A multi-analytical approach for the study of Late Bronze Age metals from Central Portugal


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The aim of this paper is to provide a chemical study and a microscopical characterization of a group of metals from Late Bronze Age (LBA) found at Porto do Concelho (Central Portugal) and consisting of 2 sickles, 2 palstaves, 3 spearheads, 5 swords, 4 daggers, 16 rings, 1 fibulae, 3 bracelets and 4 undefined objects (fig. 1) [1]. For this purpose, a multi-analytical approach was adopted by integrating chemical and micro-structural data: compositional measurements were performed using a portable XRF Analyser, Metorex X-Met 920, equipped with a Si(Li) detector and an Am-241 source. The metallographic study was made with an optical microscope (OM) Leica, model DMLM, equipped with a digital camera DFC480. Finally, analyses by Scanning Electron Microscopy with X-ray microanalysis (SEM-EDS) was performed with an Hitachi S-3700N interfaced with a Quanta EDS microanalysis system with a Bruker A.XS Xflash® Silicon Drift Detector (129 EVE Spectral Resolution at FWHM/MN Ka). Quantitative elemental analyses were processed using the Bruker ESPRIT software. Operating conditions: backscattered electron mode (BSEM), accelerating voltage of 20 kV, working distance of ~10 mm, current emission of 120 µA, detection limit c. 0.1 wt%.

From a chemical point of view, the objects can be divided into two types of copper alloys: thirty-five objects are binary bronzes (Cu+Sn) with a low amount of Pb, while five are leaded bronze alloys (>2.0 wt% Pb). Tin ranges between 7.3 and 29.1 wt%, with a tendentially higher amount in the group of rings. Impurities of Fe, Ni, As, Ag and Sb also appear.

OM and SEM-EDS was realized on twenty-two artefacts allowing the identification of the microstructure of the metal, the presence of inclusions, casting defects and phases. Under the optical microscope, ten of the objects exhibit the characteristic features of as-cast microstructures (i.e. dendrites). This suggests that after removing the newly manufactured objects from the mould, the ancient metalworker did not apply any thermo-mechanical treatment to the artefacts. Twelve objects show equiaxial microstructures with annealing twins and, in some cases, slip bands. In this case, the objects were finished with annealing and forging operations. From a mechanical point of view, this treatment makes the metal more resistant and suitable to endure stronger impacts (fig. 2).

SEM-EDS displays that the occurrence α+δ eutectoid, irregular shaped unalloyed copper grains and Cu-S inclusions are common feature for almost all the items (fig. 3). Quantitative microanalyses made in corroded layers have also displayed a significant Sn enrichment in the patina by a depletion in Cu content (fig. 4) [2]. To conclude, the archaeometallurgical study of the metals from Porto do Concelho provides data that contribute to the knowledge of the LBA metal productions in Portugal and, by extension, in the Iberian Peninsula and the so-called Atlantic Europe.

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Figure 1: The metals from Porto do Concelho

Figure 2: OM-BF (etched) images of an axe with forging and annealing work (left) and of a sword showing a dendritic microstructure characteristic of an "as-cast" metal (right).

Figure 3: Unalloyed copper and Cu-S inclusions (SEM-EDS)

Figure 4: SEM-EDS image showing the distribution of element in the superficial corrosion layer and in the metal.