaxe, a plough (III-II B.C.) and two sickles (medieval period) are at the center of this study, using different physical analytical methods in order to determine the elemental composition and production technology. To reach these goals μ-XRF, SEM-EDS, OM, Vickers microhardness tester, as well as C-S system for carbon content calculation were used. From the XRF results all objects consist of over 99%Fe with minor elements such as Co, Mn (<1%), Cu (<0.06%), as (<0.04%). The first sickle contain 0.18%C and its mean Vickers microhardness value is 201HV while for the second one is 151HV. After etching the two sickles' microstructure the granules of ferrite in polygonal shapes with small islands of perlite were visible with OM. SEM revealed wüstite inclusions located on the glassy Fe matrix. The shape and directions of these inclusions suggested that these objects were hammered after casting.

Keywords: Shkodra, Illyrian, iron working tool, μ-XRF, SEM, OM.

Përmbledhja

Shkodra është një qytet veriperëndimor në Shqipëri, themeluar gjatë shekujve V-IV p.e.s., ndërsa Melgusha është një fshat me pak banorë që ndodhet 10km në jug të Shkodrës. Bujqësia në Shqipëri daton që nga epoka Neolitike, e ndjekur nga zhvillime të mëdha shoqërore. Shumë objekte hekuri janë nxjerrë në dritë gjatë gërmimeve arkeologjike. Një lopatë, një kazmë, një parmendë (III-II p.e.s.) dhe dy drapëra (periudha mesjetare) janë në qendër të studimit, duke përdorur metoda të ndryshme analitike fizike për të përcaktuar përbërjen elementore dhe teknologjinë e prodhimit. Për të arritur këto qëllime janë përdorur μ-XRF, SEM-EDS, OM, testuesi Vickers i mikrofortësisë dhe sistemi i C-S për llogaritjen e përmbajtjes së karbonit. Nga rezultatet e XRF të gjitha objektet përbëhen nga mbi 99%Fe me elementë minor Co, Mn (<1%), Cu (<0.06%), As (<0.04%). Drapëri i parë përmban 0.18%C dhe vlera mesatare e mikrofortësisë Vickers është 201HV ndërsa për të dytin është 151HV. Pas atakimit të mikrostrukturës së dy drapërave, ishin të dukshme me OM granulat e ferritit në forma poligonale me ishuj të vegjël perliti. SEM zbuloi inkluzionet wüstite të vendosura në matricën e qelqtë Fe. Forma dhe drejtimet e këtyre inkluzioneve sugjeruan që këto objekte ishin goditur me çekan pas derdhjes.

Fjalë kyçe: Shkodra, Ilire, vegël pune hekuri, μ-XRF, SEM, OM.

Introduction

Iron objects excavated in Albania have been studied by archaeologists and very few with physical analytical methods which would reveal information about iron extractive metallurgy. Metal working in Illyrian cities is represented mainly by working tools and weapons production. There are many findings that testify iron smelting in Illyria but until now there are few traces of iron ore extracting in our country. Agriculture in Albania began in the Neolithic era, its birth was followed by major changes in human society. Agriculture has been to Illyrians and later to Albanians a primary economic activity. Many ancient tools and later ones, have similarities with each other. They speak about ancient traditions, the continuity of techniques generation after generation and ancient agricultural rules. (Anamali, 1979; Prendi, 1982; Prendi, 1985; Prendi, 2008).

Archaeologists have long hypothesized that iron production technology spread from a single point of origin, divided into two sections: smelting and hot forging. In ancient times metallic iron was produced in solid state by chemical reduction of its ore at about 1200ºC in the presence of charcoal. After metallic iron was solidify, annealing at 700ºC and cold hammering was in order, in most cases. Iron smelting is thought to have been practiced by the Hittites in today Turkey around XVI-XII century B.C., and the technique slowly migrated outward, reaching China, Britain and Nigeria during the first millennium B.C. (Tylecot, 2002; Schmidt & Childs, 1995)

On a hill where Melgushë village lies, near the district of Shkodra, three agricultural (working) tools have been excavated and dated to the III-II century B.C. While the two sickles (I and II), according to archaeologies, belonged to the medieval period. All objects were exposed in the Shkodër History Museum. The purposes of this study are to determine the elemental composition and the production technology for these objects. (Anamali, 1979; Ceka, 2002)

Materials and methods

In order to fulfill the purposes of this study, investigation with archaeometallurgical methods is necessary but only when it is possible to sample the object. We were allowed to sample the two sickles but not the spade, pickaxe and plough. On table 1 the objects are presented along with their dating, place of excavation, object / file number, culture and mass in grams.

Table 1. The objects of this study along with their dating, place of excavation, object / file number, culture and mass in grams.

Object	**Period**	**Excavated**	**Object no**	**File no**	**Culture**	**Mass**
Spade	III-II century B.C.	Melgushë (Shkodër)	14786	132	Hellenistic	985gr
Pickaxe	III-II century B.C.	Melgushë (Shkodër)	14605	214	Hellenistic	437gr
Plough	III-II century B.C.	Melgushë	14788	288	Hellenistic	197gr
Sickle I	Medieval	Shkodër	41519	192	Illyrian	172gr
Sickle II	Medieval	Shkodër	14718	133	Illyrian	164gr

Figure 1 below shows the spade, pickaxe, plough and the two sickles (photos and sketches) with their dimensions. The spade, pickaxe and plough belong to the Hellenistic culture (III-II century B.C.) while the two sickles are evidence of the Illyrian tools production (medieval period). According to archaeologists the technique used to give the final shape of these objects was cold hammering. A high-quality tool's edge could be produced using low carbon steels, just like most ancient ones that contained about 0.1-0.5% carbon. (Scott, 1991; Scott, 2013)

The analyzed objects were covered in varnish to protect them from corrosion so it was necessary to remove it in certain points where the μ - XRF analysis was performed. The samples of the two sickles were mounted in acrylic resin and polished with SiC abrasive papers (Buehler P600, P800, P1000, P1200, P2500) along with diamond paste (Kemet 6, 3, 1 μm). The polishing process is necessary to eliminate the mechanical damages of the samples' surface that could negatively affect the analytical examinations. (MIT, 2003)

The devices used for the examinations are: μ - X ray fluorescence (μ - XRF, ARTAX Bruker, Mo anode, Rh target, 60μm examining spot, voltage 45kV, current 300μA, 60sek exposure time, detective capacity from Na to U); optical microscopy (OM, KOZO XJP304); scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS, XL30 ESEM-FEI and EDAX Genesis Spectrum with ZAF correction; Vickers microhardness tester attached to Metalloplan Leitz optical microscope; carbon & sulfur systems (CS-244-784-000) for a single carbon content calculation. (Potts & West, 2008; Wayne, 2009; Goldstein *et al.*, 2003)

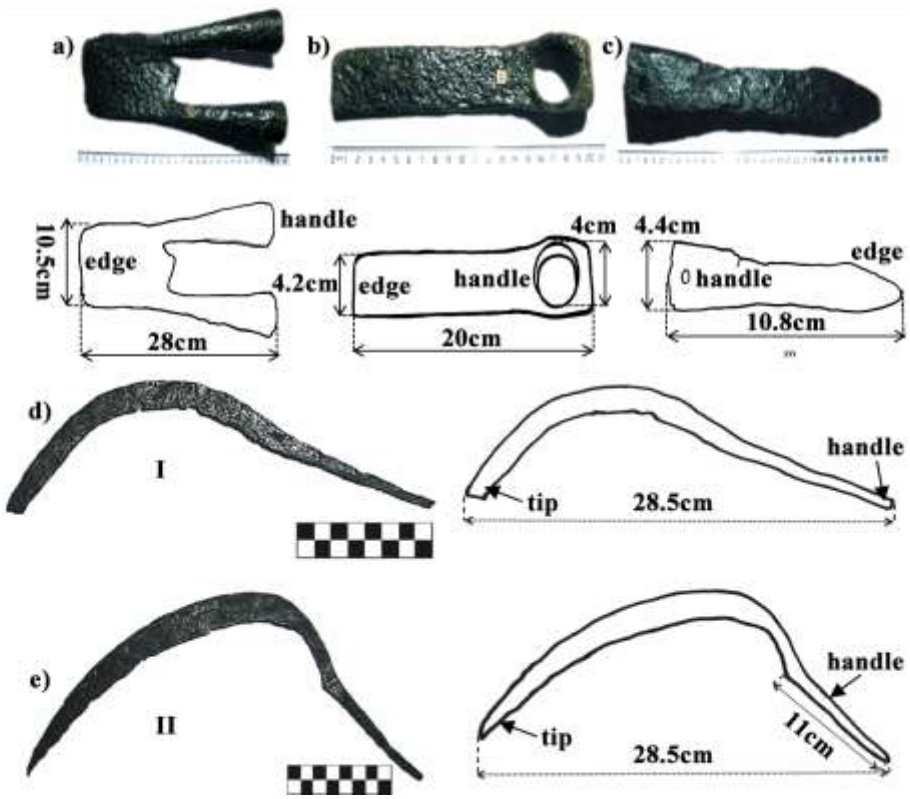

Figure 1. Photos and sketches of the: a) spade, b) pickaxe, c) plough and the two sickles (d) I and e) II), along with their dimensions.

Results and discussions

Cementite Fe_3C is a hard and brittle component, influencing on the properties of steels and cast irons. Alloys, containing up to 0.51% of carbon, start solidification causing the formation of δ-Fe crystals. Carbon content in δ-Fe increases up to 0.09% in the course of solidification, and at 1493ºC part of the system exists in liquid phase while δ-Fe perform a peritectic transformation, resulting in the formation of austenite γ-Fe. Alloys, containing carbon more than 0.51%, but less than 2.06%, form primary austenite γ-Fe crystals in the beginning of solidification and when the temperature reaches the curve ACM primary cementite stars to form.

Iron-carbon alloys, containing up to 2.06% of carbon, are classified as steels. Alloys, containing from 2.06 to 6.67% of carbon, experience eutectic transformation at 1147 ºC with a carbon concentration of 4.3%. All Fe-C alloys experience eutectoid transformation at 723ºC with a carbon concentration of

0.83%. When the temperature of an alloy reaches 733ºC, austenite γ-Fe transforms at slow cooling conditions to pearlite (87.5% α-Fe + 12.5% Fe_3C). Figure 2 shows these phase transformations on the F-C alloys diagram. (Scott, 2013)

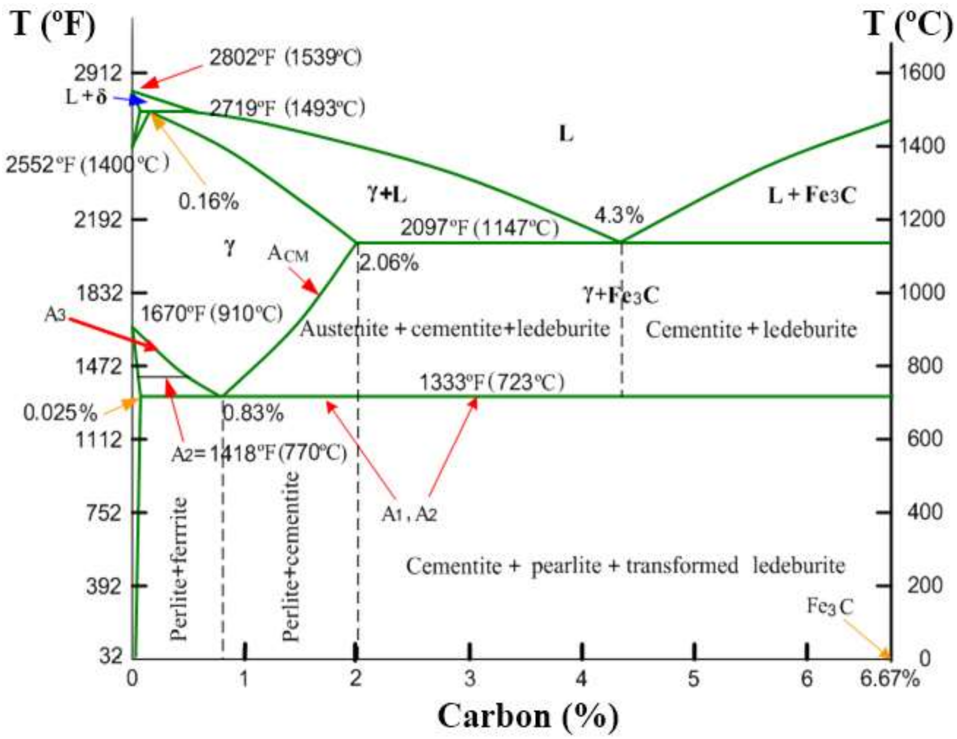

Figure 2: Iron-carbon phase diagram.

Non-destructive μ - XRF is an unreplaceable tool to determine the chemical composition and to investigate the provenance of cultural heritage objects in the last decade. (Potts & West, 2008)

μ - XRF analysis for all objects on various points were performed in the premises of the Shkodër History Museum. The results of the μ - XRF examinations (qualitative and quantitative results in %) are shown on table 2, along with the standard deviation and figure 3 represents three of the spectra obtained in the case of the spade, pickaxe and plough. The points analyzed with μ - XRF were chosen in different parts of the objects regarding usage, on the tips / edges and handles. We can see that these objects are over 99% iron with minor elements such as Co, Mn (both less than 1%) and Cu, As (less than 0.06%). Co and Cu might be present as a result of impurity diffusion from soil; C, which is the main element in steels, is not detectable with XRF; while Mn is a common alloying element of steels.

No difference in quantitative percentage is detected between the various points within the object. (Scott, 2013)

Table 2. The μ - XRF results of all objects on various points; the elemental compositions are in % along with the standard deviations.

Object (point analyzed)	**Fe (%)**	**Co (%)**	**Mn (%)**	**Cu (%)**	**As (%)**
Spade (on edge)	99.30±5.10	0.45±0.29	0.25±0.02	-	-
Spade (on handle)	98.71±5.14	1.00±0.30	0.29±0.03	-	-
Pickaxe (on edge)	99.46±4.12	0.38±0.01	0.16±0.02	-	-
Pickaxe (on handle)	98.91±4.04	0.50±0.01	0.59±0.07	-	-
Plough (on edge)	99.26±4.80	0.40±0.26	0.32±0.03	-	0.02±0.01
Plough (on handle)	99.22±4.36	0.42±0.24	0.32±0.02	-	0.04±0.01
Sickle I (on tip)	99.31±5.40	0.42±0.30	0.22±0.02	0.06±0.01	-
Sickle I (on handle)	99.28±4.55	0.41±0.25	0.26±0.02	0.05±0.01	-
Sickle II (on tip)	99.19±4.77	0.47±0.27	0.44±0.03	-	-
Sickle II (on handle)	99.10±4.82	0.43±0.27	0.44±0.03	-	-

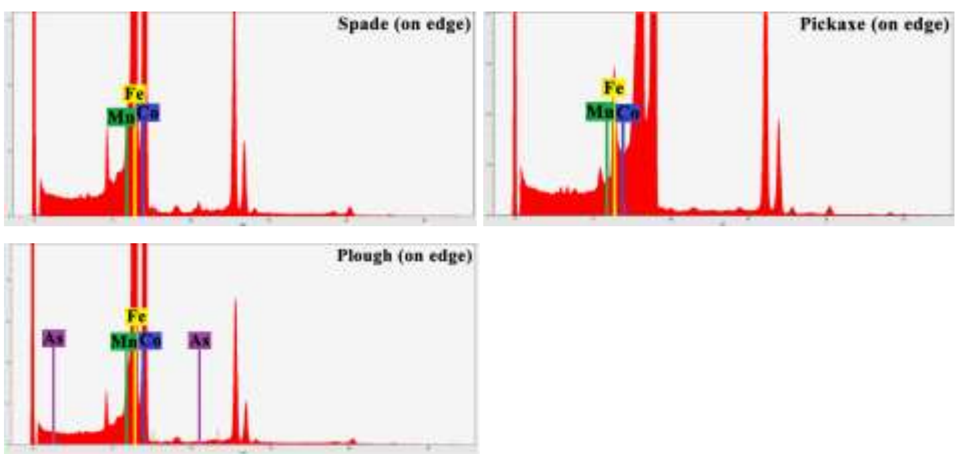

Figure 3. Three of the μ - XRF spectra: spade (on edge) up-left, pickaxe (on edge) up-right and plough (on edge) below.

Figures 4 and 5 show the OM and SEM examinations of sickle I and II samples. Optical microcopy images a) and b), in both figure 4 and 5, present the same sample's surface obtained with reflected and polarized light respectively. These OM images (a) and b)) of both samples show: the iron metallic matrix; the corrosion products penetrating deep into the metal; the absence of pores, which is related with the production technique and might suggest the low content of gases evaporating during solidification or a low cooling rate. Inclusions are visible in the sickle I sample (fig. 4 a), b)) and are missing in the second one (fig. 5 a), b)).

Images 3 c) and 4 c) are obtained with OM with reflected light after the samples were etched with nital 5% (5% nitric acid + 95% ethyl alcohol) for about 10 seconds. Ferrite (α-Fe) with small islands of pearlite (87.5% α-Fe + 12.5% Fe_3C) compose the microstructure of both etched samples.

From the SEM images (fig. 4 d) and fig. 5 d)) nodular wüstite on glassy iron matrix and inclusions / slag components are clearly visible. These inclusions / slags are oriented along a certain direction, which shows that the production technique used might have been hammering. EDS analysis show high content of CaO, SiO_2, Al_2O_3, and MgO, which might be related to the fuel or flux used by the blacksmith. While the high content of FeO derives from nodular wüstite observed in the SEM images.

The mean Vickers microhardness value of sickle I sample is 201 HV, while the one of the second sample is 151HV. The carbon content is measured for the sickle I sample with the help of carbon & sulfur systems (CS-244-784-000) equipment and resulted 0.18% C. (Einarsdóttir, 2012; Duka *et al.*, 2013; Eliyahu *et al.*, 2011)

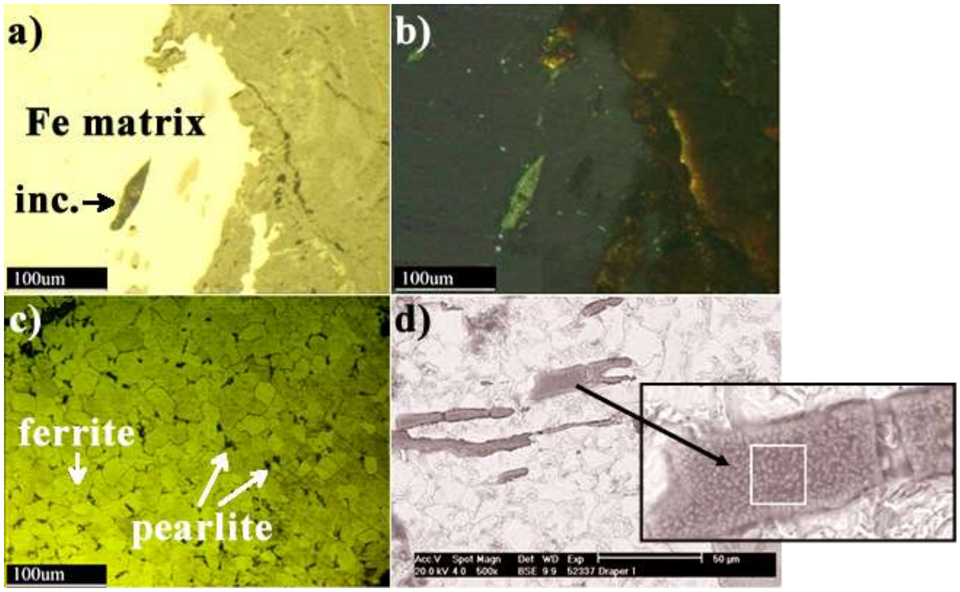

Figure 4. Sickle I: a) optical micrograph with reflected light, Fe matrix with inclusions (inc.); b) optical micrograph with polarized light (same position); c) optical micrograph with reflected light after the sample is etched, showing a ferrite-perlite microstructure; d) SEM image showing microstructure's inclusions.

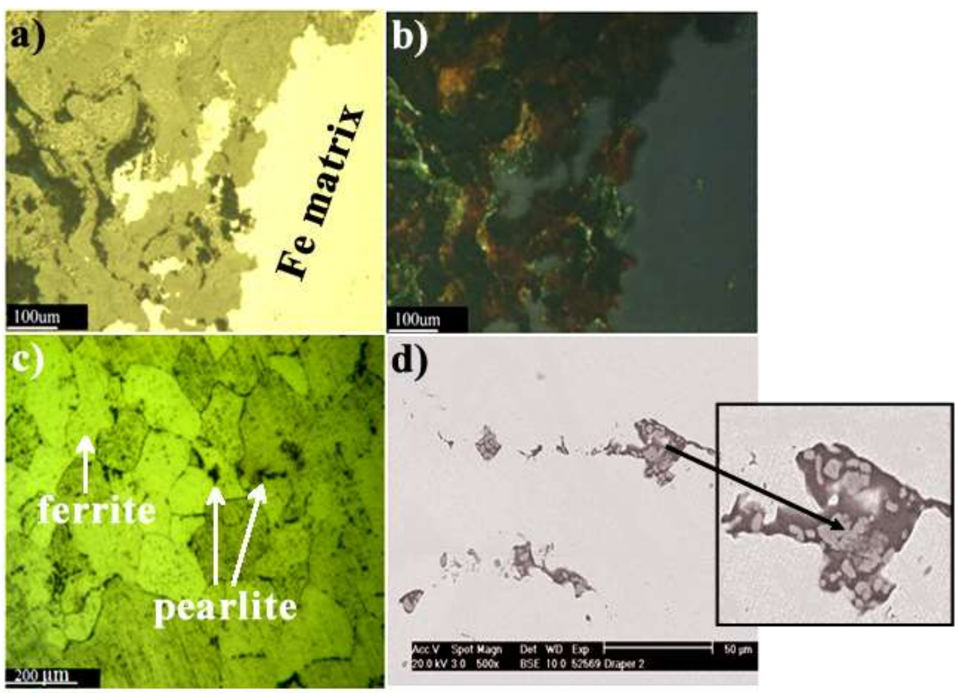

Figure 5. Sickle II: a) optical micrograph with reflected light, Fe matrix with inclusions (inc.); b) optical micrograph with polarized light (same position); c) optical micrograph with reflected light after the sample is etched, showing a ferrite-perlite microstructure; d) SEM image showing microstructure's inclusions.

Conclusions

Various working tools (from III-II B.C. to medieval period), exposed in Shkodër History Museum, were examined with different physical analytical methods in order to determine the elemental composition and production technique. A spade, a pickaxe, a plough and two sickles resulted over 99% Fe with minor elements such as Mn, Co, Cu, As (0.02-1%). Both sickles' microstructure was composed by ferrite and pearlite. The wüstite inclusions' shape and orientation suggested that sickle I and II were hammered after the casting process. Combining physical analytical methods with the archaeologist expertise is necessary to get a full picture of the object history.

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