Chemical, lead isotope and metallographic analysis of extraordinary arsenic-rich alloys used for jewellery in Bronze Age Armenia

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In this paper we discuss chemical compositions, lead isotope ratios and results of metallographic analysis of some copper based alloys extremely rich in arsenic (15.8-27.6 wt%) and touch upon technological aspects of producing of such an extraordinary alloy. Several pieces of high arsenic alloys from Gegharot and Lori Berd were subjected to chemical, lead isotope and thorough metallographic analysis using optical and scanning electron microprobe (SEM) in the Curt-Engelhorn-Centre for Archaeometry in Mannheim, Germany.

The presence of high arsenic concentrations in decorative objects in the Bronze Age of southern Caucasia has repeatedly been noted by many scholars and is a topic of ongoing discussions. But some recently studied metal objects have even higher As concentrations, much beyond average the arsenic content of the usual arsenical copper alloys.

A possible reconstruction of the necklace of EBA Gegharot consisting of 99 metallic (total weight 144.5 g), 88 chalcedony and 217 talc beads (Hayrapetyan, 2005) is shown on Fig. 1A. The EBA-LBA settlement of Gegharot was excavated by an American-Armenian expedition (Smith et al, 2004). In the necklace three types of alloys were identified Meliksetian et al. (2007): It turned out that double voluted beads consist of arsenical copper with 4.6-6.1% As, the conical and spherical teardrop-shaped beads consist of leaded arsenical copper and finally, the cylindrically shaped and barrel-shaped beads are made of a copper alloy with extremely high As contents between 15.8% and 19.4%. These beads are mainly characterized by a gray, “silvery” colour, sometimes with a yellowish, “bronze” shade. We assume that the ancient craftsman used differently coloured alloys to give the necklace an extraordinary, “precious” appearance. Lead isotope analysis of EBA objects of the necklace of Gegharot demonstrates considerable variations in lead isotope abundance ratios for the different alloys. Particularly the Cu+As alloys are clearly different from Cu+As+Pb ones. Therefore, we assume that more than one ore source was used for the production of these alloys.

Microscopic examination of one of the high arsenic beads of the necklace of Gegharot revealed a eutectic microstructure, which is responsible for the silvery gray colour of the beads (Fig. 1B). The microstructure of the leaded beads is a dendritic α_{Cu}-solid solution with some interdendritic Cu_3As and scattered lead globules.

Three exceptional bimetallic objects (Fig. 1C) were excavated from the “Royal” tomb 29 of the Lori Berd cemetery by S. Devejian and date back to the 12th century BC, following the periodisation scheme-for the Bronze Age Armenia by Avetissyan, et al. (1996). This age corresponds to the end of the LBA and the beginning of the Early Iron Age (EIA). One of these objects is a button, another a massive ring (or bracelet?) and the third object is probably a part of a sceptre. The ring consists of two metals, namely tin bronze with 11 % tin and leaded arsenical bronze with a mean arsenic content of 25% and 1.2% lead. The microstructure of the silver coloured arsenic rich part consists of dendrites of tin bearing α-solid solution and the interdendritic α_{Cu} + Cu_3As eutectic. Lead is precipitated at the interfaces and tiny non-metallic inclusions consist of copper sulphides (Fig. 1, D). The microstructure is homogenous and thus different from the microstructure of the Gegharot beads whose bulk composition is less than the eutectic composition due to the high volume fraction of non-metallic phases.

The arsenic contents of the objects from Lori Berd range between 24 and 28 wt%, the highest ones reported as yet for any ancient object. So far “only” 18-21 wt% As were reported for few small beads from Maikop (see Ravich & Ryndina, 1995).

Thus, the metallographic investigation of metal artefacts from Gegharot (EBA) and Lori-Berd (LBA-IA) revealed that the high arsenic concentration is not a result of inverse segregation arsenic rich phases or of any surface enrichment, as it was suggested for many silvery colored copper objects with much lower (2-8 %) content of As (e.g. Giumlia-Mair, 2008 with references).

Considering the fact that arsenic is extremely volatile element that is in the gas phase at the melt-

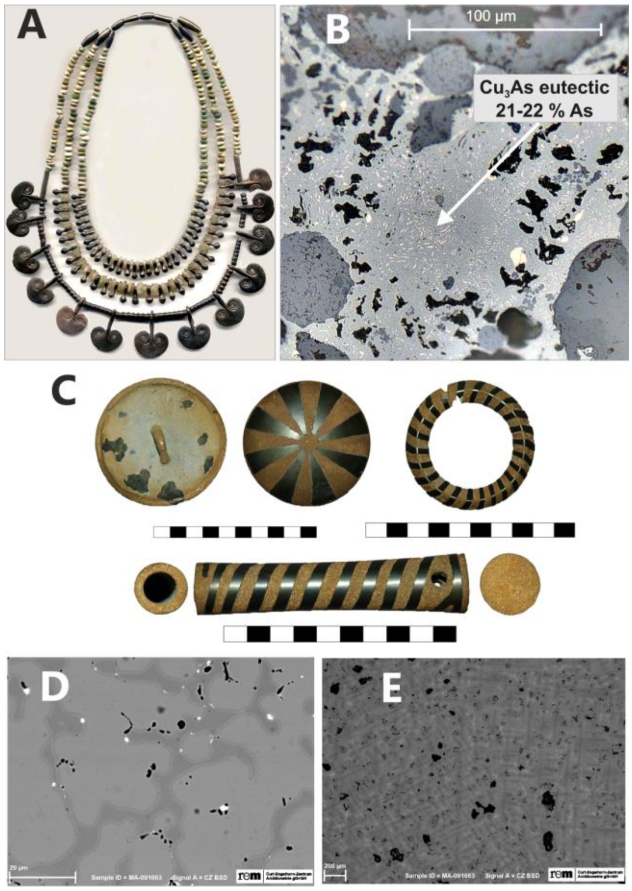

Fig. 1: A. A possible reconstruction of the necklace of EBA Gegharot. B. Optical bright field micrograph of Gegharot object showing α_{Cu} +Cu_3As eutectic with Cu_2S and cavities. C. Bimetallic object from the Royal tomb 29 of Lori Berd: big button, Massive ring (bracelet?) and part of scepter. D. Backscattered scanning electron image of the arsenic rich part of the Lori Berd object showing dendritic tin bearing solid solution with interdendritic α_{Cu} +Cu_3As eutectic. E. Backscattered scanning electron image of the tin bronze part as cast.

ing point of copper (1085°C). Thus, the production of Cu-As alloys is certainly a problematic task. Although the temperature of the eutectic in the Cu-As system is much lower (685 °C for melt containing 21% As) it is nevertheless much higher than sublimation point of As (615 °C), so that ancient craftsmen must have used an advanced smelting technology to produce such unusual alloys.

Besides difficulties associated with the production of high arsenic alloys, ancient craftsmen solved another complicated technological problem in order to implement the design idea and produce such nice looking bimetallic objects (Fig. 1 C). These objects seem to consist of interlaced tin and arsenic bronzes and are certainly not the result of “gilding” or thin appliqué. For instance, the massive ring (bracelet?) looks like an interlaced “rope” made of two almost equally thick but differently coloured “threads”. One possible explanation may be that the tin bronze part was casted first and then the copper-arsenic alloy later cast on. The fact, that the melting point of tin bronze with 9-10 % Sn is remarkably higher (about 850 °C) than the melting point of the eutectic Cu-As alloy (685 °C), strongly supports this assumption.

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