Chapter from the book *Copper Alloys - Early Applications and Current Performance - Enhancing Processes*

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1. Introduction

The history of metals and metallurgy is rooted in the history of civilizations as the "Archaeometallurgy" and has been a subject of great interest for over a century. Due to the relatively good preservation of metallic goods and the modern values related to metals, metal artefact typologies often served as the very basis for prehistoric sequences during the late 19th and early 20th centuries. In many ways, it was V. Gordon Childe who placed metallurgical technology at the front, arguing as he did for the roles of "itinerant metal smiths" and bronze production in the rise of social elites and complex societies. Childe was also one of the first to systematically argue for the transmission of metallurgy from the Near East to the Eurasia (Thornton & Roberts, 2009). On the other hand, many of the artefacts which excavated, as well as some of the metallurgical talent being practiced are standing examples that depict the superior metallurgical skills used by human. Archaeometallurgical investigations can provide evidence about both the nature and level of mining, smelting and metalworking trades, and support understanding about structural and technical evidences. Such evidence can be essential in understanding the economy of a settlement, the nature of the industry and craft, the technological capabilities of its craftsmen as well as their cultural relations. In order to achieve such data, it is obvious that archaeometallurgical discipline has considered at each stage of archaeological and historical investigations in the field of ancient metal working.

The development of metallurgy on the Iranian Plateau has been a topic of interest to both archaeologists and scientists for many years because of the remarkable history of the metallurgical activities in Iran (such as usage of native copper in the 7th millennium BCE and smelting of copper ores by the late 6th millennium BCE) and concerned the wide variety of the technologies, compositions, etc. Indeed, the rich and old history of the Iranian Plateau and the huge metallurgical and metal working remnants spread in various forms and different parts of this region have been an important source for archaeological and archaeometallurgical studies for many years, especially during the last decade (e.g., Arab & Rehren, 2004; Pleiner, 2004; Thornton & Rehren, 2007).
A significant number of prehistoric sites have been excavated and uncovered, especially during the second half of the 20th century in Iran. Many of them yield valuable information concerning ancient metallurgy and metal working in the Iranian plateau during prehistoric period. Various metal artefacts, moulds, slags, crucibles and other tools and materials have been recovered belonging to prehistoric metalworkers from a series of excavations in different geographical regions of Iran (Figure 1). These archaeological finds and their location in Iran have created information and materials to be studied in relation to different aspects of ancient Iranian metallurgy.

Fig. 1. Approximate location of important metallurgical sites mentioned in the text.

Ancient artefacts made by copper and its alloys belonging to prehistoric period, from the 7th millennium BCE (Thornton, 2009a) down to the 1st millennium BCE (Overlaet, 2006), discovered from different sites, are evidences for the ancient metallurgy of copper and copper alloys in Iran.

In the field of archaeometallurgical studies, there are many reports and papers about study of ancient ore mining, slags and other metallurgical remains, artefacts and so on between various archaeological investigations about Iran; such as works on Tappeh Yahya (Tepe Yahya) in southeast Iran (Heskel & Lamberg-Karlovsky, 1980; Heskel & Lamberg-Karlovsky 1986; Thornton et al., 2002; Thornton & Ehler, 2003; Thornton & Lamberg-Karlovsky, 2004);
Bronze in Archaeology: A Review of the Archaeometallurgy of Bronze in Ancient Iran

Tappeh Hisar (Tepe Hissar), Northern Iran (Thornton 2009b); Godin Tappeh (Godin Tepe) (Frame, 2007) and Tel-i Iblis (Frame, 2004); Luristan Bronzes (e.g., Oudbashi et al., in Press; Fleming et al., 2005; Fleming et al., 2006; Moorey, 1964, 1969; Birmingham et al., 1964); Haft Tappeh (Haft Tepe), southwest Iran (Oudbashi et al., 2009); and ancient slags from Meymand, Kerman, southeast Iran (Emami & Oudbashi, 2008).

The aim of this paper is to review copper archaeometallurgy in Iranian Plateau, with a special regard to bronze (Cu-Sn) technology in prehistoric period (until mid-1st millennium BCE). Also, results of a comparative study on copper and bronze metallurgy in two ancient sites from western and southwestern parts of Iran are presented.

2. Chronology of Iran prehistory

Iran is one of the oldest areas with evidence for human life and settlement. There are many witnesses from human activities in Iranian Plateau from many ages. Human settlement starts in Iran from Paleolithic age and may belong to middle Paleolithic tradition (Table 1). We cannot be certain when the Middle Paleolithic began in Iran, but it has ended before 30,000 years ago. Also there are some remains of human living from upper Paleolithic period (terminated about 17,000 years ago) and terminal Paleolithic (terminated about 10,000 years ago) in different areas of Iranian Plateau (Hole, 2008). After that, the Neolithic age has been happened about 10,000 years ago by starting and combination of agriculture (wheat, barley, lentils) and the raising of livestock (goats, sheep, cattle, pigs), formed the basis of the agricultural economy that has lasted until today and spread throughout the world.

This ended about 6500-7000 years ago. The earliest Neolithic occurred before the use of hand-made, chaff-tempered pottery which appeared around 8,500 B.P. The Neolithic ends with the appearance of new styles of pottery, generally with designs painted in black on a buff background (Hole, 2004). The next steps are the ages of metals, which are: the Chalcolithic (copper), Bronze, and Iron Ages. In Near Eastern archaeology, the Chalcolithic now generally refers to the “evolutionary” interval between two “revolutionary” eras of cultural development: the Neolithic, during which techniques of food production and permanent village settlement were established, and the Bronze Age, during which the first cities and state organizations arose (Henrickson, 1992a, 1985). In Iran the Chalcolithic dates between about 5500-3300 BCE and smelting of copper ores and casting metallic copper artefacts has been started in this period. During and after the Chalcolithic age, the usage of metal and various aspects of metallurgical technology developed (Tala'i, 2008b). As a result for developing human culture and technology, a period observed in which the rise of trading towns in Iran has been occurred, from ca. 3300 BCE to the beginning of the Iron Age, ca. 1500 BCE, that has been named as Bronze Age. As a metallurgical phenomenon, first observations about application of bronze (Cu-Sn) alloy have been occurred in early Bronze Age (Dyson Jr. & Voigt, 1989). The last step of Iran prehistory is the Iron Age. In Iran the term Iron Age is employed to identify a cultural change that occurred centuries earlier than the time accorded its use elsewhere in the Near East, and not to acknowledge the introduction of a new metal (Iron) technology. The Iron Age has been dated about 1500-550 BCE and classified in three levels: Iron Age I, II and III. Iron artefacts, in fact, were not be widespread in Iran until the 9th century BCE (the cultural period labeled Iron Age II), centuries after the phase designated as Iron Age I came into existence (Muscarella, 2006; Overlaet 2005). After Iron Age III, the Iranian Plateau entered to Ancient Persian dynasties, started with Achaemenids (550-330 BCE) and ended with Sasanians (240-641 AD).
<table>
<thead>
<tr>
<th>Period</th>
<th>Categories</th>
<th>Date*</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paleolithic</td>
<td>Lower</td>
<td>N.D.**</td>
<td>Early Stone Tools, Hunting, Cave Dwelling, Fire Discovery, No Evidence of &quot;Art&quot;</td>
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<td></td>
<td>Middle</td>
<td>N.D.-30000</td>
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<td>Upper</td>
<td>30000-17000</td>
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<td>Terminal</td>
<td>17000-10000</td>
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<td>Acercamic</td>
<td>8000-7300</td>
<td>Introduction of Agriculture, Livestock and Villages, Fine Stone Tools, Early Potteries</td>
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<td></td>
<td>Ceramic</td>
<td>7300-5500</td>
<td>Early Pottery, Early Towns, Long-Distance Trade</td>
</tr>
<tr>
<td>Chalcolithic</td>
<td>Early</td>
<td>5500-5000</td>
<td>Progress in Agriculture, Permanent Villages, Widespread Painted Potteries, Advanced Pottery Kilns</td>
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<td></td>
<td>Middle</td>
<td>5000-3800²</td>
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<tr>
<td></td>
<td>Late</td>
<td>3800-3300</td>
<td></td>
</tr>
<tr>
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<td>Early</td>
<td>3000-2200</td>
<td>Painted Pottery, Early Towns, Long-Distance Trade</td>
</tr>
<tr>
<td></td>
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<td>2200-1800</td>
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<td>Late</td>
<td>1800-1500</td>
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<td>Iron Age</td>
<td>I</td>
<td>1500-1000</td>
<td>Local Traditions, Special Cemeteries, Grey Pottery</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1000-800</td>
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<td></td>
<td>III</td>
<td>800-650</td>
<td></td>
</tr>
<tr>
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<td>Proto-Elamite</td>
<td>3200-2800</td>
<td>Appearance of Writing (Proto-Elamite), First Dynasty in Iran, Under Influence of Mesopotamia, Significance Architecture, Seals, Cuneiform Inscriptions</td>
</tr>
<tr>
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<td>Old Elamite</td>
<td>2200-1500</td>
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<td>Middle Elamite</td>
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<td>Neo Elamite</td>
<td>1000-640</td>
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* The Paleolithic dates are before present and from Neolithic afterward, the dates are presented as BCE.
**N.D.: Not Determined.
1 Ceramic Neolithic doesn’t start in Northern and Eastern Iran until much later (ca. 6500-6000 BCE).
2 This date is related to Zagros Highlands in Iranian Plateau, Please see: Henrickson, 1992b.

Table 1. A diagram showing chronology, characteristics and metallurgical events of Iranian Prehistory.
On the other hand, the plain of Khuzestan in the southwest Iran played a major role with the origin of urban societies in the Middle East besides Mesopotamia, which called Elam. The earliest evidence mentioning the country of Elam is from Mesopotamia and belongs to the 3rd millennium BCE. The Elamite region was not restricted to the plain of what is Khuzestan today but included wide parts of the Zagros Mountain to the North and East, as well as the region of Fars. Chogha Zanbil (Dur Untash), Haft Tappeh and Susa are the main cities that have been discovered from Elamite civilization. The Elamite period has divided to four specific categories: Proto, Old, Middle and Neo Elamite. This period is between last 4th/early 3rd millennium BCE and mid of 1st millennium BCE (Mofidi Nasrabadi, 2004; Potts, 1999).

3. Copper metallurgy in prehistoric Iran

3.1 Native copper

Copper is one of the most useful metals, and probably is the first metal that has been used for manufacturing different tools and artefacts. The characteristics of copper caused to use it for making jewelry in middle of Neolithic period. First application of copper to use as primary tools comes back to about 10 thousand years ago in the Near East and namely Iranian Plateau. It has already been mentioned that the first metal objects appear in southwest Iran, Deh Luran plain at the base of the Zagros Mountains which lies on a traditional route between Mesopotamia and the Susiana plain (Pigott, 2004a).

In fact, the first usage of copper for making an artefact in Iran may comes from the Neolithic site in southwestern Iran, namely Ali Kosh, where one piece of rolled bead of native copper has been found (Figure 2) (Smith, 1967; Moorey, 1969; Pigott, 2004a; Thornton, 2009a). This is recently dated to the late 8th/early 7th millennium BCE (Hole, 2000; Thornton, 2009a). Also, some witnesses about early copper finds have observed in Tappeh Zaqeh (North central Iran) and Choqa Sefid (Western Iran) (Pernicka, 2004; Bernbeck, 2004). Analyses of these metal artefacts have revealed that all were made of native copper (like Ali Kosh) with the application of heat treatment (annealing) on metal between various deformation steps in order to avoid work-hardening (Pernicka, 2004). Of course, implementation of metal usage occurred much later in the early-mid 6th millennium BCE, when native copper artefacts were utilized consistently in various parts of the Iranian Plateau such as Tal-i Mushki archaeological site in Marvdasht, southern Iran (Moorey, 1982; Thornton, 2009a).

Fig. 2. a) Native copper rolled bead from Ali Kosh Neolithic site, western Iran (mid 7th millennium), b) Polished cross-section of the copper bead. Metal is corroded but the resulting corrosion products have preserved its original shape (Pigott, 2004a; Smith, 1967).
3.2 Copper casting and smelting

It has been assumed that the melting and casting native copper may have been the early stage of pyrometallurgy before ores smelting (Wertime, 1973). The first clear evidence of copper casting is distinguished in late 5th/early 4th millennium BCE (e.g., Level III at Sialk, central Iran) (Moorey, 1969). The 5th millennium BCE on the Iranian Plateau witnesses the transition from the use of pure native copper to the smelting of copper ores chosen for their natural impurities such as arsenic (Thornton et al., 2002). At the same time metal is more commonly used for tools previously made by bone and stone (Moorey, 1969). Arsenic has found even in first smelted copper artefacts and even earlier in native copper objects as accidental alloying element or impurity (Thornton 2009a). Although, the arsenical copper production may assume more as an important stage of casting process than producing an alloy (Tala'i, 2008b; Tala'i, 1996).

The Cu, As-bearing minerals contained in the native copper are very important because the early metalworkers in Iran began to melt the native copper in order to cast it, and it caused producing arsenical copper (accidental alloying). This phenomenon may also have occurred by melting native copper containing arsenides in crucible (Pigott, 2004a). Anarak economical resource area in central Iran is notable for copper casting because there are two large outcrops of native as well as arsenical copper. The orogeny zone of Talmessi and Meskani, is important according to high enrichments of copper arsenides, as algodonite (Cu$_6$-7As), enargite (Cu$_3$AsS$_4$) and domeykite (Cu$_3$As) (Pigott 2004a; Thornton et al., 2002). Another copper ore deposition with arsenic enrichments in literature is Taknar, closed to the metallurgical site, Tappeh Hisar, northern Iran. As a matter of fact, the use of furnace as evidences for copper smelting has been carried out in Tappeh Hisar (Pigott et al., 1982).

Metallurgy of copper has followed by the manufacturing of artefacts with arsenical copper from 4th millennium BCE. The copper extraction from different ore resources (furnace-based metallurgy) may occurs as next step of copper metallurgy. The copper ores smelting in furnace has begun in 5th millennium BCE by smelting oxidic ores such as cuprite or malachite, for example in Tal-i Iblis (southeast Iran), Tappeh Qabristan and Sialk (north-Central Iran), Tappeh Hisar (northeast Iran) and Susa (Southwest Iran) (Figure 3) (Thornton, 2009a; Thornton et al., 2002; Pernicka, 2004; Dougherty & Caldwell, 1966). One of the important sites in copper smelting is Arisman, Central Iran. Archaeological excavations executed in this site (with slag concentrations) cleared that extensive copper smelting took place at the site during the late 5th to the early 3rd millennium BCE (Pernicka, 2004; Chegini, et al., 2004).

Analytical results from various archaeological areas in the Near East and the eastern Mediterranean region have made clearly that an intentional arsenic-copper alloy was often, if not invariably, an important stage in the transition from cast copper to the use of a tin-copper alloy. First trying to make an alloy may be producing copper-arsenic alloy or arsenical copper in prehistory (Tala'i, 2008a; Scott, 2002; Thornton, 2010). This alloy became widespread in the Near East sometime in the second half of the 4th millennium BCE and might well have arisen from an accidental use of an arsenic-enriched copper ore (Moorey, 1969).
As amount of lower than 2 percent may show that it has entered into composition as an impurity from copper ores such as tennatite, \((\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}\) (Grey Copper) and this can be considered as accidental alloy (Coghlan, 1975). With high amount of As, Coghlan (1975) suggested that the intentional alloying may be occurred by three metallurgical procedures:

1. Contemporaneous smelting of copper oxide ores with realgar \((\text{As}_2\text{S}_3)\) or orpiment \((\text{As}_2\text{S}_5)\).
2. Use of ores with high As-content such as arsenopyrite or tennatite mixed with copper sulfides.
3. Adding realgar or orpiment to the melt.

On the other hand, Thornton et al (2009) suggest the speiss (iron-arsenide alloy) as a quasi-metallic material usually formed as an accidental by-product of copper or lead smelting. It has been produced to provide arsenic as an alloying component for arsenical copper.

### 3.3 Tin bronze

In archaeometallurgical literature, bronze is a copper alloy which mostly consists of tin. It can be assumed as the real copper alloy that has produced in antiquity by adding Sn to Cu by different procedures to increase mechanical and chemical characteristics of copper. Tin make copper more fluidity and easier to cast like As and Zn, but about 10% tin, the metal would be harder and stronger than As and Zn addition (Maddin et al., 1977). Intentional alloying of copper with tin is usually considered to be indicative by a tin content of more than 1% or in some cases more than 5 percent.

Tin bronze \((\text{Cu-Sn})\) alloy became known in the late 4th millennium BCE and the beginning of the 3rd millennium BCE in Mesopotamia and western Iran (Khuzestan and Luristan regions). Nevertheless, the extensive consumption of tin and tin bronze in Mesopotamia emerges at middle of 3rd millennium BCE and in Iran even later (Thornton, 2009a).

The first appearance of producing the intentional bronze \((\text{Cu-Sn})\) alloy in Iran may be occurred in Kalleh Nissar graveyard in Luristan, western Iran at late 4th millennium BCE (Thornton, 2009a; Fleming et al., 2005). There are the evidences that direct mixing difference ores has used to create a single alloy in Kalleh Nissar artefacts by combining local copper...
and tin ores from the recently reported Deh Hosein deposit (Nezafati et al., 2006; Thornton, 2009a). The appearance of copper-tin alloys in Luristan about 3200–2800 BCE is a surprising phenomenon because the complete lack of even minor amounts of tin at many of other Iranian sites has observed until the end of the 3rd millennium BCE (Thornton, 2009a).

Of course, tin bronze examples have identified in other important sites such as Susa, Sialk, Tappeh Giyan, and Tappeh Yahya in Iran and Mundigak in Afghanistan at the early and mid-3rd millennium BCE (Thornton et al., 2002; Lamberg-Karlovsky, 1967). Even tough, an archaeometallurgical study on the site of Malyan, Fars region, showed the use of tin bronze in Middle Bronze Age of Iran between 2200-1800 BCE (Pigott et al., 2003).

In many texts, tin amount lower than 2-3 percent may be due to entering impurities from ores, but in higher amounts intentional alloying has occurred to produce tin bronze. Coghlan (1975) described four probably ways to making bronze:

1. Melting metallic Cu and metallic Sn with together as a mixture.
2. Adding (reducing) cassiterite (SnO₂) to melted copper under charcoal cover in crucible.
4. Smelting a mixture of a copper ore with together cassiterite (SnO₂).

In first procedure, by adding metallic tin to metallic copper, tin acts as deoxidant and increase fluidity of melt and casting ability. Also, adding metallic tin cause to decrease melting point of copper and it lowers by adding more tin (Pigott et al., 2003). The reducing SnO₂ in molten copper (second procedure) occurs at about 1200 ºC in presence of charcoal in the crucible charge. The charcoal covered metal helps to maintain reducing conditions in crucible (Pigott et al., 2003; Coghlan, 1975). The third and fourth are named mixed smelting (or co-smelting) and has reported in relation with Luristan Bronzes (Nezafati et al., 2006).

Determination of tin resources in ancient time is one of the main problems and questions concerning of the starting bronze metallurgy in Bronze Age (3300-1500 BCE) in southwest Asia (Pigott, 2004a). It has long been discussed about tin sources for this huge amount of bronze production in Iranian Plateau in a long period of time from mid-Bronze Age to the end of Iron Age (Muhly, 1985; Maddin et al., 1977; Pigott et al., 2003; Coghlan, 1975).

It should be considered that the earliest tin sources might have probably been also copper ones. It is possible that the first bronze makers gained it accidentally. Probably at first a tin bearing copper ore had been smelted for production of metallic copper (or arsenical copper), but then because of the presence of tin in ore, bronze has been made accidentally. The final product of such process (arsenical copper and bronze) was identified by its golden color, its hardness and better casting properties. On the other hand it is possible that early smelters did not know cassiterite as an economical ore. They just knew that the ore of some specific mines result in better quality for metal products (Muhly, 1985).

One of the strongly probable sources of tin for Iran in ancient time was Afghanistan. There are many resources and mines of tin in this region and the probably cultural relationship between Iran and Afghanistan regions in prehistoric time has caused to tin sources in Afghanistan and Central Asia would be under considerations as main tin source for bronze metallurgy in Iran more than tin sources in Anatolia (Pigott et al., 2003; Muhly, 1985; Fleming et al., 2005). Of course late P. R. S. Moorey (1982) suggests two potential tin sources in Iranian Plateau: the Central Lut, a desert in central Iran, for which there is some minimal
evidence, and a west or northwest Iranian source, maybe in Azerbaijan, for which there is still no special evidence. As noted above, Nezafati et al (2006) consider the mining region of Deh Hosein in Zagros Mountain, west central Iran as a source of tin for making bronze artefacts from Bronze to Iron Age, by combining local copper and tin ores and smelting them to produce bronze alloy (co-smelting).

Apart from sources of tin to use in bronze production, application of Cu-Sn alloy continued from Bronze Age to Iron Age in Iran. There are many examples from bronze production and use for making tools and artefacts in Iranian Iron Age, besides iron producing. Among copper-base artefacts from Iron Age sites that have been analyzed, bronze is the most common alloy, especially in western and northwestern Iran (Moorey, 1982). As a result, it is assumed that most Iron Age copper-base artefacts were of bronze and that the use of arsenical copper had waned considerably. Although, arsenical copper continued to be produced in this period and was excavated at Dailaman and Gilan regions (Pigott, 2004b).

The archaeological and experimental studies in different sites of Iron Age proved extensive archaeometallurgical finds, especially bronze artefacts. Examination of the archeological evidence suggests that the Gilan region by the Caspian Sea's littoral has been a bronze making center (Haerinck, 1988). In Marlik, the ancient site in northern Iran that is dated to late 2nd/early 1st millennium BCE, many bronze artefacts (figure 4) have found in graves beside of gold and silver vessels and decorative potteries. These are consisting of various classes of decorative artefacts such as spouted vessels, small statues of animals like deers, swords and daggers and etc (Negahban, 1999, 1996).

Fig. 4. Two bronze artefacts from Marlik graves, Left: a spouted vessel decorated with lion reliefs, Right: fantastic statue of a deer (Negahban, 1999).

At Hasanlu, an important Iron Age site in northwest Iran, more than 2,000 copper and bronze artefacts in the major various categories has found in archaeological excavations. Many of these artefacts have ornamented and decorated (Pigott, 1990). On the other hand, many bimetallic (two part artefacts made by bronze and Iron) artefacts have found such as
pips with bronze lion head (Figure 5), spears with iron sockets and bronze blades, iron daggers with bronze cast-on hilts, and repoussé tin-bronze belt plaques with iron rivets (Pigott, 2004b, Thornton & Pigott, 2011).

Fig. 5. Three bronze artefacts from Hasanlu, Northwest Iran, 1st millennium BCE, a) Lion statue, b) decorative ring, c) bimetallic pin with bronze lion statue and iron pin shaft, Photos: M. Charehsaz and M. Ahmadi.

The Luristan Bronzes are one of the significant bronze collections from Iron Age of Iran. The name of “Luristan Bronzes” introduces a series of decorated bronze artefacts in a specific local style dating from the Iron Age (about 1500/1300 to 650/550 BCE) that belong to the geographical region of Luristan, central western Iran. These artefacts became known through large-scale illicit excavations started in the late 1920s, but their cultural context and provenance remained unspecified for a long time (Overlaet, 2006, 2004; Muscarella, 1990). Of course some controlled excavations has done in Luristan Region by various archaeologists such as late E. F. Schmidt in Surkh Dum site (Schmidt et al., 1989), Belgian Archaeological Mission in Iran (BAMI) under supervision of the late L.Vanden Berghe in Pusht-i Kuh Iron Age sites, western Part of Luristan (Overlaet, 2005; Muscarella, 1988) and M. Malekzadeh and A. Hassanpour in Sangtarashan (Oudbashi et al., in press) in Pish-i Kuh Region, Eastern Part of Luristan.

The Luristan bronzes are various in shapes and include lost wax casts as well as sheet metal objects consisting of different categories such as Horse gear includes horse-harness.
trappings and horse bits with decorative cheek pieces, arms and equipment include spiked axe heads, adzes, daggers, swords, whetstone handles, and quiver plaques, jewelries include rings, bracelets, pendants, and pins with cast or hammered sheet metal heads, an important series so-called “idols,” also labeled “finials” or “standards,” placed on tubular stands (Figure 6) and sheet metal vessels and jars (Overlaet, 2006, 2004; Muscarella, 1990, 1988; Moorey, 1974, 1971).

Fig. 6. a) A "Master of Animals" Standard from Luristan, with detached man head held by 4 animals. b) The upper part of an Animal Headed Pin, Luristan that shows combination of two goats and a felidae. Falakolaflak Museum, Khorramabad, Iran, Photo: O. Oudbashi.

The metallurgy in Elamite period was an important industry for producing various tools and artefacts especially religious and non-religious sculptures. There are many evidences from different parts through Elamite period by which the usage of copper alloys and especially bronze as well as craftsmanship of Elamite metalworkers will be obvious. One of the most significant examples of metallic sculpture from Middle Elamite period is the life-size statue of queen Napir-Asu discovered from Acropole of Susa that has dated to 14th century BCE (Figure 7). It is a bronze sculpture that has been casted in one piece and is 129 cm in height (without head). This impressive sculpture shows the ability and craftsmanship of Elamite master metalworkers in work with bronze and casting techniques. Another example is a three dimensional representation bronze model called the Sit-Shamshi (Sunrise), from Acropole of Susa, 12th century BCE, 60 cm in Length (Figure 8) (Harper et al., 1992, Potts, 1999).
Fig. 7. Elamite Life-size bronze statue of queen Napir-Asu discovered, Susa, 14th century BCE, (Harper et al., 1992).

Fig. 8. Bronze model, Sit-Shamshi (Sunrise), Susa, 12th century BCE, (Harper et al., 1992).
4. Experimental study on Iranian bronzes

The study of bronze technology and the examination of copper based alloy artefacts from prehistoric time is one of the more interesting subjects in archaeometallurgical investigations around the world from some decades ago (Thornton et al., 2005; Paulin et al., 2003; Giumlia-Mair, et al., 2002; Thornton et al., 2002; Laughlin & Todd, 2000; Çukur & Kunça, 1989; Moorey, 1964). For technical studies, some metallic artefacts belonging to two Iranian archaeological sites, Haft Tappeh and Sangtarashan, have investigated and the results will be presented here. The aim of this investigation is to show metal production in these sites and a comparative study between metallurgical aspects of making copper based alloys. The investigations have done in two individual research projects and their results will be presented and compared here showing two specific metallurgical processes to make bronze and copper artefacts.

4.1 Description of sites

The investigated sites are among important archaeological finds in Iranian Plateau. The Haft Tappeh ancient site is located in Southwest Iran, in the central part of Khuzestan Province. Based on excavations done by late E. O. Negahban between 1965-1978, this site is belonging to early phase of Middle Elamite period (14th century BCE) and is remains an Elamite city named Kapanak, capital of Elamite's King Tepti Ahar (Negahban, 1993; Mofidi Nasrabadi, 2004; Potts, 1999). In the course of these excavations, many archaeological finds such as architectural remains, pottery, stone, bone, terracotta and metal artefacts are discovered (Negahban, 1993; Potts, 1999). Among these finds there are many metallurgical materials and remnants such as a two part furnace for making pottery and smelting ores, slag, matte as well as metal artefacts such as arrowheads, knives, swords, nails and pins, axes and other objects. Many of these findings were found in a workshop located at the east of excavated area (Negahban, 1993).

The recent archaeological activities in the field of Luristan Bronzes are excavations in Sangtarashan site between 2006-2011 by M. Malekzadeh and A. Hassanpour. This site is located in western Iran, Luristan region (Pish-i Kuh). The site is consisting of one cultural and historical layer belonging to Iron Age and type of discovered bronze collection suggests that this site can be dated to Iron Age II A-B of western Iran about 1000-800 BCE (Oudbashi et al., in press; Overlaet, 2005; Overlaet, 2004; Azarnoush & Helwing, 2005). The Sangtarashan Bronze collection includes swords and daggers, axes, arrowheads, round vessels, spouted vessels, cups, decorative and ceremonial finials, decorative plaques, some bi-metallic (bronze-iron) artefacts and so on. This collection consist of individual group of excavated Luristan Bronzes, in high amount of founds as well as variety of manufacturing bronze artefacts. They have manufactured in a high level of craftsmanship and artistic skill (Oudbashi et al., in press).

4.2 Experimental

The experiments have designated to identification of chemical composition and microstructure of metallic artefacts from two sites. For this reason, 10 samples from different excavated metal pieces of Haft Tappeh and 10 samples from broken vessels of Sangtarashan (Figure 9) have selected and analyzed. To indentify chemical composition of samples, they analyzed by semi-quantitative chemical analysis with Scanning Electron Microscopy with
Energy Dispersive X-ray Spectrometry (SEM-EDS)\(^1\) (Pollard et al., 2006; Pollard & Heron, 1996; Olsen 1988).

Metallographic samples were prepared by cutting a small piece from each sample, and then they mounted, polished and investigated through the optical microscope as well as SEM. It helps us to characterize microstructure of metal with its various details and aspects via high magnifications (Scott, 1991; Smith, 1975; Norton, 1967). To reveal microstructure and also for explaining the manufacturing methods, mounted samples have etched in ferric chloride (FeCl\(_3\)+HCl solution in H\(_2\)O) and examined under metallographic microscope (Caron et al., 2004; Scott, 1991).

### 4.3 Results and discussion

#### 4.3.1 Alloy composition

The SEM-EDX results of 10 samples from different metallic artefacts and pieces belonging to Haft Tappeh are presented in Table 2. The major element in all samples is Cu and varies from about 67 to 95 percent in weight.

![Fig. 9. left) 10 copper alloy samples investigated from Haft Tappeh, Middle Elamite Period, Right) One of the broken vessels from Sangtarashan Iron Age site, No. ST.08.](image)

Other metallic elements in minor amount are Pb, Sn, Ni and Zn where have detected in an amount higher than 1% in weight. The elements such as Ag and Fe are lower than 1 percent and variable in content and may be considered as impurities from smelted ores. On the other hand, Al, Cl, Mg, S and Si show a minor amount in composition that they may be originated from soil, with the exception of S that can have another source, main ore.

\(^1\) The SEM-EDS analyses were performed by 1) XL30 model, Philips in the SEM-EDS laboratory of Tarbiat-e Modarres University, Tehran, Iran, and 2) TESCAN model VEGA II, with a RONTEC BSE detector in SEM-EDS laboratory of RMRC, Tehran, Iran.
Table 2. Chemical composition of Haft Tappeh Metallic Samples by SEM-EDS method in wt.%.

The samples are consisting of copper (HT.35, 71), leaded copper (HT.31, 37, 43, 54, 56) and leaded tin bronze (HT.44, 47, 53). As a matter of fact, nickel shows a significant role in samples No. HT.31 and HT.54 and zinc also in No. HT.56. Based on the results it can be suggested that the copper alloying in the analyzed Haft Tappeh artefacts has not been done by similar and controlled procedures and different compositions can be identified at them, although leaded copper and bronze are apparent in samples. The Pb is detected in 9 samples and it may be recommended that the alloyed samples are leaded with exception of 3 copper artefacts: HT.35, HT.53, and HT.71 (lower than 1 percent).

The variety of alloy composition and determining different alloys, various amount of alloying elements in similar classes (such as lead and tin in bronzes) and presence of metallic elements such as Ni in minor content shows that the metalworking in Haft Tappeh may not followed from a specific process and an uncontrolled smelting and alloying procedure has been applied in this period of time.

On the other hand, the ore sources of Elamite metallurgy has not been identified yet and it can be state that the different metal sources may be used to metal smelting in this site.

Table 3 shows the results of SEM-EDS analysis performed on 10 broken vessels from Sangtarashan Iron Age site. The results determine that only two elements play main role to form alloy composition in sample: Cu and Sn. The tin content is variable from 7.75 to 13.56% and cannot consider as an alloying pattern based on Sn.

Other elements such as Ag, As, Fe, Ni, P, Pb, Sb and Zn are lower than 1% in many samples and don't play an important role in alloying process. They can be considered as impurities that may originated from mother stone ores.
4.3.2 Microstructure

The microstructures of the unetched samples of both sites observed by optical microscope (OM) and SEM consist of many fine gray-green inclusions spread in the metallic matrix (Figure 11a, 12a). To identify chemical composition of these inclusions, three samples from each site has analyzed by SEM-EDS microanalysis. The results of main elements detected in analyses are presented in Table 4.

In Table 4, only elements detected more than 1% wt. in amount are presented. The major elements detected in all samples are Cu and S. Also, Fe, Sn, Si and Pb are available in minor content in samples. The elemental composition of inclusions suggests that the inclusions are composed of copper sulfides with some iron sulfides. Sn (and Pb in sample HT.37) constituents probably associated to the bronze matrix and have no relation with the composition of inclusions.

<table>
<thead>
<tr>
<th>Cu</th>
<th>Fe</th>
<th>Pb</th>
<th>S</th>
<th>Si</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT.35</td>
<td>77.88</td>
<td>1.25</td>
<td>–</td>
<td>14.79</td>
<td>–</td>
</tr>
<tr>
<td>HT.37</td>
<td>75.50</td>
<td>2.08</td>
<td>1.30</td>
<td>15.04</td>
<td>1.30</td>
</tr>
<tr>
<td>HT.44</td>
<td>79.03</td>
<td>–</td>
<td>–</td>
<td>15.19</td>
<td>–</td>
</tr>
<tr>
<td>ST.03</td>
<td>83.48</td>
<td>1.10</td>
<td>–</td>
<td>12.48</td>
<td>–</td>
</tr>
<tr>
<td>ST.05</td>
<td>79.50</td>
<td>0.95</td>
<td>–</td>
<td>18.44</td>
<td>–</td>
</tr>
<tr>
<td>ST.08</td>
<td>79.21</td>
<td>2.77</td>
<td>–</td>
<td>15.77</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 4. Results of SEM-EDS analysis of inclusions for three samples from each sites (wt.%). The elements with higher amount than 1% are presented.

Figure 10 presents ternary phase diagram of the Cu-Fe-S system based on SEM-EDS analysis of inclusions. The proportion of Cu/S and location of points in Figure 10, strongly suggests
the presence of chalcocite (Cu₂S) or digenite (Cu₉S₅). Also, with regard to the appearance of low to variable amounts of Fe in the composition, this may reflect the existence of iron sulfides like Pyrrhotite (Fe₁₋ₓS) (Klein & Hurlbut Jr., 1999). In fact, the composition of inclusions suggests they are residues of sulfidic ores (Singh & Chattopadhyay, 2003; Bachmann, 1982). Sulfidic inclusions have been observed in many copper alloy artefacts from other examined sites in prehistoric Iran such as Luristan Iron Age sites (Fleming et al., 2006; Fleming et al., 2005) and some Chalcolithic and Bronze Age sites in southeastern Iran (Thornton & Lamberg-Karlovsky, 2004).

Fig. 10. Ternary phase diagram of Cu-Fe-S system with respect to the inclusions' composition. The main component is copper sulfide.

To identify microstructure in detail and to make clear the manufacturing method of the artefacts, three mounted samples from each site were etched in ferric chloride solution and examined under metallographic (optical) microscope (Caron et al., 2004; Scott, 1991). The etched microstructure of samples HT.31, HT. 43 and HT. 44 have studied from Haft Tappeh. The microstructure is consisting of worked and recrystallized grains of α solid solution of copper with twinning lines in grains (Figure 11b-d).

FCC metals such as copper (α solid solution in Cu-Sn system) recrystallize by a twinning process (except for aluminum). New crystals that grow following the annealing after cold-working in copper and its alloys produce the effect of a mirror reflection plane within the crystals, with the result that parallel straight lines can be seen in etched sections traversing part or all of the individual grains of the metal. The straight twin lines shows that the final stage of shaping operation has been annealing but the deformed (curved) twin lines suggest that the metal has been worked finally and if heavily worked, the slip lines can be seen in grains (Scott, 1991).
Fig. 11. Microstructure of Haft Tappeh samples: a) SEM micrograph of an inclusion, Sample HT.37, b) microstructure of sample HT.43, c) sample HT.44, d) sample HT. 31. All are etched in ferric chloride solution and show equi-axed grains with twinning.
The etched microstructure of Sangtarashan samples (ST.01, ST.03, ST.04) is even more similar than Haft Tappeh ones and of course shows worked and recrystallized grains of $\alpha$ solid solution (Figure 12b-d). The twinning microstructure in these samples also occurred due to hammering and annealing of cast bronze and demonstrates that ancient metalworkers shaped the vessels by hammering as well as subsequent heat treatment. This process of hammering could have been used to shape a cast bronze ingot into sheet metal vessel, and in the course of the mechanical working the sheet metal was work-hardened. To remove this work hardening, (like Haft Tappeh samples) the metal has treated with heat between 500 to 800 °C (i.e. for copper alloys). This annealing process returns workability to the sheet metal (Siano et al 2006; Caron et al 2004; Scott 1991).

Fig. 12. Microstructure of Sangtarashan samples: a) SEM micrograph of elongated inclusions, Sample ST.08, b) microstructure of sample ST.01, c) sample ST.03, d) sample ST.04. All are etched in ferric chloride solution and show equi-axed grains with twin and slip lines.

5. Conclusion

Iran is a considerable region in archaeological researches and events and about 150 years has been taken into attention of many archaeologists, historians and scientist from worldwide. In fact, Iranian Plateau was one of the pioneer regions in many aspects of technological and manufacturing history from ancient times. The investigations and researches on the history
of metallurgy and metalworking states that the earliest experiences and events in metal usage in the world have occurred in Anatolia, Caucasus, Iran and Levant.

Copper is the first metal for making tools and ornaments in Iran (like other regions). The Archaeometallurgy of copper can be classified in four main stages in Iran prehistory. Initially, the ancient metalworkers have used native copper to making artefacts from about 9000 years ago. The second stage has been melting native copper and casting it to specific shapes in early Chalcolithic period. Some of native copper resources in Iran contained arsenic and it caused to occurrence of early accidental alloying and emergence of arsenical copper. The third stage is smelting of copper from ores that is started by smelting oxidic copper ores such as cuprite and malachite and then polymetallic sulfidic ores in Chalcolithic; and consequently, many of objects made by smelted copper also have arsenic as an impurity or alloying elements. In last stage, by progressing metallurgical experiences in prehistory, production of a new alloy has occurred in the late 4th millennium BCE (early Bronze Age). Tin bronze has observed about 3000 BCE but has been common about 1000 years later and even in Iron Age (1500-550). Bronze usage in Iron Age is an important stage of copper alloys metallurgy in Iran. There are many examples of decorative bronze collections and artefacts from Iron Age sites especially in graves. These are discovered in many Iron Age graves and may assume as vows religious cemeterial objects, such as Luristan and Marlik bronze collections. Bronze production has been continued in the next periods although some changes in metallurgical traditions have occurred in that time.

The examination of some metallic samples from Haft Tappeh (Middle Elamite period) and Sangtarashan (Iron Age) sites shows differences and similarities in alloying and shaping processes. The main difference between these sites is alloying. Haft Tappeh shows a variable alloying process to make copper alloys. There are three significant composition in samples: copper, leaded copper and leaded tin bronze. The considerable subject in all samples is presence of tin, even in low amount. This may cause to assume all samples as bronze (low tin bronze and tin bronze). Nevertheless, presence of Sn may be due to application of copper tin-bearing ores. On the other hand, alloy composition in Sangtarashan shows an apparent pattern in bronze production; although tin content in samples is variable and it state that the alloying has not done in a controlled condition. Presence of copper sulfide inclusions in microstructure suggests the employed ores in both sites were copper sulfidic ores. Low amount of As in both and Pb in Sangtarashan are two interesting aspects of alloy composition and may related to ore sources, although need to be considered as a research subject in the future. The microstructure is consisting of equi-axed and worked grains of copper solid solution explaining the shaping method has been cold working on casted or smelted copper or bronze ingot, continuing with annealing as a stage to remove work hardening, especially in thin vessels of Sangtarashan.

Despite of history of metallurgy in Iran, especially bronze, many investigations about Iran archaeometallurgy only focus on archaeological subjects and relations and connections between cultures and civilizations and the technical studies are very limited in compare of archaeological ones. It seems to need to a large scale study on metallurgical technology in ancient and historic Iran to reveal various aspects of archaeometallurgical activities in Iran, especially with regard to bronze technology.
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Bronze in Archaeology: A Review of the Archaeometallurgy of Bronze in Ancient Iran


Copper has been used for thousands of years. In the centuries, both handicraft and industry have taken advantage of its easy castability and remarkable ductility combined with good mechanical and corrosion resistance. Although its mechanical properties are now well known, the simple f.c.c. structure still makes copper a model material for basic studies of deformation and damage mechanism in metals. On the other hand, its increasing use in many industrial sectors stimulates the development of high-performance and high-efficiency copper-based alloys. After an introduction to classification and casting, this book presents modern techniques and trends in processing copper alloys, such as the developing of lead-free alloys and the role of severe plastic deformation in improving its tensile and fatigue strength. Finally, in a specific section, archaeometallurgy techniques are applied to ancient copper alloys. The book is addressed to engineering professionals, manufacturers and materials scientists.

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