COMPOSITIONAL AND TYPОLOGICAL STUDY OF SOME ISLAMIC COPPER-BASED ALLOYS BRACELETS

ZIAD AL-AHMED AND SALEH SARI *
Yarmouk University, Irbid, Jordan

Abstract

This study is part of a large project devoted for the typological and analytical study of Islamic metal work turned up from excavations all over Jordan. The importance of the project stems from the fact that most studies conducted so far concentrated on the description of the surface and style and totally ignoring the intrinsic value of the studied objects.

In this part of the project, eight well preserved copper based bracelets from an Islamic site (Dohaleh in northern Jordan) have been analytically and typologically investigated using microscopy and Atomic Absorption Spectrometry (AAS).

The results of the compositional analyses reveal very significant information regarding the technical understanding of the Islamic metal smith of metal alloying and processing.

Introduction

Most research concerning Jordanian collections of ancient materials in general and ancient metalwork in particular is approached from a purely typological viewpoint. Most studies are purely descriptive and do not go beyond what is present on the surface of the studied objects. This approach ignores the intrinsic value of the
objects. In most cases questions regarding the source of the original materials of the object, the technological processes used by ancient man in its manufacture and its real use are left unanswered. This type of information is badly needed for the reconstruction of a detailed and coherent image about the human past activities and his technical knowledge.

The present authors believe that there should be a change in our approach of studying man's material remains. The adopted approach should have the ability of maximising the quantity and quality of the information which could be deduced from studying these remains. This could be achieved by taking advantage of the recent developments in scientific analysis by applying these sophisticated methods in studying and analysing artefacts. Therefore, the best approach is to look at the artefacts from both angles, typological and analytical. Both approaches must co-exist to maximise the amount and quality of the extracted information.

In this sense the combined approach will be used to study collections of Islamic metalwork made of various metals and alloys. The present study is part of a larger project devoted to the study of metals extraction, manufacturing and processing practised by the Muslim craftsmen in Jordan. This project aims at revealing the level of technical knowledge acquired by the Muslim metal smith and to fill the present gap in the analytical studies of Islamic metalwork where very little of such studies were done (Craddock, 1979, Allan, 1979).

Historical Background:

This study deals with eight copper alloy bracelets that have been recently uncovered at Dohaleh archaeological site in northern Jordan (see map). The ongoing excavations at this site have been conducted under the supervision of Dr. Sari of the Institute of Archaeology and Anthropology, Yarmouk University, Irbid, Jordan (Sari, 1991, 1992).

All the collected archaeological evidences from the site indicate a continuation of the occupation of the site from the early Roman period up to the Ottoman. The bracelets under investigation came from an Islamic cemetery (area C) that have been unearthed. Based on the stylistic and typological analysis of the excavated archaeological materials, especially pottery and coins, that have been turned up from the cemetery, the bracelets could be dated to the Ayyubid/Mamluk period (Sari, 1992).
Typological description of the objects:

The bracelets under study could be classified based on their surface decoration patterns into two main groups (see fig. (2)): Group I (Nos. 1-4) which are plainly decorated and group II (Nos. 5-8) which are undecorated. Below is the detailed description for each bracelet:

Group I (No. 1): copper based bracelet, open rounded shape, the surface is covered with a thin layer of green patina which consists mainly of basic copper carbonate (malachite). Mechanical cleaning reveals that the surface is decorated by three engraved parallel lines of dots.

Group I (No. 2): copper based bracelet, very good condition, open rounded shape, covered with a thin layer of green patina, decorated with five motifs, two symmetrical ones on each side of the bracelet with a different geometrical motif on the centre of the bracelet. In addition, engraved triangles and parallel lines are spread all over the body.

Group I (No. 3): copper base bracelet, open rounded shape, decorated by three patterns; two similar motifs, one at each end of the bracelet and one larger and geometrically different at the centre. The surface is covered with a heavy layer of green patina. The central shape is covered with a well preserved piece of textile. This is mainly due to the inhibition action of corrosion products of the biodeterioration processes. The textile piece could be interpreted as a piece of the winding sheet used to shroud the dead body before burial.

Group I (No. 4): copper based bracelet, open rounded shape, consists of four twisted metal sheets. The surface is covered with green patina with scattered bright and lustrous spots of cuprous chloride which are a strong indication of spreading bronze disease.

Group II (Nos. 5, 7, 8): all are copper based bracelets with an open rounded shape. No engraving or decoration was detected even after the surface was mechanically cleaned. All are small in size which suggests that they were worn by children.

Group II (No. 6): copper based bracelet with a closed rounded shape, covered with a thick layer of patina overlaid by a layer of concretions. Small in size like the others in the group with no decoration.

It is obvious from the inspection of the typology of the bracelets that they were roughly made and decorated. The sophistication of inlaying and decoration of Islamic
jewellery was not observed in the bracelets. This might be attributed to the socio-economic circumstances of the area at that time. That period was accompanied by wars and unrest due to the attacks by the Franks and the Mongols. Time of wars and unrest was accompanied with a deterioration in the jewellery production and decoration. However in the time of peace, manufacturing, processing and decoration of metals and jewellery flourished in Syria during the 13th and 14th centuries (Rice, 1965, p 137).

Experimental procedures:

(1)-Sampling:
Care was taken to obtain a representative samples of the studied objects. Therefore, surface corrosion products and surface metal were mechanically removed and discarded since these surface materials may have a composition which is different from that of the interior.

Fig. (1): Geographical map showing the location of Dohaleh archaeological site
Fig. (2): Photograph of the studied bracelets

To eliminate the differences in composition due to the inhomogeneity caused by segregation and coring of metal alloys upon casting and manufacturing, samples were taken by drilling deep into the different objects. Samples were taken with a portable hand-held mini drill. 1 mm tungsten carbide drill bits were used to avoid any contamination of the taken samples.
(2) Samples preparation:

Samples were prepared by a modified method of Huges et al. (1976). 10-25 mg of the copper alloy drillings was weighed to an accuracy of ± 0.01 mg using an analytical balance. The samples were then transferred to a 250 ml beaker. 25 ml of aqua regia (1 vol. of conc. HNO₃ and 3 vol. of conc. HCl) was added to each sample. The sample was then placed on a hot plate at 60°C until all the sample was completely dissolved. The sample was then removed from the hot plate and left to cool at room temperature. After that a further 1 ml of aqua regia and 10 ml distilled water were added. The samples were then transferred to a 25 ml Erlenmeyer flask and distilled water was added to the mark.

(3) Analysis by Atomic Absorption Spectrometry (AAS).

Atomic Absorption Spectrometry is an analytical technique used for the quantitative determination of most elements. It has a high degree of versatility, sensitivity and accuracy. For more details about theoretical principle, operation and fields of application of the technique, interested readers are referred to the literature (Hughes, 1976, Parker, 1965, Price, 1974, Perkin-Elmer, 1973).

The analysis were carried out using Perkin-Elmer Atomic Absorption Spectrometer model SP9 stationed at the Geology Department, Yarmouk University.

Elements analysed together with their detection limits and detection wavelengths are listed in table (1). The concentration of an element has been determined on a sample solution in terms of ppm (parts per million) of the element in solution and then converted to weight percentages in the original object by using the following equation:

\[
\text{% Wt of element in the original object} = \frac{C \times V}{10 \times W}
\]

Where:

- \( C \) = Concentration in ppm of element in solution.
- \( V \) = Volume of the original solution in ml.
- \( W \) = Weight of the taken sample in mg.

**Results and Discussion:**

The compositional analyses of the studied bracelets are listed in table (2). The analytical results show that the bracelets were made of brass (an alloy of copper and
zinc) with a large proportion of lead and a small quantity of tin. This type of alloys is commonly called leaded brass.

This type of ternary (3-metals) or quaternary (4-metals) alloys of copper, zinc, lead and tin were so common during and after the Roman period (Tylecote, 1962, pp 53-55). Before the Roman period the common additions used to form an alloy with copper were tin and lead (Craddock, 1978).

Brass was first introduced by Romans and they used it extensively at least from the time of Augustus (Craddock, 1978). The widespread use of brass in the Mediterranean area followed the collapse of the empire in the west and the consequent loss of the two principal tin-producing provinces of Britannia and Hispania. Therefore, it is not surprising that the Islamic metal smith inherited such type of alloying tradition. The few published analyses suggest that brass was the usual alloy before the tenth century AD. and almost the sole copper alloy after that with very few of tin bronze (Craddock, 1979, Allan, 1979, Barnes, 1973).

In order to throw light on the technical understanding and knowledge of metal alloying and processing acquired by the Muslim metal smith, the variation in the nature and percentages of the elements obtained by the compositional analysis should be fully discussed and explained. Questions such as : to what degree craftsmen sought to control their alloying processes and the resulted proportions of the alloying metals ? Was the additions of various elements deliberate or accidental ? should be answered.

Dependence of the brass composition on the manufacturing process:

The elemental analysis of any object in isolation will yield little more than a chemical composition. For meaningful conclusions to be drawn, results of such analysis must be related to the processes involved in the objects' manufacture and to the possible source of the original materials. Elemental analysis could also be used to assess the process used in the metal extraction and the subsequent refining processes (Tylecote and Boydell, 1978).

The zinc content of the bracelets largely varied and ranging from 8.5% to 13.6% as shown in table (2) and illustrated in figure (3). How could these percentages related to the manufacturing process used in producing brass by the Islamic metal smith ?
<table>
<thead>
<tr>
<th>Elements analysed</th>
<th>Detection limit in solution (ppm)</th>
<th>Wavelength used (nm)</th>
<th>Concentration range (ppm in solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.08</td>
<td>324.8</td>
<td>800-1250</td>
</tr>
<tr>
<td>Zn</td>
<td>0.01</td>
<td>213.9</td>
<td>1-10</td>
</tr>
<tr>
<td>Sn</td>
<td>1.7</td>
<td>224.6</td>
<td>10-150</td>
</tr>
<tr>
<td>As</td>
<td>0.5</td>
<td>193.7</td>
<td>1-50</td>
</tr>
<tr>
<td>Pb</td>
<td>0.08</td>
<td>217.0</td>
<td>10-55</td>
</tr>
<tr>
<td>Fe</td>
<td>0.04</td>
<td>248.3</td>
<td>5-50</td>
</tr>
<tr>
<td>Ni</td>
<td>0.04</td>
<td>232.0</td>
<td>10-50</td>
</tr>
<tr>
<td>Ag</td>
<td>0.02</td>
<td>328.1</td>
<td>2-10</td>
</tr>
<tr>
<td>Sb</td>
<td>0.35</td>
<td>217.6</td>
<td>0.5-10</td>
</tr>
<tr>
<td>Co</td>
<td>0.08</td>
<td>240.7</td>
<td>1-5</td>
</tr>
</tbody>
</table>

Data collected from Perkin Elmer AAS tables

Background correction applied to AAS analysis
### Table (3): Results of the elemental analysis of the bracelets.

<table>
<thead>
<tr>
<th>Number</th>
<th>% Cu</th>
<th>% Pb</th>
<th>% Zn</th>
<th>% Sn</th>
<th>% Ni</th>
<th>% Co</th>
<th>% Sb</th>
<th>% Ag</th>
<th>% As</th>
<th>% Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>74.30</td>
<td>10.2</td>
<td>9.2</td>
<td>3.70</td>
<td>0.02</td>
<td>0.017</td>
<td>0.007</td>
<td>0.004</td>
<td>0.006</td>
<td>0.082</td>
</tr>
<tr>
<td>2</td>
<td>72.20</td>
<td>13.6</td>
<td>8.6</td>
<td>4.34</td>
<td>0.07</td>
<td>0.004</td>
<td>0.006</td>
<td>0.006</td>
<td>0.005</td>
<td>0.277</td>
</tr>
<tr>
<td>3</td>
<td>70.32</td>
<td>12.3</td>
<td>10.4</td>
<td>4.00</td>
<td>0.03</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.277</td>
</tr>
<tr>
<td>4</td>
<td>75.40</td>
<td>11.3</td>
<td>8.9</td>
<td>2.30</td>
<td>0.16</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.277</td>
</tr>
<tr>
<td>5</td>
<td>77.70</td>
<td>9.0</td>
<td>7.4</td>
<td>3.50</td>
<td>0.07</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>0.277</td>
</tr>
<tr>
<td>6</td>
<td>73.30</td>
<td>9.8</td>
<td>12.4</td>
<td>2.70</td>
<td>0.09</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.277</td>
</tr>
<tr>
<td>7</td>
<td>74.40</td>
<td>9.4</td>
<td>11.3</td>
<td>2.90</td>
<td>0.05</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>0.277</td>
</tr>
<tr>
<td>8</td>
<td>71.80</td>
<td>8.5</td>
<td>15.1</td>
<td>3.20</td>
<td>0.04</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.277</td>
</tr>
</tbody>
</table>

47
Analysis of some early metal objects which pre-date the general introduction of brass detected several percent of zinc (Craddock, 1978, Halleux, 1973). The mechanism proposed by Craddock (1978) that these objects were made of a smelted zinc-rich copper ores could explain the presence of these small quantities of zinc in addition to other metals. However, the zinc content of the studied bracelets is too high to suggest such a method in producing the bracelets.

The other possible method of producing brass is by alloying metal zinc with copper. This type of alloying produces brass containing more than 30% of zinc with a very low iron concentration (Werner, 1972). This method of producing brass was first known in India (Craddock, 1981, pp. 1-32) and the obtained results suggest that this technique of producing brass was not practised by the Islamic metal smith despite that the Indian production centres were geographically quite close.

Due to the difficulty in isolating zinc from its ores, metallic zinc was not available for the metal smith in Europe or the Middle East until the nineteenth century (Craddock, 1981). The problem was that zinc boils at about 950 °C i.e. at a much lower temperature than any other common metal. In order to reduce it from its ores, it needs to be heated in contact with charcoal at 1000 °C which is above its boiling point. So that it comes off as a vapour and is promptly reoxidiseds and lost. Due to this difficulty zinc was alloyed with copper to produce brass by the direct addition of zinc ores to copper (Tylecote, 1962, pp 39-55 Tylecote, 1987, pp 28-44, Bayley, 1990, pp 7-27). This process is known as Cementation. This process was discovered in Anatolia at the end of the 2nd century BC, (Craddock, Burnet and Prestone, 1980) and persisted until well into the nineteenth century AD. Producing brass by the Cementation process was the common practice of the Roman metal smith and therefore it is not surprising that this knowledge was inherited by the Muslim metal smith.

Cementation process was first described in detail by Theophilus (Smith and Hawthorne, 1963) in the twelfth century AD. In the Cementation process, finely divided copper metal was mixed with zinc ore, normally zinc oxide (Calcined) or zinc carbonate (Calamine), and charcoal and put in a closed crucible. Based on the Islamic texts on brass making (Allan, 1979) and recent finds (Barnes, 1973), it would seem that the zinc oxide was produced by the calcination of zinc carbonate. Heating of the copper metal and zinc ore at around 1000 °C results in the reduction of the zinc ore to the vapour form of zinc which diffuses into the copper, forming brass.
Fig. (3): Histogram of the analysed bracelets showing the negative correlation between zinc and lead contents.

Laboratory experiments by Haeckel reported by Werner (1970, pp 138-140) demonstrate that the maximum zinc content at a working temperature of 1000 °C is 28%. This represents equilibrium between the zinc vapour in the sealed crucible and the zinc dissolved in the copper.

The zinc content of the analysed bracelets does not approach the equilibrium figure. This is mainly due to the presence of high percentages of lead and tin. The
presence of high levels of lead and tin lowers the melting point of the metal and consequently reduces the amount of zinc that could be absorbed. Tin reduces the zinc absorption in an amount equal to its percentage while the presence of lead reduces the zinc percentage twice of its percentage (Craddock, 1985). The wide variation of the zinc content as shown in figure (3) is an indication that the Cementation process used in the production of the bracelets was not carefully controlled. This might be due to the variations in the purity of the zinc ores used and in the reduction conditions and the subsequent refining and processing of the metal. However, it would not be easy to exert an accurate control over the process as in the production of tin bronze where tin was added as a metal. Therefore these variations are not altogether surprising.

The high percentages of lead present in the bracelets (fig. (3)) is a strong indication that the bracelets were made by casting. The presence of lead in the casting alloys has the advantage of facilitating castings by improving the fluidity of the metal and depressing its melting point (Craddock, 1979, Tylecote, 1962, pp 39-49, Bayley, 1990). The important question to be raised at this stage is whether the presence of lead was a deliberate addition by the Islamic metal smith or an accidental incorporation from a secondary source? I.e. Did the Islamic metal smith realise and understand the addition of lead for casting metals?.

In order to answer such a question all possible sources of lead in the bracelets should be examined and tested against the obtained results. Lead could come from different sources. Zinc ores always contain some lead, and if Calcined calamine was used then lead would present in the Cementation crucible. This could explain the presence of small amounts of lead and 5% of lead in brass probably represents the absolute maximum amount which could be originated from the zinc ores (Craddock, 1985). Small amounts of lead could also come from the copper ore and fluxes used in the smelting process. The large amounts of lead found in the bracelets (7.4-13.1%) demonstrate that lead addition was intentional and not a result of contamination from secondary materials.

It has been proved (Craddock, 1979, Tylecote, 1962 pp 34-44) that the maximum limit of lead content that improves the casting properties of the copper alloys is 2%. No further improvement occurs above this percentage. On the contrary, higher percentages of lead is detrimental. This is because lead is not soluble in copper and if the percentage of lead in the alloy is too high globules of lead appear and form lines of weakness when hammered (Craddock and Giiumia, 1988, pp 317-326).
The high percentages of lead found in the bracelets (7.4-13.1%) indicates that the Islamic metal smith was not aware of this fact or it might be a calculated risk in using a cheap metal (lead) as a dilutant for a more expensive metal (copper) for economical reasons. Other possible reason for the large additions of lead is that heavily leaded brass has a silvery appearance which is a relatively cheap imitation of silver jewellery.

Tin was found to be present in all of the analysed bracelets in small quantities (fig. (4). However the origin of these small amounts is not certain.

Due to the lack of tin in or even near the Islamic world, tin was not a common alloying element in the Islamic metal work. On the other hand zinc was readily available throughout the area especially in Iran and Anatolia.

The important point regarding tin is whether it was an intentional addition by the metal smith to produce a quaternary alloy of copper, zinc, lead and tin as suggested by Allan (1979) or was it an accidental addition from secondary materials. Tin, unlike lead, provides no noticeable improvements to the casting properties of the alloy. Its presence reduces the absorption of zinc by copper and therefore hindered the possibility of producing high quality brass. The low percentage of tin obtained in addition to its rarity make the deliberate addition of tin highly unlikely.

If tin was not intentionally added to the Cementation process then where did it come from? One suggestion is that tin may have been coming inadvertently with lead or with copper scraps (Craddock, 1979). Leaded casting brasses were made by adding to the Cementation process not only lead but also its own weight of scrap copper and bronze. Also scrap solder and pewter (lead tin alloy) might have been used as a source of lead.

Silver presents in low percentages (Ag% ranging from 0.59-0.96) in all the bracelets. This indicates that silver was not a deliberate addition by the metal smith. Silver probably came with lead since natural lead ores (especially galena) usually contain some silver and these ores were used in the ancient time for extracting silver by a process called cupellation (Tylecote, 1962, p.79).

Bracelet No. 2 contains an appreciable amount of antimony (Sb% = 3.61) which rises a question about the source of antimony since antimony was not a major alloying metal in that period. Antimony occurs in the copper sulphides ores and it should be
lost in the roasting of these ores to extract copper. There are examples of copper having such a high percentage of antimony due to the incompletion of the roasting process (Craddock, 1977). Therefore, we believe that this bracelet was made of copper extracted from a sulphide ore which was incompletely roasted.

**Fig. (4):** Comparison of the Sn (%) of the weight of different bracelets
Acknowledgements
The authors would like to express their appreciation to Dr. Ibrahim Dwiri, Mr Gazi Smadi, Mr. Wajih Yousuf and Mr Mustfa Naddaf of the Geology Department, Yarmouk University for their assistance in obtaining the AAS results.

A great measure of appreciation must go to the Deanship of Research and Graduate Studies Yarmouk University for providing the grant which supported this study.
References


Barnes, J. W., Ancient Clay Furnace Brass From Iran, Bulletin Of The Historical Metallurgy Group, 1973, 7(8), 17.


