METAL ANALYSES: SOME CASE STUDIES FROM MOTYA

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The aim of this investigation is to reconstruct the archeometallurgical processes, manufacturing techniques, and cycle-life of Motyan (Sicily, Italy) metallic artefacts from metals extraction to corrosion. The research was developed through five case studies, for which metallurgical and corrosion processes are reconstructed.

Keywords: Phoenician - Punic metallurgy; weapons; slags; bronze artefacts; corrosion

1. INTRODUCTION

The study of metal artefacts from Motya sheds new light on the manufacturing processes and technological skills of the Phoenicians. They were renown in ancient times as "metal producers" and/or at least "diffusers" of technological transfer and advancements of the *ars flaturae* during the first centuries of the 1st millennium BC.[1] For several centuries, from the 9th to the 5th century BC, much of their metal products were exchanged in the Mediterranean, together with precious goods and stuffs on cargos and ships. Although several research have been carried out on different typologies of metal artefacts from Phoenician sites in the Iberian Peninsula, Sardinia and North Africa, scientific studies on archaeometric characterization of metalworks from Motya have never been performed before.[2]

The main issue of this project was the assessment of the original microstructure and composition of the alloys, including microstructural features induced by manufacturing process and the evolution of the corrosion processes over time, including selective dissolution, and formation of new phases during burial conditions.

1.1. *Microstructure and chemical composition of a Sardinian bronze axe*

MCM.18.200 is a bronze two-looped socketed axe attributed to a mature stage of Motya IIIC Period (1100-950 BC), found in a sounding in the so-called *Casa dei mosaici*, dated to the 10th century BC, buried under several strata of the Phoenician colony.[3]

Scanning Electron Microscope (SEM) analysis shows a Cu-Sn matrix and numerous brighter inclusions, having different shapes and sizes, formed due to the low miscibility of Pb in copper (fig. 1:a). The number and distribution of Pb-inclusions in the matrix depend on casting parameters. In particular, the big globules suggest that the cooling rate is very slow and there was time for the bulk of Pb to be refused from the solid ahead of the freezing front.[4]

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1 Whitaker 1921; Markoe 1985; Matthäus 1985; Giumlia-Mair 2015.

2 Valério *et al*. 2010; 2012; 2015; Kaufman *et al*. 2016; Rovira - Renzi 2017; de Caro 2017; de Caro - Angelini - Es Sebar 2021.

3 Nigro 2016; Nigro *et al*. 2020.

4 Hughes - Northover - Staniaszek 1982.

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Regarding corrosion process, the concentration of Cu and Sn in the external layer, corresponding to the patina, is highly depleted for decuprification and de-stannification processes, where these elements are dissolved and leached from metallic structures. Indeed, a large quantity of Pb, in time, migrated from core to the surface through porosity system of the alloy and reacted with water, oxygen, chloride, sulphate and carbonate ions from the environment, forming Pb- salts. X-ray Diffraction (XRD), performed on the surface of leaded bronze axe, confirmed the occurrence of cuprite (Cu_2O), cassiterite (SnO_2), laurionite (PbClOH), cerussite ($PbCO_3$), litharge (PbO), anglesite ($PbSO_4$) and plumbonacrite ($Pb_5O(OH)_2(CO_3)_3$).

Electron Microprobe Analysis (EMPA) showed that the matrix is composed by Cu 86.9-95.4wt.% and Sn 2.8-6.9 wt.% with arsenic impurities (0.6-1.3 wt.%). Instead, Pb in distinct micro-domains reached concentrations up to 95wt.%. The high concentration of Pb suggested a deliberate addition in the alloy to improve the fluidity of the molten bronze, thus increasing the temperature of the solidification range. However, these big islands completely immiscible in the Cu–Sn solid phase, representing points of weakness and possible fracture in the metal artefact, are not suitable alloy features for weapons productions that should have high mechanical properties. This apparent contradiction can be explained taking into account that this kind of weapons were usually employed in ritual and cult contexts, such as deposits and hoards[5] and was characterized by the presence on the surface of lead globules functional to produce the loops. This hypothesis is supported by the presence of leaded bronzes in many axes from Atlantic Europe, such as the British Isles, Western France and North-Western Iberia, whereas in the regions around the Mediterranean Sea binary bronze was employed until Early Iron Age.[6]

1.2. *Corrosion pattern of Iron Age bronze arrowheads*

The Iron Age bronze arrowheads at issue were long range offensive weapons involved during the siege by Dionysius, the tyrant of Syracuse (Sicily, Italy), who conquered the island of Motya in 397/6 BC.[7] On the basis of their typology, morphological features and geographical areas of attestation, the arrowheads are classified in different types: Type A.1 or “Crete type”, characterized by a flat and lanceolate body with two lateral barbs; Type B.1, *i.e.*, short conical points with two lateral wings; Types C.1 and Type C.2 also known as “Scythian type”, that are short pyramidal points and Type D.1, *i.e.*, conical arrowhead.[8]

SEM and EMP data revealed that the presence of Sn played a key role in the corrosion process of conical arrowhead (Type D.1). These arrowheads are Pb-free bronze alloy and are characterized by the occurrence of periodic corrosion layers, called Liesegang rings with streaks of Sn-oxide interposed between Cu_2O and $Cu_2(OH)_3Cl$ layers. These banded structures are involved by environmental changes in burial conditions, *e.g.*, temperature, relative humidity, duration and intensity of rain, sea salinity, soil corrosivity, interdiffusion

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5 Taramelli 1921, fig. 27; Bernabò Brea - Cavalier 1980, 76, pl. 284:25; Begemann *et al*. 2001, 49, fig. 5:10714; Lo Schiavo 2003, 159; 2013, fig. 8:3.
6 Bernabale *et al*. 2019; Nigro *et al*. 2020.
7 Nigro 2022.
8 Termini 2005.

of metallic components and soil salts. On the contrary, the arrowheads with more accessory elements (*i.e.*, wings and barbs) and high quantities of lead, which occurred at microscale in form of large globules (Type B.1 and C.2) or as Pb fine dispersion in grain boundaries (Type A.1 and C.1), are characterized by multi-layers consisting of lead compounds. Indeed, in a chlorine-rich environment, the less noble metal Pb acts as an anode, involving selective corrosion of Pb in form of pitting and formation of a porous structure (fig. 1:b).

Based on X-ray Powder Diffraction (XRPD) results, the corrosion mechanism identified in all samples was bronze disease, characterized by the presence of chlorides in the alloy interface. It has been observed that a greater stratification of copper trihydroxychlorides and mixed salts of Cu and Pb, *i.e.*, pseudoboleite, is favored in alloys with smaller Pb microdomains, whereas in alloys with large Pb globules lead salts prevail, *i.e.*, penfieldite and cotunnite.

The harder type of binary alloy, having high Sn content, was used for the conical arrowheads attributed to Motyan production, suggesting that, although the Motyan have been tragically defeated, they have defended themselves with weapons of good quality. On the contrary, the pyramidal and lanceolate arrowheads, ascribed to the troops of Dionysius I of Syracuse - since the greater number of attestations of arrowheads “on arrival” – consisted of a more modern type of ternary alloy, but with worse mechanical properties due to the presence of a soft metal as Pb.[9]

1.3. *Archaeometric investigation of copper and iron waste*

Microstructure, mineralogy, and chemistry of fourteen copper and iron slags from the Phoenician site of Motya, dating back to 8^{th}-4^{th} centuries BC[10] were investigated. The samples were analyzed by a multi-analytical approach, based on Scanning Electron Microscope (SEM-EDS), High-Resolution Field Emission Scanning Electron Microscopy (HR-FESEM), Micro-Raman spectroscopy (μ-RS) and Electron Microprobe Analysis (EMPA). The results showed different typologies of by-products, such as base metals speiss, copper slags from smelting sulphide ore with matte and iron smelting and smithing slags, suggesting different stages of copper and iron productions.

Group 1, corresponding to the more recent Motyan copper production (6^{th}-4^{th} centuries BC), is composed by high amount of copper and has numerous Cu-S inclusions. The occurrence of these wastes could be due to working processes of final refining stage of copper metallurgy in Motya.

Group 2 (7^{th}-mid 6^{th} centuries BC) is considered the remains of base-metal speiss, *i.e*., a complex mixture of copper arsenides and antimonides, characterized by copper dendrites and interdendritic micro-domains, containing As, Sb, Bi, Pb.

Group 3 (7^{th}-mid 6^{th} centuries BC) wastes suggest the presence of metallurgic activity in Motya, producing copper from sulphide raw materials (probably chalcopyrite) by partial smelting of ores.

Group 4 (8^{th}-4^{th} century BC) is composed by Fe-rich slags. On the base of macroscopic features and chemical and mineralogical markers, two types of slags are distinguished:

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9 Bernabale *et al*. 2021.

10 Nigro 2009; Spagnoli 2019.

furnace slags, corresponding to the primary process of iron production, and hammerscales, corresponding to materials removed during smithing, when the bloom was heat-treated in the hearth and hammered on the anvil to produce the iron artefact.

1.4. *Corrosion models of Iron weapons from Motya and Lilybaeum*

This study contributed to the investigation of corrosion behaviors of iron artifacts in two different conditions, *i.e.*, lagoon-like and calcarenitic hypogea environments. A multi-analytical approach that includes µ-RS, Scanning Electron Microscopy (SEM-EDS) and Field Emission Scanning Electron Microscopy (HR-FESEM) was applied. The samples consist of a set of weapons and armors found in the "Archaic Necropolis" of Motya[11] (8th-6th centuries BC), along the northern shore of the island, and in the Punic Necropolis of Lilybaeum[12] (4th century BC).

Microstructural observation with SEM and HR-FESEM show that all weapons were made of wrought iron, with complex microstructures recognized as a) sandwich-type, b) active corrosion layers and c) high temperature/reconstructive corrosion. Micro-Raman results revealed the presence of magnetite, goethite, lepidocrocite and hematite as the main corrosion products and soil minerals as quartz, calcite, barite, actinolite, microcline, zircon and Ti-oxides.

The occurrence of lepidocrocite in the outer rust layer of most of the samples from Motya indicated that the artifacts are not yet thermodynamically passivated.

The chain-mail from Lilybaeum is shaped by hot-working processes, using high-temperature forge-welding, involving the formation of hematite at the forge-welded interfaces.

The occurrence of magnetite and metal, survived in armors buried in hypogea site of Lilybaeum, suggests more stable environmental conditions than Motya.[13]

1.5. *Integrated approach for the study of iron nail corrosion*

A preliminary investigation of the corrosion system of an iron nail (MF.03.53) from Motya was performed by traditional and advanced techniques. Micro-Raman spectroscopy allowed to confirm the presence of an active corrosion on the external patina as confirmed by the presence of red-brown clusters of lepidocrocite. SEM-EDS analyses showed the lack of metal core in the tip of the nail and the occurrence of corroded iron phases in the dense product layer (DPL) and transformed medium (TM). In order to evaluate if the studied section was representative of the entire sample, a low-resolution scan of the nail with Multiscale X - ray Microscopy (XRM) has been performed. The challenge was to extract as much useful information about the spatial distributions of phases in iron-based archeological nail from 3D visualization and image segmentation. XRM revealed the existence of an internal metal core, starting from a few millimeters above the tip of the nail and showing that the tip is completely corroded away. In contrast, the head and upper part of the shank are well preserved. Nail 3D reconstruction and segmentation allowed

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[11] Tusa 1972; 1978; 2012; Ciasca 1979; 1980; 1990.
[12] Bisi 1970; Bechtold 1999; Giglio 2016.
[13] Bernabale *et al*. 2022a.

evaluating quantitatively the presence of each phase of the nail in virtual slices. However, the low-resolution scan represented a limiting factor for the identification of the corrosion sub-layers. Thus, to tackle the complete characterization of the virtual section which included the metal remaining, high-resolution scan is also performed, covering all length scales from micrometric resolution to centimeters. The evolution of internal nail corrosion has been tracked by combining SEM-EDS data with XRM images of the entire nail.[14]

2. Conclusive Remarks

The research carried out on metal artifacts, weapons, nails, and slags from Motya, dated between the beginning of the 1st millennium and the 4th century BC provides additional information on local metallurgy and the role of Motya in the exchange network of this category of products.

Motya, therefore, participates in the Mediterranean metallurgical *koinè* between the end of the Late Bronze Age and the beginning of the Iron Age, which involves the spread of Atlantic and Iberian types of eastwards, as evidenced by the discovery of the two-looped socketed axe.

A metallurgical activity of some importance has been performed in Motya since the 8th century BC, both for copper and iron working, and both primary (smelting) and secondary (melting) production took place on the island. This data thus suggests that either minerals or ingots and semi-finished metals arrived on the island and were locally processed.

In conclusion, Motya actively participates in the metallurgical innovations that spread in the Central and Western Mediterranean during the 1st millennium BC and shares the most widespread types and forms.

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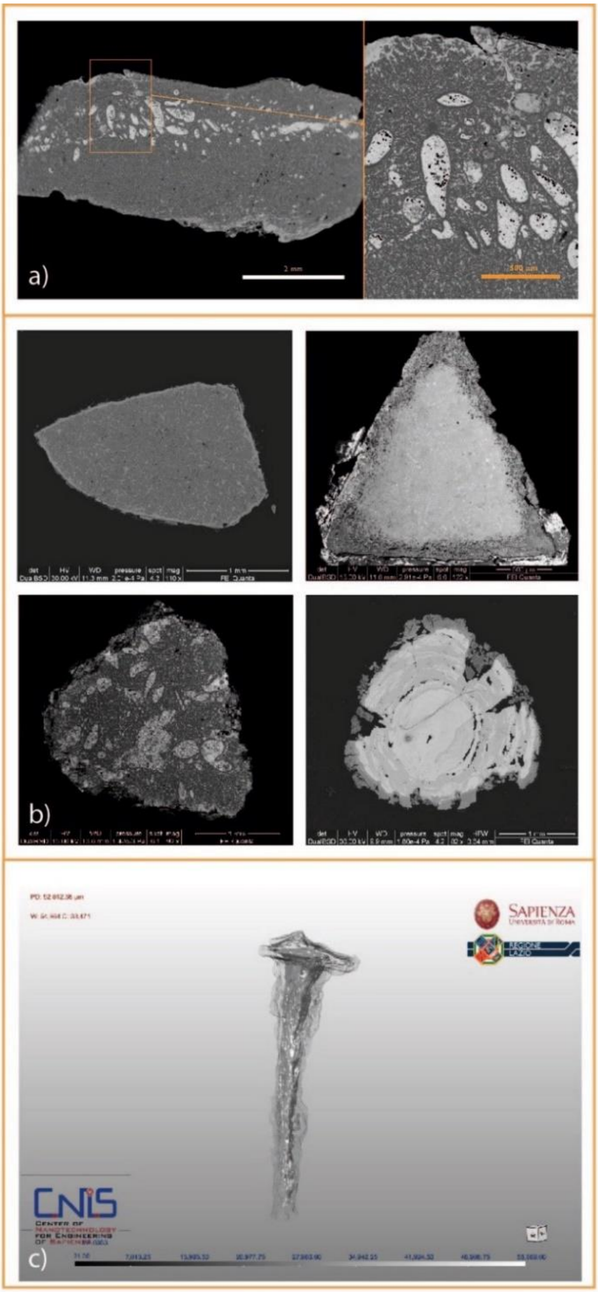

Fig. 1 - BSE images of axe MCM.18.200 (a), arrowheads MM.78.151/8, MM.16.162, MM.16.13, MM.79,61 (b) and 3D tomographic image of nail MF.03.53 (c).