Aegean Metallurgy in the Bronze Age

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20. THE TECHNOLOGICAL EVOLUTION OF COPPER ALLOYS IN THE AEGEAN DURING THE PREHISTORIC PERIOD

George Papadimitriou

In this paper a new approach to understanding the evolution of prehistoric copper alloys in the Aegean region, from the point of view of both the metalsmiths and the end users of the metal products, is presented. The effect of alloying additions and impurities on both: metalworking properties and properties of interest to the end user of the products are critically reviewed and discussed. The main developments in the alloys' constitution and in metalforming techniques characterising the principal sub-divisions of the prehistoric period (EBA, MBA and LBA) are described.

1. Copper alloys and their terminology

In addition to the precious metals of gold and silver, copper and bronze were known and used for the manufacturing of metal articles in prehistoric times.

Copper (Cu) is, strictly speaking, a chemical element, i.e., a pure substance. However, in common speech copper means a more or less impure metal of everyday technological applications. In prehistoric times, as at the present time, copper contained a number of impurities, too. It was initially collected from metalliferous veins as native metal and later on it was produced from smelting of copper ores (mainly oxides) in small primitive furnaces. Alloys were accidentally discovered or invented and were progressively substituted for copper for their enhanced properties.

From the physical metallurgy point of view, an alloy is defined as "a material with metallic properties, homogenous in macroscopic scale, and consisting of two or more elements, of which one at least is a metal". Thus an alloy, apart from its base metal contains impurities and intentional additions, the latter called alloying additions or alloying elements.

The alloys of copper used in prehistoric times satisfy the above definition and are actually called bronzes.[1] In addition to copper, which is the base metal of the alloy, bronze contains both main and secondary alloying elements as well as impurities.

An alloying element aims to provide the alloy with enhanced properties. The main alloying additions to copper in prehistoric times were arsenic (As), tin (Sn) or, rarely, both of them. Lead (Pb) may also be present and should be considered as a secondary alloying addition, but sometimes it is found alone as a main alloying element.

When arsenic is the main alloying addition to copper, the alloy is more specifically called arsenical copper,[2] the term bronze being usually but not exclusively reserved for tin bronzes.

Zinc (Zn) does not enter into the composition of prehistoric bronzes and remains unknown in the Aegean region up to the Hellenistic or Roman period. If zinc was occasionally present in alloys of the prehistoric period, its presence should probably be considered as accidental. Alloys of copper with zinc are actually called brasses.[3] The Greek term 'ορείχαλκος' was used in some cases by ancient authors in

1. In modern Greek *μπρούντζος* or in Greek *katharevousa* *κρατέρωμα*.
2. In modern Greek *αρσενικούχος χαλκός*.
3. In modern Greek *ορείχαλκοι*.

Classical times, but it is not clear what exactly was meant by this term. In any case, brasses, which are alloys of copper and zinc, should not be confused with bronzes,[4] which as we have explained, contain one or more of the elements of arsenic, tin and lead as alloying additions, but not zinc.

It should be emphasised that in classical literature no distinction was made between copper and its alloys, all of them called indifferently *χαλκός*. It is thus reasonable to believe that by the term *χαλκός*, bronze rather than copper was meant, since unalloyed copper was less frequently used. The same seems to be true in Linear B inscriptions of LBA, where a single term *ka-ko* (*χαλκός*) is used in order to designate, without distinction, both copper and its alloys.

In the present symposium I heard for the first time the very interesting interpretation by Hubert Le Marle that in Linear A inscriptions distinct terms were used to designate different copper alloys or compositions.[5] This is clearly in contrast with what happened later, from Mycenaean to Classical times.

An impurity is an element coming from the ore or other raw materials eventually used during smelting or melting and going through the metallurgical process into the metal or the alloy produced. When impurities are at a low level, they are tolerated. If present in significant amounts, they become harmful to the properties of the alloy and may adversely affect or even inhibit working, e.g., by hammering. Although refining techniques (i.e., metallurgical processes aimed at lowering the impurity level of the alloys) were used in antiquity, they were probably unknown as late as LBA. As a matter of fact, impure alloys were sometimes used, as evidenced by imperfections and defects, such as open pores and cracks, present on the surface of metallic articles. In order to achieve technically correct artefacts, the ancient craftsmen had to select materials convenient for a specific application by experimentation and trial. Raw materials which were difficult to proccess were not rejected, but reserved for simpler applications, for example for casting. This practice, which was perhaps the first scientific experimentation, progressively led to the sense of quality and created specific grades (or classes) of alloys, according to their content in alloying additions and impurities. Finally, the quality of metals was perfectly mastered in the Mycenaean period.

A very unwelcome, but frequent, impurity in bronzes is iron (Fe).[6] Other common impurities are nickel, cobalt, antimony, bismuth, silver, etc, all of them affecting the ability of the alloys to be hammered. Tin, arsenic and lead in low quantities, if they were not deliberately added as alloying elements, may be considered as impurities coming either from the metallurgical process or from recycling (re-melting) of older bronzes.[7]

Impurities at very low levels are usually called oligo-elements or trace elements and have been considered sometimes as an indication of the origin of metals. Such deductions should, however, be considered with great reservation, as the initial level of impurities in the ores and their mutual ratios are in general modified during the metallurgical processes. As a matter of fact, each chemical element has a different tendency to divide between the metal and the slag during smelting or melting processes and this partition depends on the particular parameters of the metallurgical process, i.e., temperature, strength of reducing/oxidising atmosphere in the furnace and overall slag composition.

4. In modern Greek *μπρούντζοι or κρατερώματα*.

5. H. LA MARLE, "Minoan Metallurgy and Linear A: Definitions, Lexical Slides and Changes in Metal Processing," (this volume).

6. G. PAPADIMITRIOU, "Copper and Bronze Metallurgy in Ancient Greece," *Archaeometry* (1991) 117-126; G. PAPADIMITRIOU, "Simulation Study of Ancient Bronzes: their Mechanical and Metalworking Properties," in Y. BASSIAKOS, E. ALOUPI and Y. FACORELLIS (eds), *Archaeometry Issues in Greek Prehistory and Antiquity* (2001) 713-733.

7. G. PAPADIMITRIOU, "The Evolution of the Copper Alloys in the Helladic Area to the End of the Geometric Period: Alloying Additions and Technological Development," in Y. BASSIAKOS, E. ALOUPI and Y. FACORELLIS (eds), *Archaeometry Issues in Greek Prehistory and Antiquity* (2001) 587-608.

2. Forming techniques

Forming techniques are by means of casting and plastic deformation.

Following casting, the solidification of the melt in a mould usually leads to a characteristic microstructure of columnar (elongated) crystals with their major axis parallel to the direction of heat flow during cooling, which is perpendicular to the walls of the mould. These common characteristics in form and orientation of grains are called solidification texture.

The elongated crystals sometimes possess a characteristic internal microstructure with main and secondary branches or presenting concentric layers of different chemical composition, called dendritic (Fig. 1). This feature is usually evident in copper alloys under the optical and scanning electron microscope and it is the result of microsegregation of the alloying elements (e.g. tin) within the growing grains. For this reason, the dendritic microstructure is not identified in relatively pure copper (Fig. 2).

Forming by means of plastic deformation is always carried out on a casting of simple geometrical form, called an ingot.[8] In order to save work by hammering, the ingot was sometimes designed to approximately the shape of the final item. Final shaping was then performed either by forging, while the metal was at a high temperature, or by hammering, with the metal cold.[9]

During deformation by hammering, the metal strengthens, becoming harder and loosing its ductility, i.e., its deformation capacity. This phenomenon of hardening during cold plastic deformation is called work or strain hardening.[10] The degree of work hardening may be expressed as the percentage of decrease of the initial thickness of a sheet of metal. From a microscopic point of view, after plastic deformation, all the grains become compressed or elongated in the same direction and almost by the same amount as the whole piece of metal

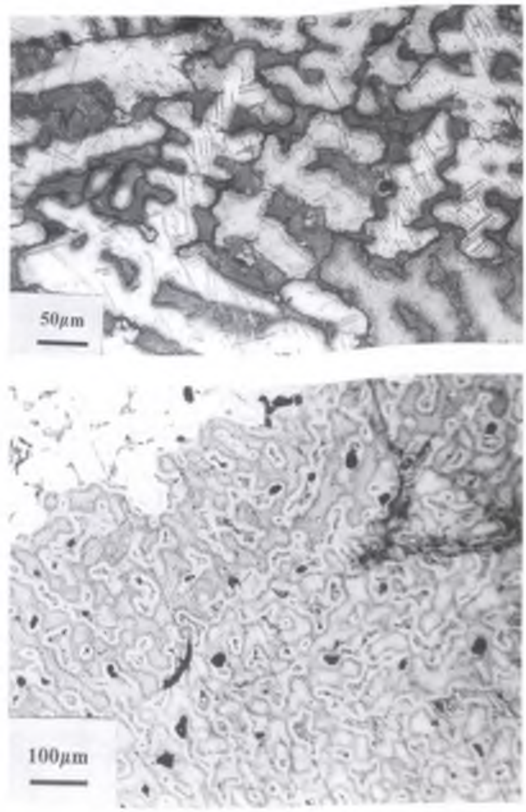

Fig. 1 Dendritic microstructure and microsegregation (a) Dendritic microstructure in 8.5% wt tin bronze casting (Late Mycenaean period); (b) Dendritic microstructure in the form of concentric layers with increasing tin content (coring). Experimental bronze casting with about 11 % wt tin.

8. In modern Greek *πλίνθωμα or χελώνα*.
9. In modern Greek *θερμή* and *ψυχρή σφυρηλασία*, respectively.
10. In modern Greek *ενδοτράχυνση* or *κράτυνση*.

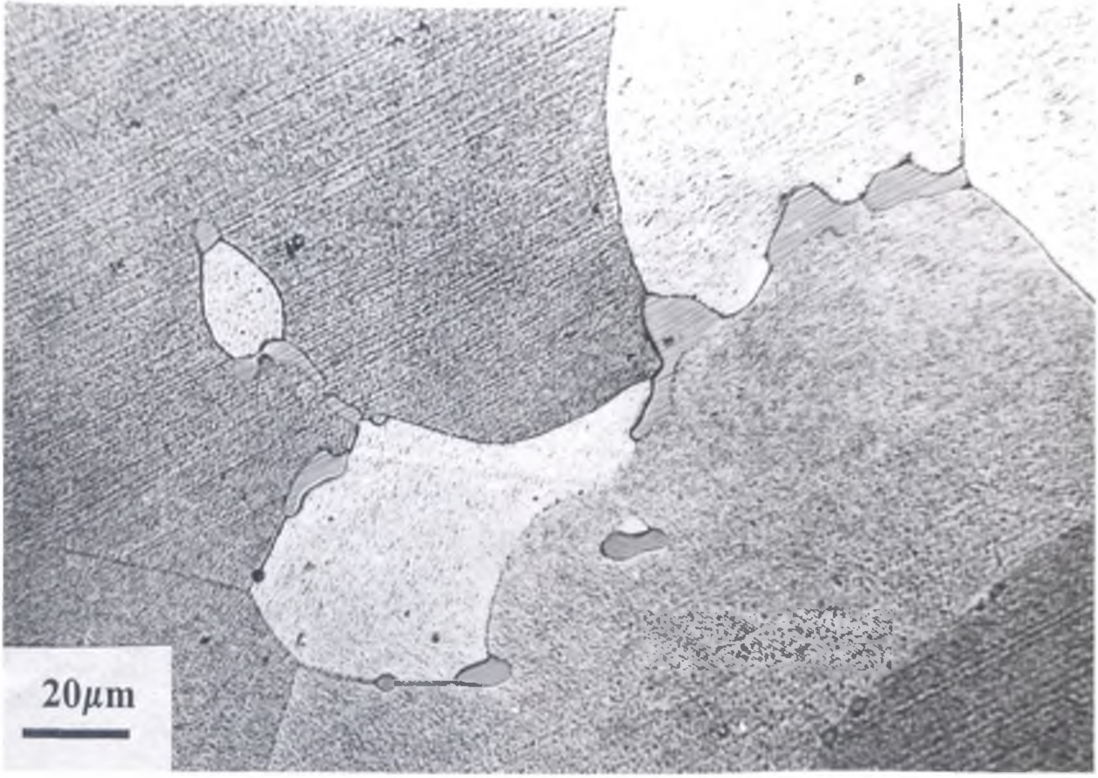

Fig. 2 Hellenistic copper with about 1% wt tin as impurity. Coarse grained microstructure, with copper oxide inclusions (small grey particles) mainly on the grain boundaries.

(Fig. 3). This common elongation of grains is called deformation texture.

Work hardening is due to the creation of crystal defects within the grains (the most important of them are called dislocations). As the density of defects increases, plastic deformation becomes more difficult. When a certain degree of work hardening is exceeded, the metal becomes full of dislocations, it looses its ability to deform further and cracks appear on its surface. Finally, fracture may occur.

To avoid cracking, the experienced craftsman stops hammering in time and heats the metal to a convenient temperature, rendering it again plastic and ductile. This heat treatment is called 'recrystallisation annealing'.[11] During this treatment the metal recrystallises, i.e., its grains are regenerated, taking on a regular equiaxed (not elongated) shape. At the same time the number of crystal defects and dislocations diminishes and the metal becomes soft and workable again. Figs 4a and b show the microstructure of prehistoric bronze wires in the cast and in the recrystallised condition, for comparison.

Each metal or alloy is characterised by a recrystallization temperature, i.e., a minimum temperature at which the alloy has to be heated for recrystallisation to proceed. Furthermore, a critical (minimum) degree of work hardening is necessary.

For copper alloys the recrystallisation temperature lies between 200 and 400°C, depending on composition and degree of work hardening.

The original dendritic microstructure of al-

11. In modern Greek *ανόπτηση για ανακρυστάλλωση*.

loys may disappear during recrystallisation, if annealing takes place at a relatively high temperature, between 600 and 700°C. If the annealing temperature is lower (say 400-500°C), the alloy may recrystallise without loosing its dendritic microstructure, as is evidenced in Fig. 5.

An alloy in recrystallised condition can be recognised under the microscope from its fine equiaxed grains, sometimes containing parallel bands, called annealing twins[12] (Fig. 6). However, a prolonged annealing treatment may cause excessive grain growth following recrystallisation. A coarse-grained microstructure is undesirable, since the metal becomes too soft and susceptible to cracking on hammering (overaged condition).

Forging is normally performed at a temperature higher than the recrystallisation temperature of the alloy; for this reason the alloy does not harden and its microstructure remains equiaxed. Forging is usually employed to facilitate shaping, i.e., to save strength and time, when important deformation is required. In the case of copper and its alloys, forging is a secondary process compared to hammering, since it does not take advantage of the hardening effect produced by hammering. As a matter of fact, alloys of copper are intrinsically soft and need work hardening in order to become hard and resistant to deformation.

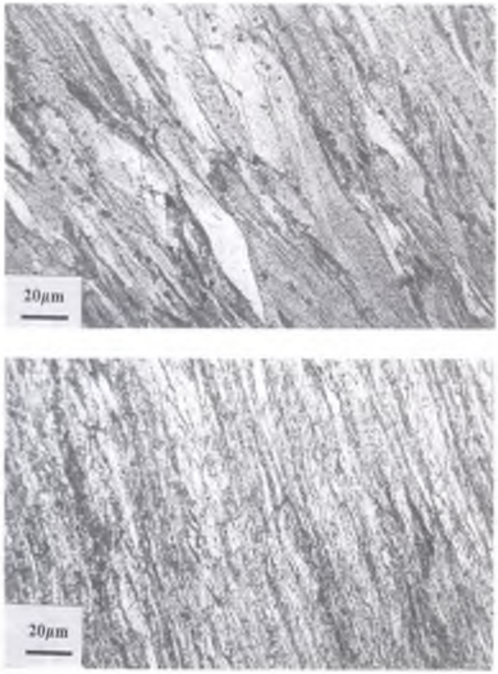

Fig. 3 Deformation texture in cold hammered bronze of the Hellenistic period, with 8% wt tin. (a) Strong deformation with elongated grains; (b) Extremely strong deformation, the grains have taken on a fibrous appearance.

3. Crucial Alloy Properties

The evolution of the composition and the technological development of alloys of copper during Prehistoric times was guided by the properties which are of interest to both the coppersmith and to the end-user of the items produced.

The main properties which are of interest to the user are:

• The colour, which may change from the characteristic red of copper to golden or silvery, depending on the nature and percentage of the alloying elements present. The colour is very important for certain categories of objects, such as decorative objects, adornments and vessels.

12. In modern Greek *δίδυμοι κρύσταλλοι από ανόπτηση*.

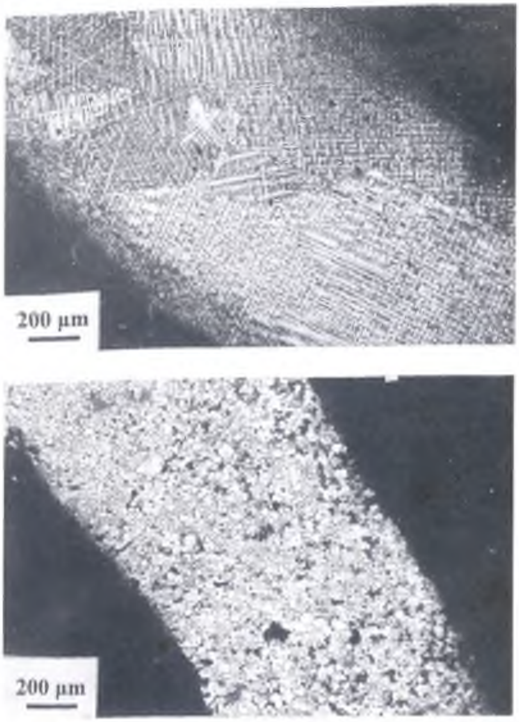

Fig. 4 Comparison of cast and recrystallised microstructures in wires. (a) Mycenaean ring, about 8% wt tin, in the as cast condition, with characteristic dendritic microstructure; (b) Geometric ring, about 3% wt tin, recrystallised after strong plastic deformation (black spots are corrosion products and inclusions).

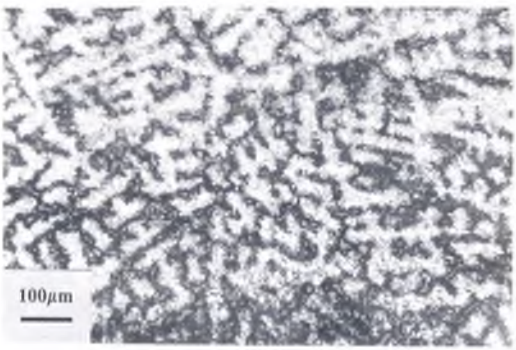

Fig. 5 Proto-Geometric bronze with about 8% wt tin. After limited plastic deformation, the subsequent annealing treatment led to recrystallisation within the dendritic branches. The low temperature of annealing was not able to homogenise the alloy, i.e., to suppress the segregation of tin, so that the overall dendritic microstructure was preserved.

• The hardness is proportional to the strength of the alloy and may change from 50 to approximately 200 HV (degrees of Vickers hardness) or even higher. A high hardness is mainly useful for cutting tools and blades, which have to be able to cut and resist wear, without blunting.
• Stiffness is in particular required in the case of long swords, in order to avoid excessive elastic bending during hits.
• Toughness is required for daggers, knives and tools, in order to resist strokes; these are allowed eventually to be deformed, but not broken.

The main properties which are of interest to the coppersmith are completely different from those cited above.

• For casting purposes the castability of the alloy is of main concern. Castability is the ability of the melt of an alloy to run easily into the cavities of the mould, reproducing with accuracy all the details of the model. For good castability it is crucial to have good fluidity of the alloy.
• A low melting point (as for example for bronzes, which is typically equal to or lower than 1000°C, as compared with that of copper, which is 1083°C) is advantageous, since the alloy is easier to melt and does not react strongly with the refractory materials of the melting furnace and of the mould, destroying them.
• For hammering, the ability of an alloy to be extensively cold worked is very important and is called workability. The term forgeability is used for forging to designate the ability of an alloy to be hot worked (say above 600 or 650°C). In both cases this property ensures a smooth condition of the surface without cracking. Cracking and surface defects due to low workability are shown in Fig. 7.
• The stability of an alloy during heating is very important. Unstable alloys are those containing arsenic or significant amounts of lead. Lead liquefies within the solid mass of the alloy (melts alone) when heated above 330°C, leading to cracking during forging or hammering. Arsenic may evaporate during hot forging,

causing softening of the alloy. These problems arise often in practice, since heating is always required for shaping by plastic deformation. As a matter of fact, heating is necessary to render the alloy soft and plastic for forging. In the case of hammering, heating is required for recrystallisation annealing, as explained earlier.

On the basis of the above discussion, it would not be wrong to say that, as in modern times, the alloys dominating a certain period were dictated by both social needs and existing technological progress. Of course, there was a strong interaction between them, leading to further developments.

4. Alloys and Forming Techniques in the Early Bronze Age

The metallic materials of EBA, extending roughly in the Aegean region between 2900 and 2000 B.C., were copper and arsenical copper.

For that period, the main property of interest for the users was hardness, since the articles produced were mainly tools (axes, chisels, saws, nails, hooks) and weapons (arrowheads, daggers). These metal items were intended to satisfy basic needs and co-existed with stone tools. There were also some adornments (beads, rings and pins), while vessels and statuettes were virtually absent.

Indicative values of hardness for the materials in use (copper and arsenical bronze), in both the cast and hammered (work hardened) condition are presented in Table 1.

It is evident that in the as cast condition both copper and arsenical copper have almost the same hardness. Arsenical copper may become very advantageous as compared to copper only in the work hardened condition, i.e., after hammering.

From the coppersmith's point of view, there are some advantages of arsenical copper over copper-metal in terms of casting, since arsenic acts as a de-oxidant, suppressing brittleness due to the presence of copper oxide inclusions in the metal.[13] Oxide inclusions have already

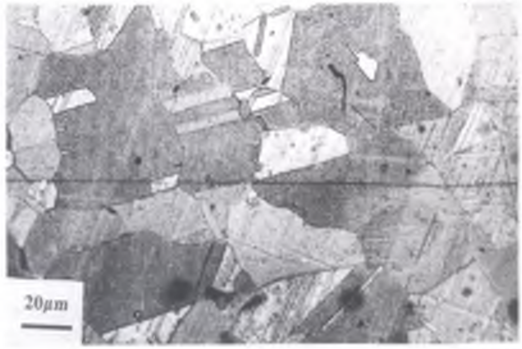

Fig. 6 Fully recrystallised bronze with annealing twins (bands) within coarse grains. Geometric bronze with about 4% wt tin.

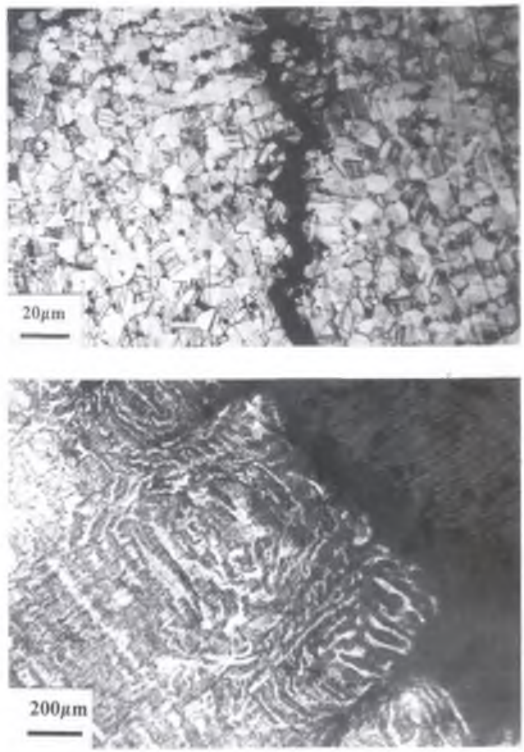

Fig. 7 Cracking due to low workability. (a) Internal cracking in experimental bronze with about 16% wt tin. Cold deformation as low as 17% led to internal cracking. The subsequent recrystallisation at high temperature (6000°C) led to the microstructure observed. The δ-phase eutectic was almost completely dissolved and the alloy recrystallised, but the crack persisted; (b) Deformation bands and cracking on the surface of an experimental bronze with about 7% wt tin, after 73% cold deformation. The low workability was due to the presence of 1.25% wt iron in the alloy.

13. J.A. CHARLES, "Early Arsenical Bronzes, a Metallurgical View," *AJA* 71 (1967) 21-26.

Comparison of Vickers hardness (HV) of the two basic metallic materials of the EBA in cast and cold formed condition		
	Copper	Arsenical Copper (2%-4% wt arsenic)
Cast metal	50-60	55-70
Hammered metal	100-120	150-160

Table 1

Alloying Element or Impurity	Copper (10 objects)	Arsenical Copper (24 objects)
Tin (Sn)	0.05	0.10
Arsenic (As)	0.05	4.33
Lead (Pb)	0.27	0.16
Iron (Fe)	0.10	0.15

Table 2

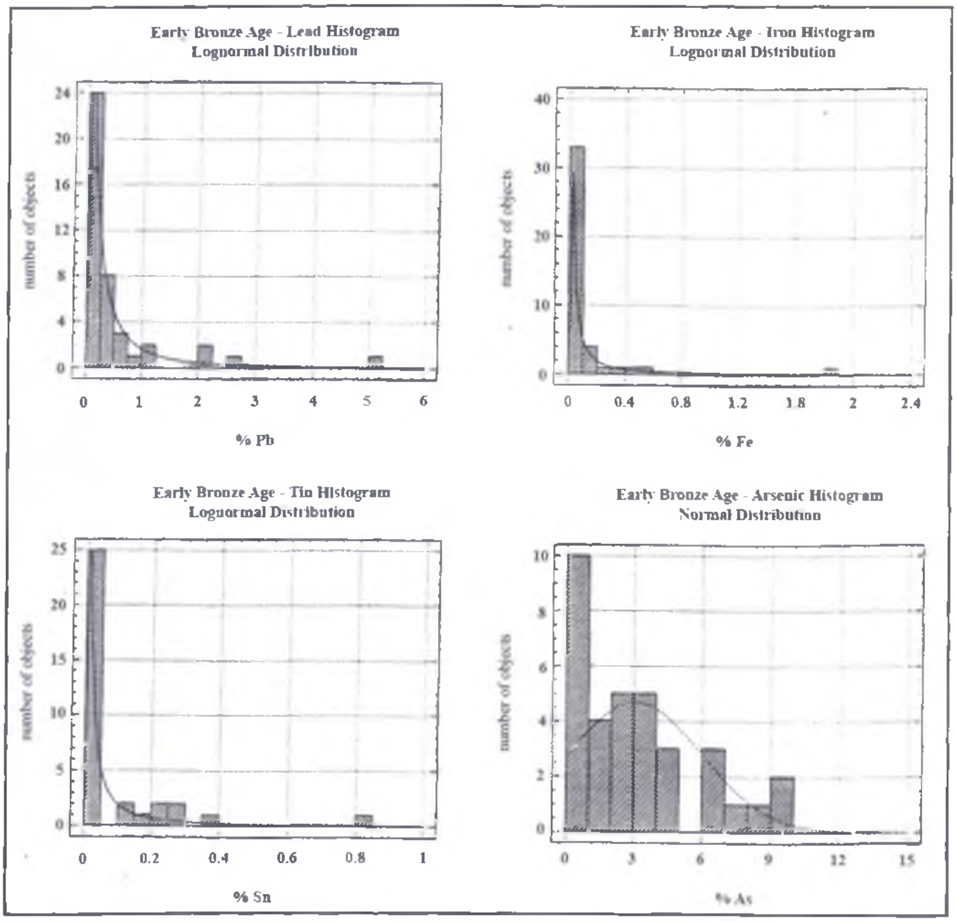

Fig. 8 Histograms of the elements Pb, Fe, Sn and As on a set of artefacts of EBA (taken from Papadimitriou, 2001a).

been shown in Fig. 2. On the other hand, arsenic contents up to 6% wt or 7% wt improve workability, so that the material can be work hardened by hammering without cracking to strengths almost equivalent to tin bronzes[14]. Less than 1.5% wt arsenic in copper does not appear to provide advantages over the use of copper-metal.

Unfortunately, in most collections of objects quoted in the literature only the chemical composition is given, whereas the art of fabrication (by casting or hammering) is not mentioned. This is apparently because an unambiguous distinction between cast and hammered articles requires metallographic examination. Archaeologists should consider in conjunction with chemical analysis both parameters, use and art of fabrication of an item, if they wish to facilitate the interpretation of a specific type of alloy for the manufacturing of specific articles.

However, even without sufficient metallographic evidence for arsenical copper, it is justified to agree that the metalsmiths of this period took advantage of these alloys by using forging and/or hammering, after casting. For example, the initial shape (model) of a dagger could be obtained by casting in a simple stone mould. Then the formation of the midrib, which requires extensive deformation while the metal remains in a plastic condition, could be carried out by forging. The cutting edges, however, which should be hard and wear resistant, had to be formed by local hammering, in order to take advantage of the strong work hardening occurring with arsenical bronze.

In a previous investigation,[15] based on chemical analyses of published bronze collections[16] the histograms of the main alloying elements and impurities of EBA coppers and bronzes were presented in Fig. 8.

From these histograms it emerges that 10 objects of the collection are made from copper without any arsenic addition, 17 objects have an arsenic content centred around 3 per cent (from 1% wt to 5% wt arsenic) and some alloys have even higher arsenic contents (from 6% wt to 10% wt). The average compositions (in wt %) of coppers and arsenical coppers are shown in Table 2.

From the present histogram on arsenic distribution, it appears that there exists a recipe (formula) of arsenical copper with 3% wt. As this composition is not accidental, since it was preserved in later periods.

Tin and lead are present as low level impurities with a mean value of about 0.10% wt and 0.20% wt, respectively, if we exclude some accidental values which are relatively high and should be attributed to insufficient control of the metallurgical extraction process. Iron, which is always an impurity in copper alloys, is also a low level impurity with a mean value of 0.13% wt.

The low level of impurities in copper and arsenical copper may be interpreted in terms of low temperatures and weak reducing conditions prevailing in the metallurgical furnaces, i.e., they may be considered as an indication of a primitive metallurgical process. The low impurity level is a net advantage for the stage of forming, because a low impurity level improves the ability of the metal to be forged or hammered without cracking.

During the Early Bronze Age, casting was the main technique used for metal shaping. Stone moulds for casting, open or bivalve, have been found in the Aegean islands. They were used mainly for casting of knives and axes. In Poliochni on Limnos a mould which was probably used for the casting of an axe with the lost wax technique was found.[17]

14. D. HANSON and C.B. MARRYAT, "Investigation of the Effects of Impurities on Copper, Part III the Effect of Arsenic on Copper," *Journal of the Institute of Metals* 37 (1927) 121-143; J.R. MARECHAL, "A Study of the Mechanical Properties of Arsenical Copper," *Métaux, Corrosion Industries* 33:397 (1958) 377-383.

15. PAPADIMITRIOU (*supra* n. 7).

16. C. RENFREW, "Cycladic Metallurgy and the Aegean Early Bronze Age," *AJA* 71 (1967) 1-20; P.T. CRADDOCK, "The Composition of the Copper Alloys Used by the Greek, Etruscan and Roman Civilizations," *Journal of Archaeological Science* 1 (1976) 93-113.

17. R. TREUIL, P. DARQUES, J.-C. POURSAT and G. TOUCHAIS, *Les civilisations Égéennes du Néolithique et de l' Âge du Bronze* (1989) 160-161.

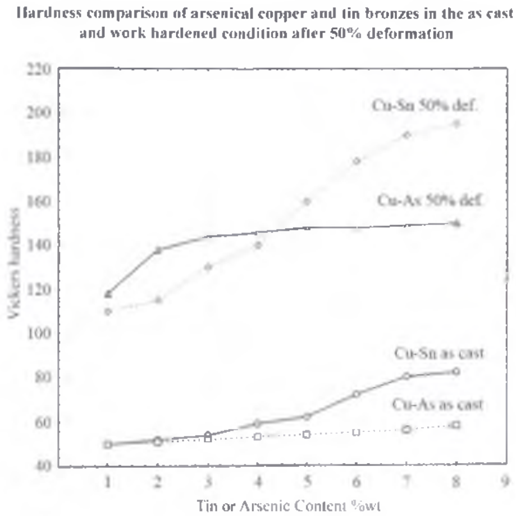

Fig. 9 Comparative diagram of hardness measured on experimental arsenical coppers and tin bronzes in the as cast condition and in the work hardened condition after 50% deformation.

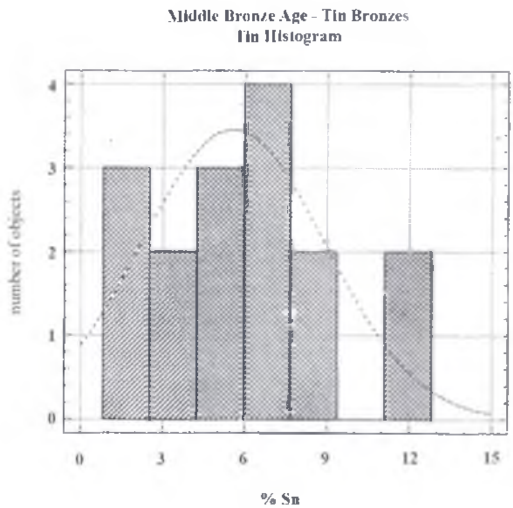

Fig. 10 Tin histogram on a set of artefacts of MBA (Papadimitriou, 2001a).

Hammering was not so far a fully controlled process and was mainly used for the purpose of finishing objects produced by casting. Hammering had not reached the status of an independent shaping technique for arsenical copper. although it was already a master technique for gold and silver. A possible explanation is that the production of thin sheets for the fabrication of vessels requires repeated annealing treatments for recrystallisation, but this is not quite convenient, since arsenic is an unstable alloy. Another possible reason is that both forging and hammering require a constant quality of raw materials, with controlled impurity levels, which had not been achieved up to that time frame.

5. Alloys and Forming Techniques in the Middle Bronze Age

During MBA. extending roughly from 2000 B.C. to 1600 B.C., arsenical copper progressively recedes and tin bronze becomes the prevailing metallic material. The advent of tin and its progressive substitution for arsenic could be associated with increased contacts of the Aegean peoples with commercial centers on the eastern Mediterranean coast, where tin was already available.

It is widely accepted by archaeologists that the MBA was a period of recession and instability and this condition is reflected in the relatively limited number of metallic objects found. This situation did not apparently interrupt metallurgical development, as tin bronzes present a number of advantages over arsenical copper.

As far as hardness is concerned. harder products can be produced with tin bronzes. This can be seen from Fig. 9. showing the hardness of tin and arsenical bronzes with increasing alloying content. in both the as cast and the work hardened condition. It is clear that tin bronze castings are slightly harder than arsenical bronze castings. but the difference in hardness becomes remarkable in the work hardened condition. For example. at 8% alloying element. cast tin bronze exceeds arsenical copper in hardness by only 20 HB (Brinnell hardness). whereas in the strain hardened condition (50% deformation) this difference becomes readily 40 HB.

In MBA agricultural tools are almost completely absent, although a variety of articles were produced, mainly tools and weapons, with the same technique as in EBA. Furthermore, the use of tin bronzes allowed new hammering skills to develop, so that the first long swords and vessels with thin walls appeared. This is due to the excellent formability of tin bronzes by hammering.

Tin bronzes are stable alloys, in contrast to arsenical copper. Arsenic evaporates as metal or as arsenious oxide during melting, heating or forging, leading to undesirable modification of the alloy. The vapours emanating have a characteristic smell of garlic and are highly toxic for the craftsmen. The legend of Hephaestus, the god of metalsmiths, being ugly and suffering with a limp, is certainly not irrelevant to diseases and malformations caused by the toxic action of arsenic on metalsmiths.

It is therefore reasonable to suppose that arsenical coppers were progressively abandoned as tin bronzes became available, since the latter presented net advantages for both metalsmiths and product users. However, arsenical copper did not disappear immediately, having co-existed with tin bronzes for many hundreds of years. Arsenical bronzes survive even in the Mycenaean period. Isolated cases of the Geometric period should however be rather attributed to recycling of old metals. The long persistence of arsenical copper leads us to believe that it was of local production and its use relied, despite its disadvantages, on a strong metallurgical tradition and availability of mineral resources in the Aegean.

In our investigation cited previously,[18] among the objects of the MBA statistically analysed, 68% were of tin bronzes, 20% of arsenical copper and 12% of copper, as shown in Table 3.

As it emerges, arsenical coppers do not contain tin and conversely tin bronzes do not contain arsenic, as if metalsmiths were specialised in work-

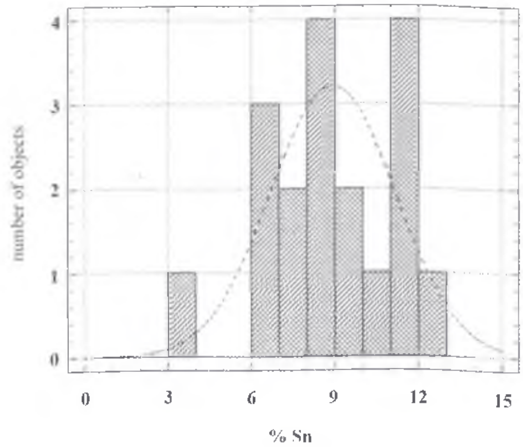

Fig. 11 *Tin histogram on a set of swords of LBA (Papadimitriou, 2001a).*

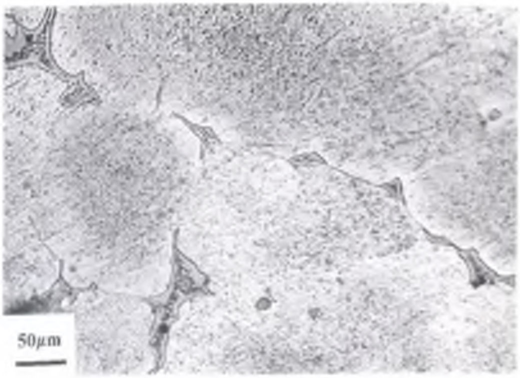

Fig. 12 *Experimental tin bronze with about 6% wt tin. A small quantity of eutectic is present on the grain boundaries. The fine precipitates within the grains is due to iron (impurity).*

18. PAPADIMITRIOU (*supra* n. 7).

Alloying Element or Impurity	Copper (3 objects)	Arsenical Copper (5 objects)	Tin Bronzes (17 objects)
Tin (Sn)	0.17	0.09	5.55
Arsenic (As)	0.17	3.60	0.48
Lead (Pb)	8.26	3.75	0.61
Iron (Fe)	0.49	0.16	0.13

Table 3

Alloying Element or Impurity	Tools and weapons	Swords	Statuettes
Tin (Sn)	6.55	8.92	2.95
Arsenic (As)	0.47	0.28	0.46
Lead (Pb)	0.69	0.25	3.21
Iron (Fe)	0.23	0.15	0.36
Nickel (Ni)	0.14	0.05	0.11
Silver (Ag)	0.027	0.04	0.027

Table 4

ing exclusively with either arsenic or tin as an alloying element, but never with both of them.

All classes of metals show good purity as in the EBA.

It is worth mentioning that some (cast) metal statuettes appear in this period. They are practically all of copper or leaded copper. The presence of lead is explained by the fact that it promotes castability and lowers the melting point of the alloys.

Arsenical copper seems to follow the recipe of 3% arsenic as in the EBA. It is now clear from the diagram of Fig. 9 that this composition was dictated by the fact that arsenical copper with 3% wt arsenic attains practically its maximum hardness, while higher arsenic contents do not further improve its strength, in either the as cast or in the as hammered condition.

Tin bronzes present a wide range of tin contents between 1% wt and 13% wt, suggesting metalsmiths vacillating and still unresolved as to which alloy composition to select. Most tin bronzes are in the range from 3% wt to 8% wt, which is not, however, the best choice from the technical point of view. These percentages are too low and could be considered as indicative of scarcity or a high price of tin. Looking at the tin histogram in Fig. 10, one can conclude that the usual and good recipes of 8% wt and 11% wt tin, which prevailed later from the Mycenaean to the Classical period, although essayed by the EBA metalsmiths, were yet not definitely adopted.

Finally, the MBA could be characterised as a period of experimentation, where the possibilities provided by three different alloying elements (arsenic, tin and lead) were a challenge to coppersmiths. However, the concept of impurity remained unknown.

As far as the shaping techniques are concerned, the novelty is certainly the development of hammering to produce thin sheets, as a result of the introduction of tin bronzes, which possess excellent cold workability, very effective work hardening and stability of the alloys in an unlimited number of annealing treatments.

6. Alloys and Forming Techniques in the Late Bronze Age

The LBA extends from approximately 1600 B.C. to 1150 B.C. and coincides with the period of Mycenaean domination in the Aegean and on the Greek mainland.

During this period the metallurgy of copper is in expansion and there is an astonishing variety of objects produced from copper alloys, including tools, weapons, everyday utensils, adornments, statuettes, etc. The Linear B tablets from Pylos refer to about 400 hundred active coppersmiths (*ka-ke-we* = *χαλκεῖς*), divided in several classes and depending on the King's court.

In the LBA ox-hide ingots, i.e., ingots with a special form weighing about one talent, have been found in excavations in Crete and other places. Chemical analysis of ox-hide ingots found in Crete[19] and in shipwrecks of 14th and 13th century B.C.,[20] found at Kaš and Cape Gelidonya, off the coast of Turkey, have shown that copper was very pure, with arsenic being the only significant impurity at a level of about 0.3% wt.

It is astonishing that similar ingots belonging to the EBA and MBA have not been found - probably because they did not exist. A possible explanation is that at those remote periods raw copper was available as small pieces and prills, since the metallurgical production scale was small. This would facilitate dividing and cutting the material into small pieces for melting purposes.

The main characteristic of MBA metallurgy is the good knowledge of the composition of the alloys and their corresponding mechanical and forming properties. It seems that alloys are divided into classes according to their alloying content and to different qualities according to their impurities. These grades are conveniently used for different metalworking processes, such as casting, forging, hammering, deep drawing, engraving, etc. Table 4 shows the main compositions of the alloys used for the fabrication of several different classes of objects.

The manufacturing of swords is the most demanding application, requiring both excellent mechanical and forming properties of the alloys. For this application, bronze with the minimum impurity content, in particular iron but also lead, nickel and arsenic, was used. High purity is required in order to obtain good forgeability and workability, as these properties are respectively crucial for shaping the long and thin blades of swords with their midrib and finishing their strongly work hardened edges. The main mechanical property required for the metal of swords is a high limit of elasticity, which is obtained by the high tin content.

Two different classes of alloys with 8% wt and 11% wt tin respectively were used, as can be seen from the histogram in Fig. 11. The 8% wt tin alloy is the most common bronze composition through the periods until Classical times, since it possesses very good properties without being particularly expensive, because of its lower tin content. It has a good limit of elasticity associated with a very good toughness and it possesses excellent workability. The specification of one part of tin to 12 parts of alloy, corresponding to 8.33% wt tin, is found on an inscription concerning poles for the construction of the Philonian Stoa at Eleusis. This inscription is exhibited at the Archaeological Museum of Eleusis.

The 11% wt tin alloy has an excellent limit of elasticity, i.e., it resists high loads before it is permanently deformed. This high tin content is, however, very unfavourable to the workability of the alloy and has to be associated with very pure materials and skillful hammering. The 11% tin content is the maximum allowed for cold forming (hammering). As a matter of fact, in the case of 11% tin, a hard and brittle intermetallic constituent (δ-phase) is present, which may cause cracks on the surface (see below section 7.2).

For the fabrication of weapons other than swords and for tools, a second quality bronze, with a lower tin content and with higher impurities was used.

Finally, for statuettes a low-quality bronze

19. N.H. GALE and Z.A. STOS-GALE, "Oxhide Copper Ingots in Crete and Cyprus and the Bronze Age Metal Trade," *BSA* 81 (1986) 81-100.

20. R. MADDIN and J.D. MUHLY, "Some Notes on the Copper Trade in the Ancient Mid East," *Journal of Metals* (1974) 24-29; R. MADDIN, "The Copper and Tin Ingots from the Kaš Shipreck," *Old World Archaeometallurgy* (1987) 99-105.

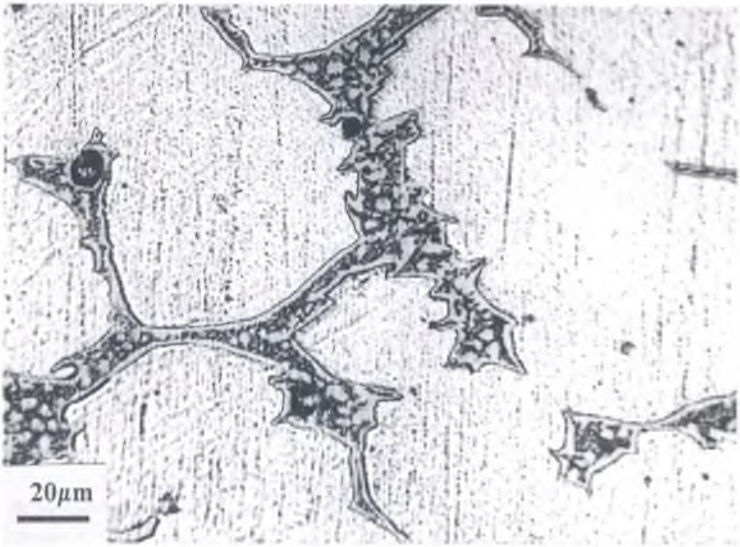

Fig. 13 High tin bronzes. (a) Typical cast microstructure of an experimental bronze with about 16% wt tin. A continuous network of δ-phase eutectic is present on the grain boundaries, making cold hammering impossible; (b) the same alloy after annealing at 6000 for 2 hours and subsequent quenching in cold water. The δ-phase has almost completely disappeared and the alloy is readily workable at room temperature as a low tin bronze.

was used. It came probably from recycling of old bronzes mixed with inferior-quality copper. Some lead was also added to improve castability. For the small statuettes of this period, however, where hollow casting was still not practised, not too much castability was required.

During this period both casting and hammering were independent shaping techniques, although they were usually combined.

7. The Effect of Alloying Elements

Although the main features of alloying elements have been quoted in the previous paragraphs, a more concise account of their effect on the copper alloys will be briefly presented in the subsequent sections.

7.1. Arsenic

The effect of arsenic on copper is not sufficiently known, as it is not involved in actual bronzes, except for contents only lower than 1% wt. In prehistoric alloys it was, however, present in percentages usually between 2% wt to 4% wt and sometimes as high as 8% wt or even more.

Arsenic discolours copper, giving to its alloys a lighter (white) colour at percentages even as low as 2% wt or 3 % wt.[21]

Arsenic is a useful deoxidising agent of copper, reducing the oxide content (Cu_2O), which is eventually formed during smelting or subsequent melting.[22] Lowering the oxide content improves the ductility and the workability of the alloys, which was very important for prehistoric metalsmiths.

Arsenical coppers have very good casting properties.[23]

The solubility of arsenic in copper is about 8% wt and it does not change markedly with temperature,[24] however, it is usually used at contents around 3% wt, since higher contents do not markedly improve its hardness.

Arsenical coppers can be both hammered and forged substantially without cracking.[25] Recrystallisation occurs in the interval between 300°C and 400°C or even higher.[26]

7.2. Tin

At the ambient temperature tin is regularly insoluble in copper, forming an intermetallic compound known as *δ-phase*. This is very hard and brittle, imparting brittleness to the alloy.

However, if the cooling rate after casting is not too slow, then tin may remain in solution for contents up to 7% wt - 8% wt (i.e., δ-phase does not form).[27] In usual practice, tin bronzes with maximum 8% tin may contain a small amount of δ-phase in the form of eutectic, which is not very harmful (Fig. 12). This explains the popularity of the alloy containing about 8% wt tin, as it is both hard and readily workable.

Tin contents above 8% wt lower the cold workability, so that the alloys require repeated annealings in order to be extensively deformed. This is because of the increasing amount of δ-phase, as tin content becomes higher.

Tin contents above 12% can be only hot formed. If one tries to hammer an alloy with more than 12% wt tin in the cold condition, cracking will occur even for low deformations. This undesirable effect is intensified if iron is present at contents above 0.2% wt.

Tin is an effective hardening agent in copper, for contents above 2% wt. To obtain an excellent limit of elasticity, tin contents between 8% wt and 12% wt are required.

Tin increases the castability of bronzes, lowering the melting point down to 950°C. Tin bronzes are, therefore, excellent alloys for rendering casting details and they are also used for

21. E.R. CALEY, "On the Prehistoric Use of Arsenical Copper in the Aegean Region," *Hesperia Supplement* 8 (1949) 60-63.
22. CHARLES (*supra* n. 13).
23. E. VADERS, "Neue Kupferlegierungen, besonders für die Herstellung von Gussteilen," *Zeitung der Metallkunde* 45/9 (1954) 528-533.
24. "Binary Alloys Phase Diagrams, in T.B. MASSALSKI, J.L. MURRAY, L.H. BENNET and H. BAKER (eds), *American Society of Metals* (1986) 197.
25. HANSON and MARRYAT (*supra* n. 14); MARECHAL (*supra* n. 14).
26. J.P. NORTHOVER, "Properties and Use of Arsenical Copper-Alloys," *Old World Archaeometallurgy* (1987) 111-118.
27. "Binary Alloys Phase Diagrams" (*supra* n. 24).

casting repairs. In the latter case, lead is usually associated with tin.

Increasing amounts of tin change the colour of copper from red to yellow and then to golden at 15% wt tin. This property was advantageously exploited in antiquity in order to imitate gold. These alloys cannot be cold worked, because of the presence of significant amounts of δ-phase. They can, however, be formed by forging at temperatures higher than 600°C, as at these temperatures the δ-phase dissolves in copper and the alloy becomes ductile.

In the classical times, alloys with about 15% wt tin imitating gold were formed to very complex shapes by hammering, using some special practice. It is not, however, known whether this practice was known in prehistoric times. A characteristic example of classical times is the *Derveni crater*, exhibited in the Museum of Thessaloniki. This crater was formed by hammering, although it contains about 14.5% wt tin.[28]

In order to resolve this problem, we have simulated the working of such bronzes in the Laboratory of Physical Metallurgy at the National Technical University of Athens and we have found that if annealing was carried out at 600°C and then the alloy was quenched, i.e., abruptly cooled by immersion in water, the ductile microstructure of the 600°C was preserved at the ambient temperature and the alloy could be cold worked equally well as a low tin content bronze. Figs 13 a and b show the microstructure of this experimental alloy in the as cast condition and after the heat treatment described. It is clear that the hard and brittle δ-phase, which is abundant in the as cast condition, has almost completely disappeared in the annealed condition.[29]

This procedure is referred to by ancient authors as *χαλκού βαφάς*, i.e., quenching of copper,[30] but it was misunderstood by ancient authors, who believed that copper was hardened by quenching, exactly as occurs with steel. On the contrary, copper becomes soft and ductile by quenching after annealing.

7.3. Lead

Lead is not used as an alloying element in alloys which had to be hammered or forged. In the case of these alloys, lead should be considered as an impurity.[31]

Lead is a voluntary addition in cast alloys, as it improves castability and lowers their melting point. However, its addition at high contents, say 20% wt to 30% wt, causes a very low strength.

Lead segregates markedly in copper and bronze alloys and may be concentrated in some parts of the castings by the action of gravity, when the cast alloy is still in a liquid state. For this reason, chemical analysis on samples taken from different places on an ancient bronze may result in quite different lead contents.

It is believed that lead was sometimes used instead of tin as a fraudulent addition, since it was an inexpensive alloying element.

Lead was frequently added to copper or tin bronze destined to repair castings, as the alloys become free-flowing and possess a very low melting point. They can therefore be melted and poured into cavities to be filled at a relatively low temperature, preserving the repaired object from local melting.

8. The Effect of Impurities

8.1. Iron

Iron is very often present in copper and bronze as a usual impurity.[32] It is practically insoluble in copper and bronze, forming a very fine dispersion of precipitates, which makes the alloy hard and brittle.[33]

The presence of iron is indifferent to casting. Iron may be tolerated up to 5% wt, as at higher contents it may considerably increase the melt-

28. G. VAROUFAKIS, "Metallurgical Investigation of the Derveni Crater," *Archaeologiki Ephemeris* (1981) 60-180.
29. PAPADIMITRIOU (*supra* n. 6).
30. Aeschylus, *Agamemnon* 612, Pollux, VII, 169, Pausanias II.3.3.
31. PAPADIMITRIOU (*supra* n. 7).
32. P.T. CRADDOCK and N.D. MEEKS, "Iron in Ancient Copper," *Archaeometry* 29/2 (1987) 187-204.
33. PAPADIMITRIOU (*supra* n. 6); PAPADIMITRIOU (*supra* n. 7); PAPADIMITRIOU (*supra* n. 6) 7.

ing point of an alloy and have an adverse effect on the castability.

Although high iron contents, even higher than 5% wt, may be found in cast objects of the Geometric period, in prehistoric times the iron content remains usually at low levels, rarely exceeding 0.5% wt to 1% wt.

In the case of forming by hammering, the presence of iron is truly harmful. It may be accepted up to 0.2% wt and marginally tolerated up to 0.4% wt. Iron is inconvenient even in the case of forging, since it delays recrystallisation, forcing the metalsmith to use higher temperatures, at which it is very difficult or impractical to work the metal.

The effect of iron on cold or hot formed objects may be manifested as cracks emerging on the surface or as other surface defects (Fig. 7b).

8.2. Lead

Lead is an impurity in alloys destined for hammering or forging.

The presence of lead decreases the ability of copper and bronze to be cold worked. In particular, in the case of tin bronzes, which work harden strongly and need repeated annealing treatments, lead is avoided because it liquefies, as is explained in Section 3 (unstable alloy), causing brittleness. The presence of lead is particularly dangerous when it forms a continuous layer on the grain boundaries. If it is uniformly dispersed in the alloy, it may be accepted at contents up to 0.2% wt - 0.3% wt, but this is not easy to control.

For the same reason it is an extremely indesirable impurity in alloys destined to be forged.

9. Conclusions

The great metallurgical movements in the development of alloys and their forming techniques during the prehistoric period in the Aegean region may be outlined as follows:

Early Bronze Age

- Invention of arsenical copper.
- Arsenical copper with 3% wt arsenic is the dominating composition.
- Use of arsenical copper similar to copper for fabrication of tools and weapons.
- Casting is the main forming technique.

Middle Bronze Age

- Copper bronzes are progressively substituted for arsenical coppers.
- Conscious selection of alloying additions.
- Arsenical copper with 3% wt arsenic remains the dominating composition for arsenical coppers.
- Bronze compositions with 8% wt and 11% wt tin appear, but do not prevail. Lower tin contents are preferred.
- Casting remains the main forming technique, but hammering begins to develop as a particular skill, because of the better workability and mechanical properties of tin bronzes. Fine wall vessels and swords, as well as statuettes, appear.

Late Bronze Age

- Concept of impurity.
- Selection of alloys according to both their alloying additions and impurities.
- Hammering becomes an independent forming technique.
- Tin bronzes with 8% wt and 11% wt tin.

Alloys dominating a certain period seem to be dictated by both social needs and existing technological progress. There was, however, a strong interaction between them, leading to further technological development.

Technological Questions

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