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Metallography and microstructure interpretation of some archaeological tin bronze vessels from Iran

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ABSTRACT

Archaeological excavations in western Iran have recently revealed a significant Luristan Bronzes collection from Sangtarashan archaeological site. The site and its bronze collection are dated to Iron Age II/III of western Iran (10th–7th century BC) according to archaeological research. Alloy composition, microstructure and manufacturing technique of some sheet metal vessels are determined to reveal metallurgical processes in western Iran in the first millennium BC. Experimental analyses were carried out using Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy and Optical Microscopy/Metallography methods. The results allowed reconstructing the manufacturing process of bronze vessels in Luristan. It proved that the samples have been manufactured with a binary copper–tin alloy with a variable tin content that may relates to the application of an uncontrolled procedure to make bronze alloy (e.g. co-smelting or cementation). The presence of elongated copper sulphide inclusions showed probable use of copper sulphide ores for metal production and smelting. Based on metallographic studies, a cycle of cold working and annealing was used to shape the bronze vessels.

1. Introduction

The investigation of microstructure and alloy composition of archaeological metal artefacts is an interesting and important subject to determine metalworking techniques in the ancient world. Tin bronze is the first alloy used in most regions around the world, for example, the first tin bronze artefacts appear in west of Iranian Plateau at the end of Chalcolithic period (end of 4th millennium BC) [1–3].

The Luristan region is located in the west of Iran, which is one of the important cradles of the Iranian Plateau. In archaeological context, Luristan is the highland folded region in the Central Zagros mountain chain, in western Iran. Thousands of ancient bronze artefacts with exquisite modelling, fine style, and outstanding manufacturing skill have been unearthed in the Luristan area. The emergence of significant bronze production is an important archaeological/technological phenomenon during the Iron Age in the Luristan region. The Luristan Bronzes include a series of decorated bronze artefacts similar in specific local style, dating to the Iron Age II/III (1000–650 BC) [4–10]. During the past 10 years, some archaeological excavations were carried out in Iron Age site of Sangtarashan in eastern Luristan (known as Pish-i Kuh). Sangtarashan is situated about 35 km of southeast of Khorramabad (capital of Lorestan province). The site has been excavated by Iranian archaeologists, Ata Hassanpour and Mehrdad Malekzadeh. Archaeological evidence proves that the site contains the remains of an Iron Age II sanctuary with stony architecture. Also about 2000 bronze artefacts have been discovered together with some other objects such as iron, bone, stone and pottery. In fact, the majority of objects recovered from Sangtarashan are different kinds of bronzes in the Luristan Bronzes style such as spouted and simple vessels, sculptural object such as finials, and weaponry artefacts. [11].

In this paper, some recent excavated bronze artefacts belonging to the Sangtarashan archaeological site were examined to determine alloying and manufacturing characteristics and processes during the Iron Age period. The metallurgical research concerning bronze production in Sangtarashan has become a unique opportunity to understand the Iron Age bronze production in this western region of the Iranian Plateau. The study also comprises a discussion concerning the elemental and microstructural features of some bronze vessels.

2. Materials and Methods

2.1. Archaeological Samples

To study the microstructure and alloy composition of bronzes from the Iron Age Luristan, a collection of twenty two bronze samples was selected from the Sangtarashan archaeological site. These include broken metallic vessels that have been unearthed during archaeological excavations between 2009 and 2011 (Fig. 1). Some samples were analysed

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Fig. 1. Some broken vessels from all selected samples belonging to Sangtarashan archaeological site.

and previously published [3,11] but these were reconsidered in this study next to other samples to compare and develop statistical interpretations. In total, twenty five pieces were chosen from 22 metallic vessels including 22 pieces from the vessel bodies (Nos. ST.01-10 to ST.22-11), a piece including the spout of a vessel (ST.02-10/2) and two small pins (ST.09-10/2 and ST.10-10/2). This selection was based on the fact that some bronze vessels from Sangtarashan are made with two separate pieces such as the case with spouted vessels in which the spout is manufactured by a bronze fragment that has been joined to the body with large metal pins. Therefore, one spout and two pins from three vessels are analysed.

2.2. Experimental

Small samples from the metal artefacts and fragments were prepared and mounted for metallographic preparation. For this purpose, a cross section from each piece was prepared by embedding samples in epoxy resin. Preparation for analysis was followed by grinding them with silicon carbide papers (400–2000 grit size). Finally, the cross sections were polished with a diamond paste (1 μm).

Microstructural observations and chemical composition analysis were carried out with optical microscopy and scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM–EDS) methods. Cross-sections were observed with a BK-POL/BK-POLR manufactured by Alltion Company, China, under bright field (BF) illumination. Samples were observed before and after etching with alcoholic ferric chloride ($FeCl_3$) solution. Mounted cross-sections were observed in a VEGA II, TESCAN scanning electron microscope equipped with a secondary electron detector (SE) and a backscattered electron detector (BSE) with elemental analysis system (EDS) model Rontec Quantax/QX2, Germany, in SEM laboratory of Razi Metallurgical Research Center, Tehran, Iran used for semi-quantitative elemental analyses. The metallic remains in cross sections were analysed by Energy Dispersive Spectrometry (EDS) on areas of about 10000 μm^2 (about 100×100 μm) to detect the entire alloy composition and to avoid effects of phase concentrations in the final results.

3. Results and Discussion

3.1. Alloy Composition

SEM–EDS investigation was employed to determine alloy components in a semi-quantitative manner. Table 1 shows results of alloy composition in 25 samples from 22 vessels carried out by SEM–EDS method. According to Table 1 it is obvious that all twenty two vessels are made of bronze alloy. Also, it is clear that the main alloying elements of all samples are Cu and Sn whereas Pb, Zn and Ni are considered to be impurities in the alloy composition. The percent of Cu content varies from 83.81 up to 95.11 and the Sn 4.18 up to 13.36. Through these analyses one can observe that the Sn contents show different values.

Lead is detected in minor concentrations in all samples. Only in two samples, ST.13-10 and ST.15-10, it is observed in a considerable amount, over 2%. Worth mentioning is that arsenic has been detected in low amounts and as a minor component (less than 1%) in all samples, while arsenic has been detected as a significant alloying element in many Iranian prehistoric copper alloys [1].

Generally, it is evident that the samples were made of a binary copper–tin alloy, and that other elements are impurities that entered the alloy during ore smelting and were not added deliberately.

According to the results of semi-quantitative chemical analysis, it is apparent that bronze vessels are produced by Cu–Sn or tin bronze alloy with a variable tin content and some metallic impurities. The variety of Sn content proves that the bronze alloy is not made by a controlled alloying process to reach a homogenous bronze composition by adding a distinct amount of tin to copper and melting them [12,13].