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ARCHAEOMETRIC STUDY OF IRON AGE COPPER ALLOY ARTEFACTS FROM SOUTH-EAST BULGARIA

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ABSTRACT. The metallurgy of copper alloys from the extraction of ores to the making of the end product is studied in compact area of South-East Bulgaria, situated between the upland of Chirpan, the Northern slops of the Eastern Rhodopes, the Bulgarian-Turkish state border, the Black Sea coast and the Southern slops of the Central and East Balkan Mountain. The chronological range of this research is from the beginning of VIII c. BC to the middle of III c. BC. An interdisciplinary method for determination of qualitative and quantitative composition of the studied artefacts – ICP-AES (emission spectrometry with inductively coupled plasma) was used. The artefacts are intentionally selected to be with different function – adornments, vessels and weapons. This gives the opportunity to clarify the different techniques of craftsmanship, applied in the period in question. The use of different alloys and techniques, allows to conclude that in the studied area during the explored period the metallurgy of copper alloy is on a very high level.

The present article is a result of the increased tendency for wider application of interdisciplinary research during archaeological investigations. The vast accumulation of bronze artefacts from the Iron Age, which is mostly a result of intensive archaeological investigations in Bulgaria, is well noted in the last decades. Their study so far concerns the following characteristics: manner of craftsmanship, time and place of production, function and parallels.

The most popular definition of bronze is that it is alloy of approximately 90% copper and 10% tin. In the different historic periods the composition of the bronze has changed, as various elements can enter in it. The earliest alloy of copper which contains arsenic is called arsenic bronze and is spread widely during the Bronze Age. Throughout the III mill. BC tin starts to replace the arsenic as basic alloy element, and prevails in the I mill. BC (at the end of this millennium brass starts to rival the tin bronze and predominates in the Roman period). One of the main reasons for this change is the improved properties of alloy as for example fluidity that gives opportunity for production of more objects in complex casts. It is argued that the increase of fluidity of the bronze is proportionally related to the amount of tin. The addition of large quantity of tin to the alloy influences the stability against corrosion. During the melting of tin poisonous vapours are dispersed that are harmful for ancient metallurgists.

The high percentage of tin worsens the mechanical qualities of the alloy and objects become friable. On the other hand, large amounts tin give the objects attractive golden colour and make the alloy suitable for production of adornments that successfully imitate gold. The tin bronze consist of several amazing properties that are not typical for other alloys. One of them is ability to indurate at slow cooling. Especially because of this property the moulds are made from rock or fired clay, where the proper conditions of slow cooling are ensured (Selimkhanov, 1970, 59-71).

The study area that includes compact region in South-East Bulgaria, is chosen mostly on the basis of origin of the analysed artefacts. To the West and South-west the border reaches the upland of Chirpan and the Northern slopes of the Eastern Rhodopes. To the South it is the state border between Bulgaria and Turkey and to the East the Black Sea coast. To the North, the study area stops at the Southern slopes on the Central Balkan mountain. During the second phase of the I mill. BC this territory is inhabited by the Thracian tribes of Odrysi, Nipsai, Kirmiads and others (Fol, Spiridonov, 1983, 105-107; Popov, 1999, 61).

The copper deposits in Bulgaria have various structural, mineralalogical, geochemical and genetic characteristics. Several types of deposits are classified according to their composition and morphology of the ore bodies: porphyry, vein, copper containing sandstones etc. Except copper they include other cardinal components as lead, zinc, arsenic, gold, silver etc. Gold and silver are accumulated in the oxidation zone and that explains the simultaneous extraction and exploitation of copper and gold in the past. The main copper deposits occur in mountain and hill areas formed in orogeny conditions of the Earth crust (Kovachev, 1994, 90-92). According to archaeological usually in the past the surface parts of copper deposits are extracted up to 20 m in depth (Cernykh, 1978, 58).

There are numerous deposits extracted in Antiquity in the studied area. In the vicinity of the village Gorno Alexandrovo, to the East of Sliven, copper minerals malachite, azurite, chalcosine, native copper and other minerals are found. The quantity of copper and arsenic in the ores is enormous and the amount of tin is higher in relation to other copper deposits (Kovachev, 1994, 103).

In the area of St. Iliiski Heights, situated to the South-west of the town Yambol, several copper occurrences are found: in Krysta (the village of Sokolovo), Tri Mogili (the village of Zlatarevo), Tekata (the village of Padarevo), Pepeliashka (Bojadjik), Chala Bair and Bakardjizata (the village of Mejda), Chervena Mogila (the village of Sokol) etc. The copper minerals malachite, cuprite, chalcopyrite as well as molybdenite are discovered. A copper deposit with main chalcopyrite ore is localized near the village of Madzharovo, district of Haskovo. There are deposits of azurite, malachite and chalcopyrite near the village of Iglika (Yambol district), Topolovgrad and the villages Lozen and Madzarovo (Haskovo district) which might have been used in Antiquity. An enormous copper porphyry deposit, consisting of malachite, cuprite and native copper, is discovered near the village of Prohorovo between Sliven and Yambol (Bonchev, 1920, 40). The copper deposits in the Strandzha Mountain are of a great significance – copper is discovered in huge quantities of slag as result of extraction, continuing for centuries (Georgiev, 1987, 27-37).

The main mineral for the other important component of bronze — tin, is cassiterite (SnO_2). This oxide is relatively stable and has high specific weight what makes it easily collectible in the sands along the river beds. Due to that reason it was extracted just like gold even probably being initialy treated as a waste material (Tylecote, 1976, 14).

The scientific literature distinguishes “natural” bronze from “artificial” bronze. The so-called “artificial” bronze was produced accidentally during the processing of copper ores, containing tin, and with time the qualities of the tin were appreciated and it had to be added intentionally to copper. It is considered that this alloy contains small amounts of tin (up to 2-4%) Despite that the natural bronze had preceded the artificial bronze in some regions, it was not recognized as a special alloy until the extraction of tin from its ore.

It is supposed that smelting of ores was performed in immediate proximity of the areas of extraction and in the form of ingot the metal was transported to the production centres. All deposits were usually situated in mountain or hill areas that provided sufficient supply of timber as fuel. The settlements were protected from polluting gases, dispersed during the smelting of ores (Giumlia-Mair, 2003, 23).

The smelting of ores was performed in furnaces that were not built of enough refractory materials but had to resist the high temperatures during this process. Shortly after their use, the furnaces were completely destroyed under the impact of flux, climatic conditions and components of ores (Giumlia-Mair, 1998, 35-50).

The next stage of the metallurgical process is the refining of the copper. After the initial reduction process the crude copper contains many admixtures such as arsenic, antimony, sulphur etc. Air blowing is necessary to purify the metal and during that process the unwanted substances oxidize and are removed either as gas or flow out in the form of a slag. For example lead, arsenic and antimony evaporate while iron, nickel and zinc pass into the slag as silicate phases (Trifonov, 1966, 28-29).

Normally this procedure was carried out in the workshops but not in the places where the ore is melted and melting-pot furnaces are used for that purpose. It is considered that their involvement in the metallurgical processes mark one more advanced state of development. The furnaces are large in size and consist of two parts, separated by a fire-grate with small apertures through which the heat access is better provided. The pots lie on the grate and above fire, sustained with timber and coal. The presence of blowers is not obligatory because this stage of the metallurgical process do not require such hard reducing conditions. Usually these structures remind ceramic furnaces (Forbes, 1958, 74-75; Tylecote, 1976, 16-17).

In the present work 41 bronze artefacts are studied that are kept in the National Archaeological Institute and Museum in Sofia, the Regional Historical Museum in Yambol, the Historical Museum in Nova Zagora and the Historical Museum in Sliven. The analyzed objects have various features depending on their function: ornaments (fibulae, bracelets and beads) (Fig. 1), vessels (Fig. 2), weapons (shield) and some with unclear function (bands and sticks). All of them are made by different technique – casting or hammering. The study of different parts of one object – orifices, walls, bottoms, handles, is an advantage. The archaeological finds have a wide chronological range from the Early Iron Age to Late Iron Age (VIII-IV c. BC). The majority of the objects are found in burial complexes, pits or are stray finds.

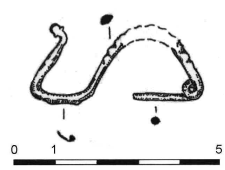

Fig. 1. Bronze fibula from Bogdanovo, Nova Zagora (Historical Museum, Nova Zagora)

Fig. 2. Orifice of bronze hydria from Novoseletz, Nova Zagora (Historical Museum, Nova Zagora)

The study of the artefacts includes determination of the origin of raw materials, chemical composition, type of the crystal structure, probable beginning of the use-life and its duration, etc. This complex analysis is difficult to perform because of several objective circumstances as shortage of funding, laboratorial equipment and skilled staff. In the present research ICP-AES (atomic emission spectrometry with inductively coupled plasma) method of chemical analysis is used, whitch determines the qualitative and quantitative composition of alloys, used for the artefacts. The advantages of this quantitative method are its sensitivity to many elements and that it is relatively fast. Its main shortcoming is that it is destructive and requires dissolution of the sample. The samples are taken by drilling of a 1.5 mm diameter hole or by breaking off a small piece. The neccessary amount is 10-15 mg. The samples are dissolved in Aqua Regia (36% hydrochloric acid and nitric acid in proportion 3:1), boiled in a sandy bath and then the real measurement was taken.

The investigated artefacts mark some important trends that concern the production of metal objects in ancient Thrace and especially in South-East Bulgaria. The qualitative and quantitative characteristics of the used alloys testify for a pronounced trend of purposeful selection of materials that depend on the function of the objects and their manner of manufacture. It was established that the alloy for artefacts, made by casting, has over 2% lead that facilitated the liquidity of the bronze. The artefacts made by hammering have a minimum amount of lead because of the possible cracks that may appear with the hitting. The amount of tin depends on function of the artefact. For example, for fibulae is used alloy with 8-10% up to 12% tin because of the necessary high elasticity, while to receive the perfect bronze for hammering alloy with 4-6% tin is used (Fig. 3). The amount of arsenic is imperceptible. This means that exceptionally clear bronze has been used, consisting mainly of copper and tin. Older artefacts which may contain arsenic have not been used. This fact indicates a very high level of development of trade and especially supply of the necessary quantity of raw material. The geographic characteristics of the region that put it in one of first places for copper deposits support such development.

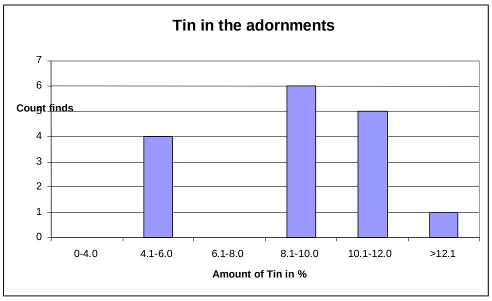

Fig. 3. Tin content in the studied artefacts

Unfortunately the problem of extraction and supply of tin did not find its solution in the Bulgarian specialised literature as well as in the European literature. Some of the artefacts have also an increased amount of antimony. However, these artefacts did not origin from a single area, they are from the entire studied territory. An explanation for the increased percentage of this element could be the fact that some of the ores from the Srednogorie area (the village of Prohorovo, Nova Zagora District) contain tetrahedrite. Chronologically these artefacts are quite different to provide more general and verifiable conclusion. It is important to note that the findings from the Sakar Mountain and its vicinity, together with the discovered moulds for bronze axes and boat fibula from the Late Bronze Age and the Early Iron Age, confirm the determination of this area as a metallurgical centre during the Late Iron Age. With special meaning is the fact that there are no considerable differences in the composition of artefacts from the second phase of the Early Iron Age and those from the Late Iron Age up to middle of III c. BC. This means that there are no noticeable differences in the technology of producing of bronze alloys during both periods and therefore the chemical composition can not be a factor of chronological determination.

In conclusion, it should be noted that serious study of the metallurgy in a certain area during a particular period is impossible without the application of physical and chemical analyses of raw materials and end products. Only in this way the entire picture of economic life could be restored, and in particular, the metallurgy in South-East Thrace. The present work made an attempt to promote the trend in a wider application of examination of the composition and manner of craftsmanship of metal artefacts.

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