



TRACING MANUFACTURING TECHNIQUE IN AN ARCHAEOLOGICAL THIN SHEET TUBE FROM TEPE SAGZABAD IN QAZVIN PLAIN, IRAN (1500-800 BC)

Mohammad Mortazavi¹, Ahmad Salehi Kakhki², Mohammad Ali Golozar³,
Hasan Tala'i⁴

^{1,2} *Faculty of Conservation, Art University of Isfahan, P.O.Box 1744, Iran.*

³ *Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran.*

⁴ *Department of Archaeology, University of Tehran, Tehran, Iran.*

Received: 09/03/2014

Accepted: 06/06/2014

Corresponding author: Mohammad Mortazavi (m.mortazavy@au.ac.ir)

ABSTRACT

Recent excavations in Tepe Sagzabad in Qazvin Plain, Iran, yielded some archaeological metal artifacts dating to the Early Iron Age. Among different metal fragments, a small tube was found. As a part of systematic analytical research, thin sheet tube was studied for elemental composition, manufacturing technique and deterioration mechanism using optical microscopy (OM), scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS) and Raman spectroscopy. The results of analyses showed that the tube has been made from a thin sheet Cu-Sn alloy. In addition, it was found that the tube was completely mineralized, and there was no sound metal remained in it. Corrosion of the tube was composed of a bilayer structure in which the original shape of the artifact has been preserved. Raman characterization of the corrosion products showed that the inner layer is composed mainly of cupric oxide (tenorite) beneath an outer cuprous oxide layer (cuprite) which has grown outward from the original surface. This is believed to be due to a corrosion phenomenon of bronze alloys known as "decuprification process". Moreover, microscopic investigation showed presence of elongated inclusions merely in the inner layer indicating both the manufacturing process and the limit of the original surface of the tube.

KEYWORDS: Archaeological Bronze, Sheet tube, SEM-EDS, Raman Spectroscopy, Sagzabad

1. INTRODUCTION

Archaeological objects are regarded as historical documents and aesthetic entities (Caple, 2000). Archaeological metal artefacts are of great importance to study the manufacturing techniques (Scott, 1991) and long-term corrosion phenomena (Robbiola *et al.* 1998; Piccardo *et al.* 2007). Technological information including materials (alloys) and methods have been the subject of studying evolution of metallurgy from ancient time (Thornton 2009). On the other hand, archaeometallurgical studies could be a subject of further investigation regarding cultural impacts of neighboring lands: Iranian Plateau, Mesopotamia and Eastern Mediterranean.

Moreover, most of metallic archaeological objects buried for a long-time are usually covered with corrosion products (Scott, 2002; Ingo *et al.* 2006; Oudbashi & Emami 2010; Schweizer, 1994; Chase, 1991). Corrosion studies on these metallic artefacts are performed with the aim of evaluating their stability (Bernard & Joiret, 2009) and tracing the original shape and inner markers which may have preserved in corrosion products. This is particularly the object regarding the copper-tin alloys (Piccardo *et al.* 2007; Robbiola *et al.* 1998; Chase, 1991; Cronyn 2004; Bertholon, 2007).



Figure 1. Sheet tube found during the excavation of Tepe Sagzabad (1500-800 BC)

The case study presented in this paper is a systematic analytical research performed on a small copper-based tube (Fig. 1 and 2) dated to the Early Iron Age (1500-800 BC) which was found during the excavation of Tepe Sagzabad (1997-1999) in Qazvin Plain,

north-central Iran (Tala'i, 1984). The aim is to investigate the manufacturing techniques and technological evidences.



Figure 2. Sheet tube found during the excavation of Tepe Sagzabad (1500-800 BC)

2. EXPERIMENTAL

The analytical studies carried out were based on optical microscopy, scanning electron microscopy combine with an energy-dispersive X-ray spectrometer (SEM-EDS) and Raman spectroscopy. In order to study the elemental composition and manufacturing technique, cross-section of the tube was taken using jeweler's saw. The sample was embedded in Buhler epoxy resin and polished using silicon carbide abrasive papers (up to 1200 grit). The final polishing was performed with diamond pastes up to 0.25 μm .

The sheet tube was heavily corroded and completely mineralized in such a way that the original shape was preserved in the corrosion products. Hence, it could provide clues for tracing manufacturing technique through corrosion products by microscopic investigation. BK-POL/BK-POLR optical microscope equipped with a Canon EOS Kiss X4 CCD camera and Breeze System image capture software was used to study the cross-section of the tub.

Layered structure in cross section was studied using scanning electron microscopy (SEM). In addition, morphology of the inclusions in the cross section was investigated using SEM. EDS was used to determine the elemental composition of different layers and inclusions in the microstructure. SEM-EDS analyses were carried out using the VEGA II TESCAN, Czech Repub-

lic. EDS: Rontec, Quantax/QX2, Germany in Razi Metallurgical Research Center, Tehran, Iran.

Moreover, Raman spectroscopy was performed on the cross-section of the tube to identify each layers of corrosion. Micro-Raman spectrometer equipment employed

was a LabRam HR600 (Jobin Horiba Scientific- France). The Raman spectra were measured with the following operational condition: laser excitation at 632.8 nm; 2-4 mW laser power; 100x objective; integration time 5s and ten accumulations.

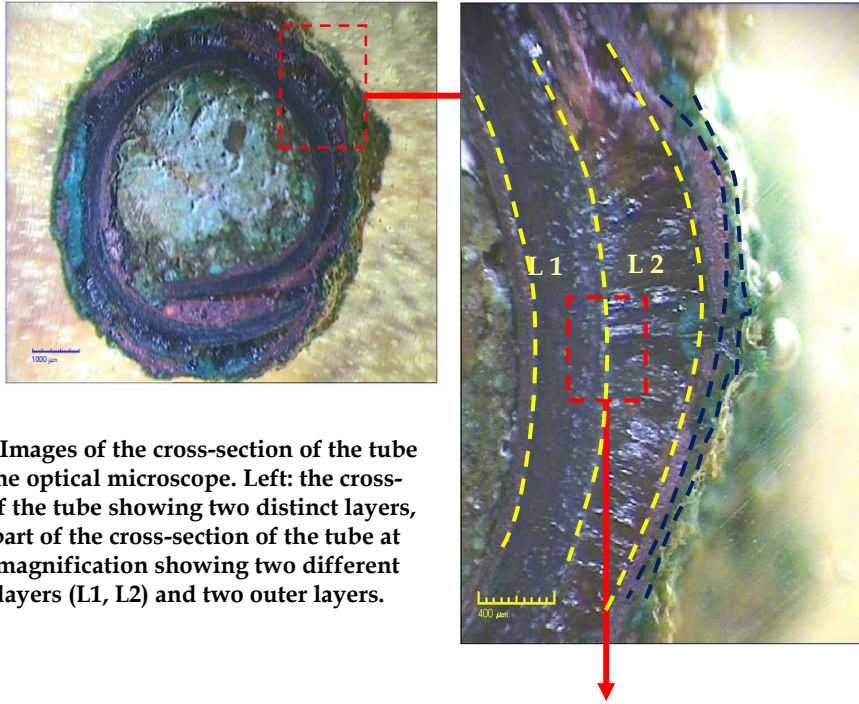


Figure 3. Images of the cross-section of the tube under the optical microscope. Left: the cross-section of the tube showing two distinct layers, Right: part of the cross-section of the tube at higher magnification showing two different inner layers (L1, L2) and two outer layers.

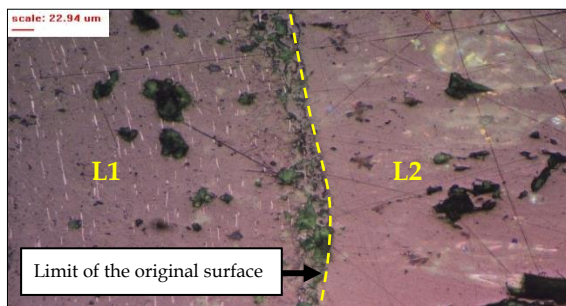


Figure 4. Microscopic image of boundary of two layers, L1 and L2, in cross-section. Note the presence of elongated sulfide inclusions individually in the inner layer (left part).

3. RESULTS AND DISCUSSION

Microscopic investigation by optical microscopy using 10x magnification clearly showed two distinct layers; L1 and L2. As tube was completely corroded, there was no sound metal in the cross-section. However, the inner layer (L1) with dark color and outer layer (L2) with pale red color

and columnar crystals of corrosion products in radial direction are clearly seen (Fig. 3). In addition, microscopic study at high magnifications illustrated the presence of elongated inclusions only in the the inner layer (L1) but not in the outer layer (L2) (Fig. 4).

Double layer structure was also identified in the SEM micrographs (Fig. 5).

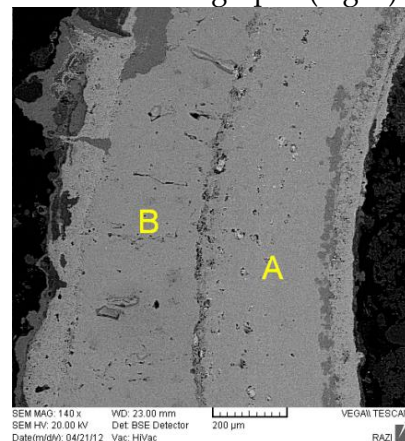


Figure 5. SEM-BSE image: detail of the cross section of the tube showing two layers and zones which have been analyzed.

EDS analyses carried out on the inner and outer layers showed copper-tin alloy as material used for tube manufacturing. Analysis the inner layer showed about 61% by weight of copper and 7% by weight of tin. High amount of Cl (30 wt%) was also identified in the inner layer (Table 1).

In contrast, analysis of outer layer showed no Sn in the composition. High amount of Cl was similar to that identified in the inner layer. Moreover, EDS analyses of inclusions showed copper, tin, chlorine, and high amount of sulfur (Fig. 6 and Table 1).

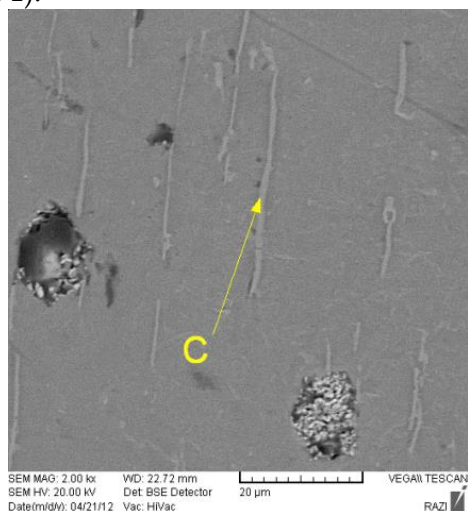


Figure 6. SEM-BSE image showing detail of inclusion presence in the inner layer

Table 1. Composition of sheet tube (wt%) in cross section as obtained by SEM-EDS

Sample No.	Cu	Sn	Cl	S	Fe	Pb
Zone A (inner layer, L1)	61.52	6.96	30.07	1.00	0.46	-
Zone B (outer layer, L2)	65.84	-	32.96	-	-	1.20
Zone C (Inclusions)	75.64	2.86	7.10	14.41	-	-

In addition, the cross section of sample was scanned and elemental maps were produced. SEM-EDS elemental mapping across the cross section clearly showed two

layers having clear differences in tin content (Fig. 7). Results obtained demonstrated the inner layer having appreciable amount of tin in contrast with the outer layer (Fig. 7A and 7C). It is particularly noticeable at the point where two ends of the sheet overlapped which four layers including Cu-Sn and Cu layers alternatively could be seen in the elemental map (Fig. 7B and 7D).

Although the Raman technique is insensitive to most pure metals and alloys, it is well suited to the identification and study of corrosion and patina layers on metal artefacts (Smith & Clark 2004: 1149). The nature of the corrosion layers was investigated by Raman micro-spectrometry (Fig. 8).

Examination of the cross-sectioned tube showed that the artefact has been made by rolling or cold-working a thin metal sheet (Thornton 2009: 308; Malek Shahmirzadi 1979: 59; Martinon-Torres *et al.* 2007: 199). The analyses showed that copper and tin are the main components of the alloy. Although copper-tin alloys first appeared in Iranian Plateau (Frame 2010: 1705), Mesopotamia and Anatolia during the third millennium BC (Kassianidou & Knapp 2005: 224), it was around the 2nd millennium BC which the tin bronze mostly replaced the copper arsenic alloys (De Ryck *et al.* 2005: 262; Eaton & Mckerrell 1976: 147; Lechtman & Klein 1999: 497).

In addition, SEM and OM images clearly showed heavily elongated inclusions along the cross-section of the tube. Sulfur compound inclusions (Cu-Fe-S) elongated along the cross-section of the artifact indicate the effects of heavy hot/cold working during the thin sheet manufacturing process (Frame 2010; Scott 1991; Artioli 2010). Moreover, presence of sulfide inclusions indicates the use of sulfidic ore sources. Iran, Anatolia, Oman and Cyprus have been identified as regions in which most of the copper deposits consist of sulfidic ores (De Ryck *et al.* 2005: 261; Kaufman 2013: 684).

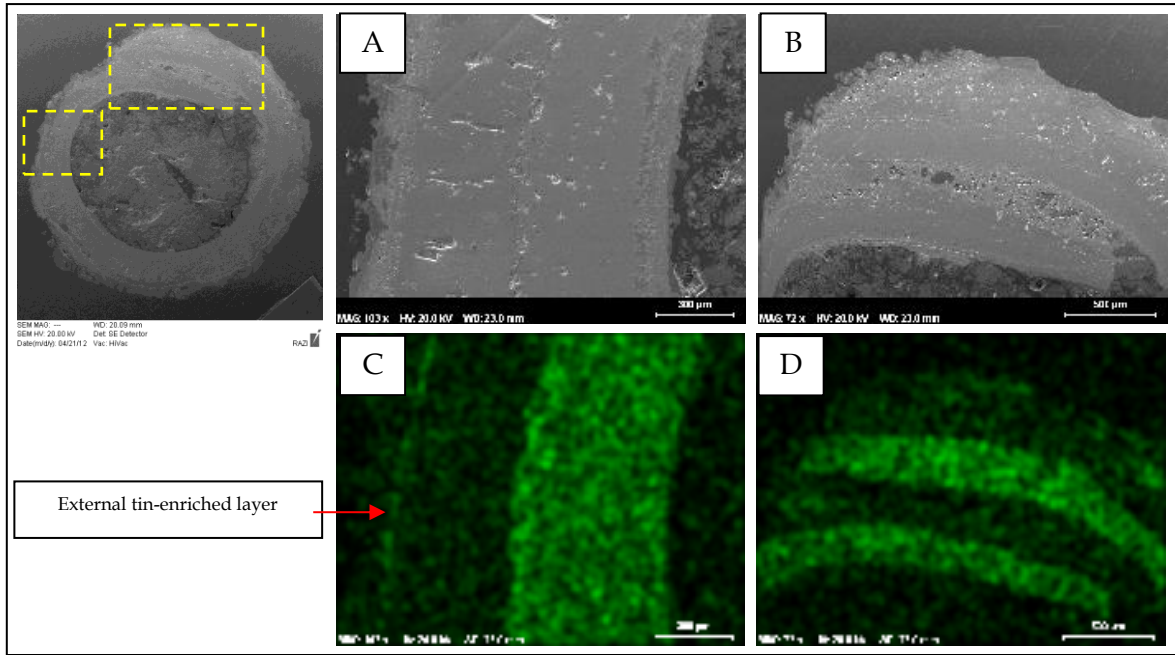


Figure 7. SEM micrographs and elemental maps of the cross-section of the tube showing differences in the tin content in two layers; Right figures (B and D) show four alternative layers where two ends of sheet overlapped.

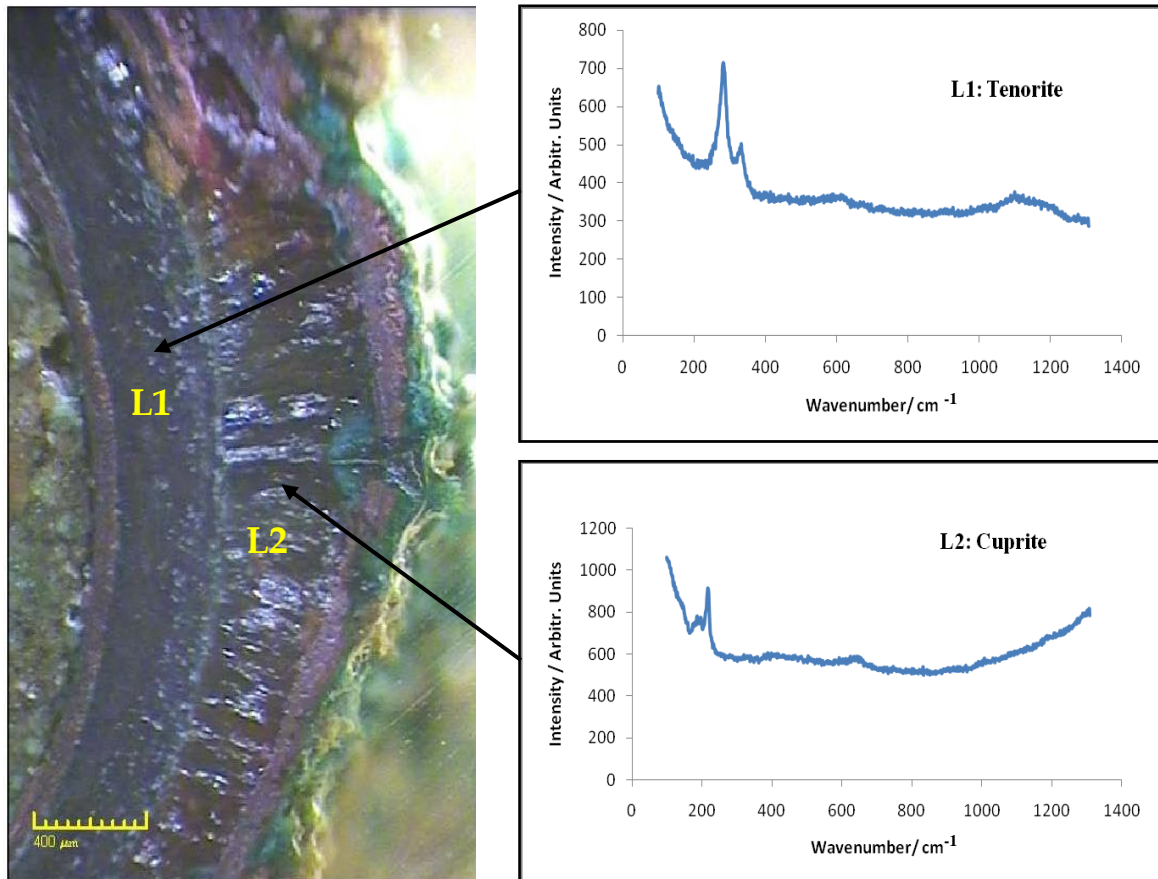


Figure 8. The Raman spectra obtained from each of the corrosion layers. The upper spectrum corresponds to tenorite (L1) and the lower spectrum corresponds to cuprite (L2).

In spite of the complete mineralization, the original shape of the artifact was preserved in the corrosion products. Locating the limit of the original surface is a major point for any study concerning corroded artefacts (Bertholon, 2007: 35). In this respect, internal markers such as inclusions remained from metallurgical structure are indications which can be used to locate the limit of the original surface between the corrosion layers (Neff *et al.* 2004: 2). Corrosion layers above the original surface are clearly recognizable, because they have no such internal structures. Accordingly, boundary between inner dark corrosion layer (L1) containing sulfide inclusions, and outer pale red (L2) is the limit of the original surface. On the other hand, the original thickness of the bronze sheet is given by L1 layer thickness.

A chemical feature of corrosion of the artifact is depletion of tin in the outer layer with respect to the inner dark layer. This phenomenon can be explained by copper selective dissolution inducing its removal from the alloy, known as "decuprification process" (Robbiola & Portier 2006: 5; Alberghina *et al.*, 2011: 136; Bernard & Joiret, 2009: 2). On the other hand, tin enrichment in the inner layer can be related to the low solubility and high stability of tin species (Alberghina *et al.*, 2011), allowing the tin ions to remain in their original location (i.e. in the inner dark corrosion layer (L1)).

Outer and inner corrosion layers (L1 and L2) were identified by Raman spectroscopy (Fig. 8). Raman micro-spectroscopy performed on the inner layer corresponds to cupric oxide (tenorite) with the bands at 294, 338 and 611 cm^{-1} (Mattei *et al.*, 2008: 304). Tenorite (CuO) is rare component of natural patinas which indicates that the object has been subjected to heating before or during burial (Scott 2002). However, converting the original artefact's thickness (L1) into tenorite is slightly confusing. The Raman spectra obtained from the outer corrosion layer (L2) corresponds to cuprous oxide (cuprite) (Bouchard & Smith 2003: 2259; Piccardo *et al.* 2007: 248; Mathis *et al.* 2007: 229). Cuprite (Cu_2O) is a com-

mon corrosion product found in the majority of buried bronze artifacts as patina (Scott 2002; Robbiola *et al.* 1998).

It is noteworthy that there are another two thin corrosion layers above the outer layer (L2); a red cuprite beneath a green copper corrosion deposits (Cu species) (Fig. 3). Elemental map of the cross-section of the tube showed high amount of Sn in the external red cuprite layer under the green corrosion layer (it can be seen as a line in the left side of the Fig. 7C). According to the presence of a tin-enriched area far from the original surface (inner bulk alloy) it can be assumed that corrosion process of the artefact consists of two steps:

- (i) an initial step of the alloy dissolution by which Type 1 corrosion structure is introduced. Hypothesis proposed by Robbiola *et al.* (1998) is likely to occurred giving such structure;
- (ii) in the second step, the presence of fissures parallel to the interface metal/corrosion layer in contact with underlying metal (Robbiola *et al.* 1988) or of cleavages at some corrosion interface in the location of the original surface (Bertholon 2001) while migration process through the corrosion layers take places, with anions inward, can lead to the formation of new corrosion products at the external layers/alloy interface. Consequently, primary tin-enriched layer moves outward (Fig. 9). At the end of this stage, inward migration of chloride anions (from environment to the bulk alloy) leads to implementation of chloride compounds occurs up to induce full metal corrosion; as in some parts, under the red cuprite, bright green chloride species can be seen (left side of the cross-section in figure 3).

In this paper, a deviation from the Type 1 model suggested by Robbiola *et al.* (1998) has been proposed. Although three-layer structure resembled Type 2 corrosion structure, the original shape of the object was left untouched, which is one of the main features of the Type 1 corrosion.

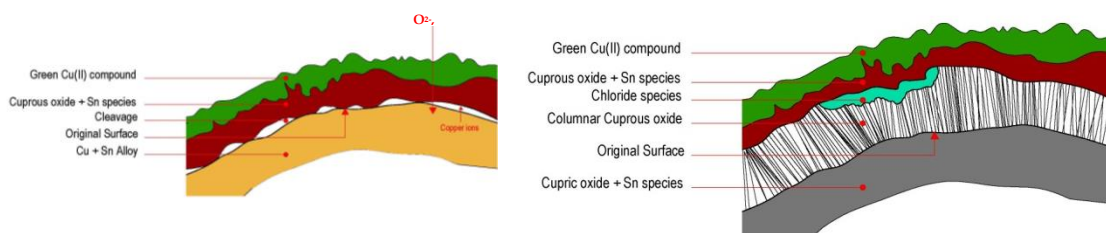


Figure 9. Schematic representation of corrosion mechanism in the tube, left: initial stage of the corrosion with cleavage at the location of original surface, right: final stage of the corrosion with growing columnar cuprite beneath the primary corrosion layers.

4. CONCLUSION

In this research it was found that the Sagzababd's tube has been manufactured by rolling or cold-working a thin sheet of Cu-Sn alloy. Although the tube was completely mineralized, presence of some inner markers (elongated sulfide inclusions) preserved in the corrosion layers could be used for tracing the manufacturing technique. Sulfide inclusions implies sulfide ores have been the main source of copper. In addition, a deviation from normal types

of corrosion structures was identified in the tube which interferes with the location of the original surface between the corrosion layers. Preservation of the original shape and size of the tube while high amount of chloride is present is of great importance in the conservation cultural copper-tin artefacts. Result presented here showed that it is possible tracing manufacturing technique in corrosion products and completely mineralized artefacts.

ACKNOWLEDGEMENTS

Every author is in debt to people who share ideas, concepts, and opinions. Dr. Luc Robbiola (Laboratoire de métallurgie structurale, ENSCP, France), Dr. Omid Oudbashi (Faculty of Conservation, Art University of Isfahan, Iran), Dr. Parviz Hoaloohei (Dipartimento di Scienze Della Terra, Ferrara, Italia) for providing important information. The authors wish to thank B. Rahmani, responsible for Razi Metallurgical Research Center, Tehran, Iran, for his assistance in SEM analyses presented here. Finally, the authors would also like to thank Institute of Archaeology of Tehran University.

REFERENCES

- Alberghina, M.F. Barraco, R. Brai, M. Schillaci, T. and Tranchina, L. (2011) Integrated Analytical Methodologies for the Study of Corrosion Processes in Archaeological Bronzes. *Spectrochimica Acta Part B: Atomic Spectroscopy*, Vol. 66, Issue 2, 129-137.
- Artioli, G. (2010) *Scientific Methods and Cultural Heritage: An introduction to the application of materials science to archaeometry and conservation science*, Oxford University Press, United Kingdom.
- Bernard, M.C. and Joiret, S. (2009) Understanding Corrosion of Ancient Metals for the Conservation of Cultural Heritage. *Electrochimica Acta*, Vol. 54, Issue 22, 5199-5205.
- Bertholon, R. (2001) Characterization and Location of Original Surface of Corroded Metallic Archaeological Objects. *Surface Engineering*, Vol. 1, No. 3, 241-245.
- Bertholon, R. (2007) Archaeological metal artefacts and conservation issues: long-term corrosion studies. In: *Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction of Long-Term Behaviour*, P. Dillmann, G. Beranger, P. Piccar-

- do, and H. Matthiessen, (eds.), Woodhead Publishing Limited and CRC Press LLC, Institute of Materials, Minerals & Mining, Cambridge, England, 31-40.
- Bouchard, M. and Smith, D.C. (2003) Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol. 59, Issue 10, 2247-2266.
- Caple, C. (2000) *Conservation Skills: Judgment, Method and Decision and Making*, Routledge, London.
- Chase, W.T. (1991) Chinese Bronzes: Casting, Finishing, Patination, and Corrosion. In: *Ancient & historic metals: conservation and scientific research*, D.A. Scott, J. Podany, and B.B. Considine, (eds.), J. Paul Getty Museum and the Getty Conservation Institute, Los Angeles, 83-117.
- Cronyn, J.M. (2004) *The Elements of Archaeological Conservation*, Taylor & Francis e-Library, London.
- De Ryck, I. Adrians, A. and Adams, F. (2005) An Overview of Mesopotamian Bronze Metallurgy during the 3rd Millennium BC. *Journal of Cultural Heritage*, Vol. 6, Issue 3, 261-268.
- Eaton, E.R. and Mckerrell, H. (1976) Near Eastern Alloying and some Textual Evidence for the Early Use of Arsenical Copper. *World Archaeology*, Vol. 8, Issue 2, 169-191.
- Frame, L. (2010) Metallurgical Investigations at Godin Tepe, Iran, Part I: The Metal Finds. *Journal of Archaeological Science*, Vol. 37, Issue 7, 1700-1715.
- Ingo, G.M. de Caro, T. Riccucci, C. and Khosroff, S. (2006) Uncommon Corrosion Phenomena of Archaeological Bronze Alloys. *Applied Physics A - Materials Science & Processing*. Vol. 83, Issue 4, 581-588.
- Kassianidou, V. and Knapp, A.B. (2005) Archaeometallurgy in the Mediterranean: the Social Context of Mining, Technology, and Trade. In: *The Archaeology of Mediterranean Prehistory*, E. Blake and A.B. Knapp (eds.), Blackwell Publishing Ltd., UK, 215-251.
- Kaufman, B. (2013) Copper Alloys from the 'Enot Shuni Cemetery and the Origins of Bronze Metallurgy in the EB IV-MB II Levant. *Archaeometry*. Vol. 55, Issue 4, 663-690.
- Lechtman, H. and Klein, S. (1999) The Production of Copper-Arsenic Alloys (Arsenic Bronze) by Cosmelting, Modern Experiment, Ancient Practice. *J. Archaeological Science*, Vol. 26, Issue 5, 497-526.
- Malek Shahmirzadi, S. (1979) Copper, Bronze and their Implementation by Metalsmiths of Sagzabad Qazvin Plain, Iran. *AMI*, Vol. 12, 49-66.
- Martinon-Torres, M. Rojas, R.V. Cooper, J. and Rehren, T. (2007) Metals, microanalysis and meaning: a study of metal objects excavated from the indigenous cemetery of El Chorro de Mai'ta, Cuba. *Journal of Archaeological Science*, Vol. 34, Issue 2, 194-204.
- Mathis, F. Salomon, J. Pages-Camagna, S. Dubus, M. Robcis, D. Aucouturier, M. Descamps, S. and Delange, E. (2007) Corrosion patina or intentional patina: contribution of non-destructive analyses to the surface study of copper-based archaeological objects. In: *Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction of Long-Term Behaviour*, P. Dillmann, G. Beranger, P. Piccardo, and H. Matthiessen, (eds.), Woodhead Publishing Limited and CRC Press LLC, Institute of Materials, Minerals & Mining, Cambridge, England, 219-238.
- Mattei, E. de Vivo, G. De Santis, A. Gaetani, C. Pelosi, C. and Santamaria, U. (2008) Raman spectroscopic analysis of azurite blackening. *Raman Spectroscopy*, Vol. 39, Issue 2, 302-306.

- Neff, D. Reguer, S. Bellot- Gurllet, L. Dillmann, P. and Bertholon, R. (2004) Structural characterisation of corrosion products on archaeological iron: An integrated analytical approach to establish corrosion forms. *Raman Spectroscopy*, Vol. 35, Issue 8-9, 739-745.
- Oudbashi, O. and Emami, S.M. (2010) A Note on the Corrosion Morphology of some Middle Elamite Copper Alloy Artefacts from Haft Tappeh, South-West Iran. *Studies in Conservation*. Vol. 55, No. 1, 20-25.
- Piccardo P. Mille B. and Robbiola L. (2007) Tin and copper oxides in corroded archaeological bronzes. In: *Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction of Long-Term Behaviour*, P. Dillmann, G. Beranger, P. Piccardo, and H. Matthiessen, (eds.), Woodhead Publishing Limited and CRC Press LLC, Institute of Materials, Minerals & Mining, Cambridge, England, 239-262.
- Robbiola, L. and Portier, R. (2006) A global approach to the authentication of ancient bronzes based on the characterization of the alloy-patina-environment system. *Journal of Cultural Heritage*, Vol. 7, Issue 1, 1-12.
- Robbiola, L. Blengino, J-M. and Fiaud, C. (1998) Morphology and Mechanism of Formation of Natural Patina on Archaeological Cu-Sn Alloys. *Corrosion Science*, Vol. 40, Issue 12, 2083-2111.
- Robbiola, L. Queixalos, I. Hurtel, L.P. Pernot, M. and Volfovsky, C. (1988) Etude de la corrosion de bronzes archeologiques du Fort-Harrouard: alteration externe et mecanisme d'alteration stratifiee. *Studies in Conservation*, Vol. 33, No. 4, 205-215.
- Schweizer, F. (1994) Chemistry and the Conservation of Archaeological Metals. *The Science of the Total Environment*. Vol. 143, Issue 1, 127-129.
- Scott, D.A. (1991) *Metallography and Microstructure of Ancient and Historic Metals*, The Getty Conservation Institute, Los Angeles.
- Scott, D.A. (2002) *Copper and Bronze in Art: Corrosion, Colorant, Conservation*, The Getty Conservation Institute, Los Angeles.
- Smith, G.D. and Clark, R.J.H. (2004) Raman microscopy in archaeological science. *Journal of Archaeological Science*, Vol. 31, Issue 8, 1137-1160.
- Tala'i, H. (1984) Notes on Bronze Artifacts at Sagzabad in Qazvin Plain, Iran, Circa 1400 B.C. *Iranica Antiqua*, Vol. 19, 31-42.
- Thornton, C.P. (2009) The Emergence of Complex Metallurgy on the Iranian Plateau: Escaping the Levantine Paradigm. *World Prehistory*, Vol. 22, Issue 3, 301-327.