It's complicated: an experimental approach towards understanding dark patinated copper alloys from the Eastern Mediterranean Bronze Age

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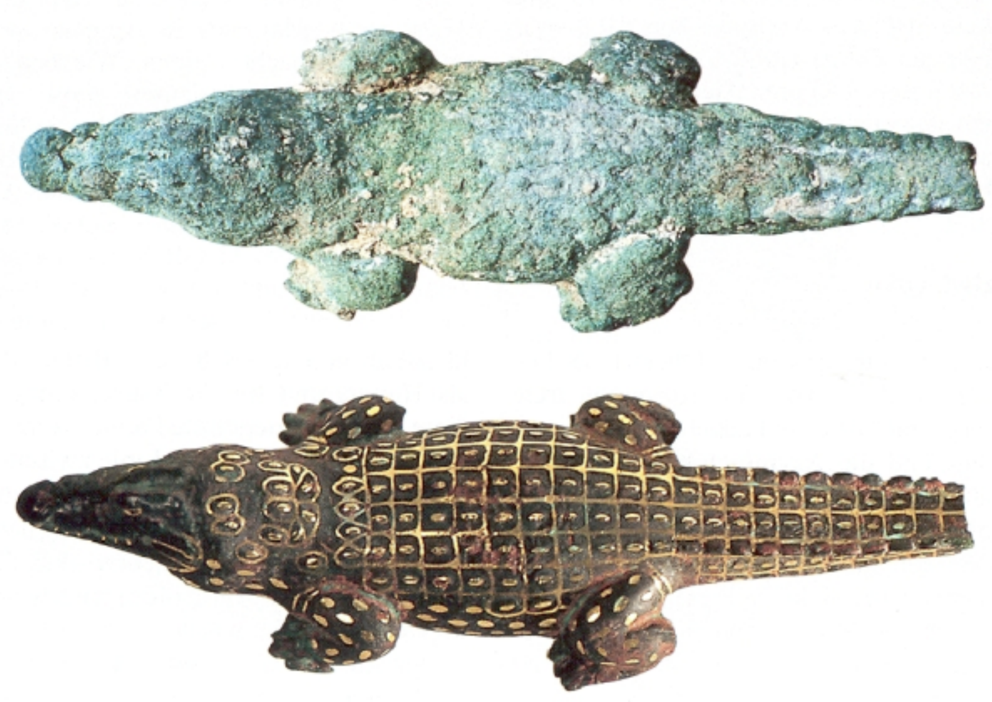
(Results from MA-Thesis Ruhr University Bochum 2015)

<Mycenaean dagger in private collection, ca.1500 BC (after Craddock& Giumlia-Mair 1993,p.20, fig. 9)

Alloy 7



The el-Faiyum crocodile statuette ca.mid 19th ct BC (Giumlia-Mair 2012, Fig. 7a, 7b.)

The Sword of Balâța-Sichem > (Palestine), second half 2nd Mill. BC. (Müller 1987, adjacent of titelpage)

Alloy 1

Introduction

Dark patinated copper alloys appear in several time periods worldwide and are typically applied in objects interpreted as prestigious, such as ceremonial weaponry, statuary and fine polychrome art. They are characterized by minor amounts of gold (Au) and often also silver (Ag), arsenic (As), iron (Fe), tin (Sn) and other trace elements in their matrix, whereas their patinas are constructed out of the copper oxides cuprite and tenorite.

Their patinas vary in colours from black to blue and purple, and only after a considerable thickness will they appear green (Giumlia-Mair 2013, 98-105). It has been suggested that arsenic (and iron) lends the patina an iridescent finish, an effect that perhaps motivated prehistoric artisans to use specific ores or compositions (Giumlia-Mair & Lehr 1998).

The Bronze Age alloys from the Eastern Mediterranean show a striking resemblance to a similar alloy in the Roman period (Corinthium Aes), that in turn has familiarities with an historically documented Japanese alloy (Shakudo) that is known since the 12th century AD, but after further development now only consists of fine copper and gold(Craddock&Giumlia-Mair 1993, Oguchi 1983).

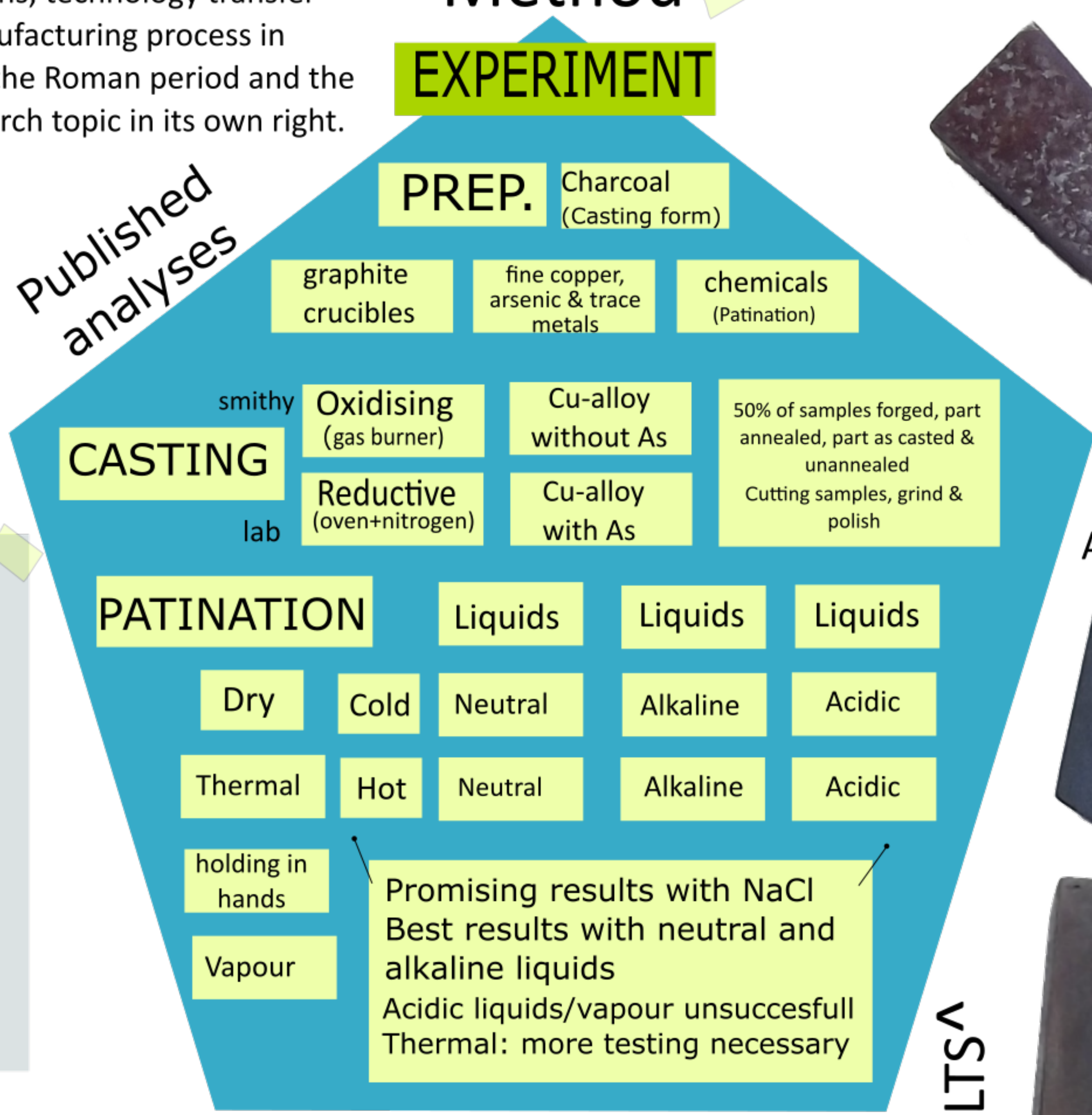
The diachronic occurence of similar alloys with similar prestige is intriguing, and poses questions about independent innovations, technology transfer and craft traditions. Little is known about the manufacturing process in prehistoric times, with only vague descriptions in the Roman period and the complex and secretive Japanese method is a research topic in its own right. Presuming that similar materials will behave in similar ways, the Japanese process was a starting point in the experiments, as an analogy to search for similar agents and processes that are feasible for the Bronze Age and as a baseline to investigate colour variations in the patinas.

Subsequently, SEM was used to exclude those samples where no cuprite or tenorite was formed.

Research objectives

- Investigate possible production sequences
- Test colour range of patina on alloys with variable composition
- Build on previous research
  - Test claimed iridescence effect of arsenic
  - Contribute towards a reference collection
  - Test notions of regenerative properties of the patina (from prehistoric alloys)

Method



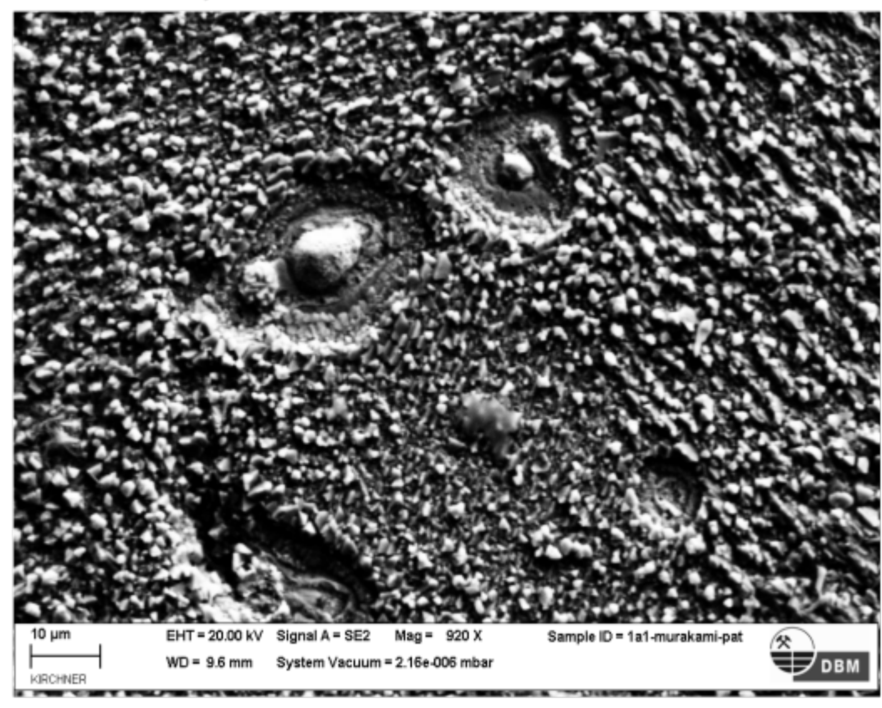
N.B.The japanese patination sequence is a combination of acidic, alkaline and neutral (PH 5 to 5,5) agents, brushing with charcoal between sessions and covering with a type of radish (alkaline). (See Gowland 1915, 92, O'Dubhghaill & Jones 2009, Uno 1929.)

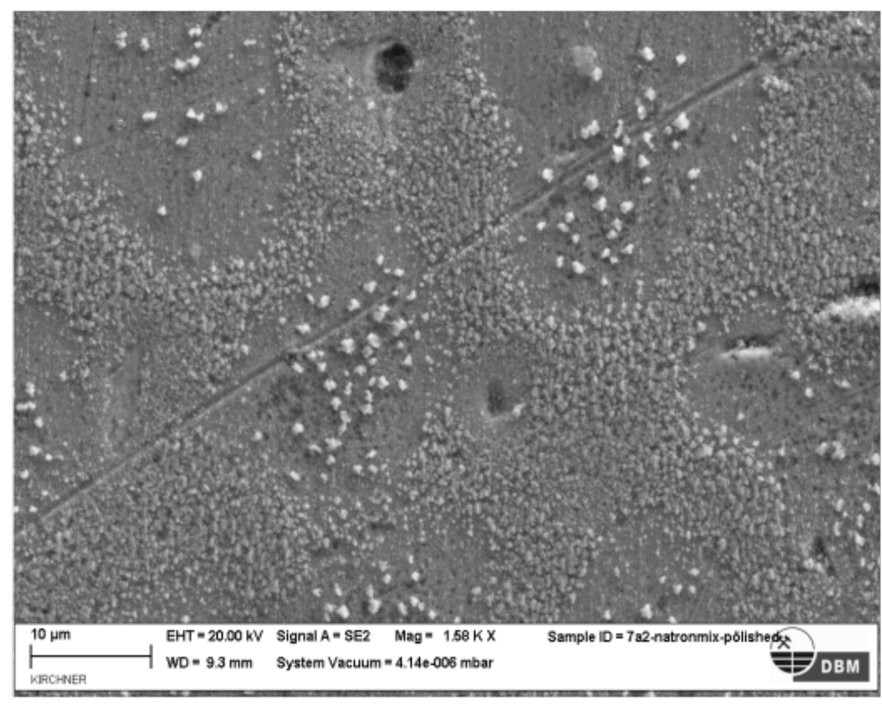
Quantification of produced alloys with ICP-OES (Dr. M.Bode, DBM)

Quantification of patinated samples with SEM (D. Kirchner, DBM)

A problem with Ag (present in large crystals bound with As) due to a polymetallic eutectic and and with Fe due to its high melting temperature was detected, but overall the produced alloys represented similar compositions to the original analyses.

Alloy 1





Alloy 7

< Alloy 1 from a similar Japanese patination method as the top but this recipe included NaCL (and the SEM image showed small crystals). The second SEM image (Alloy 7) shows small cuprite crystals from a natron mixture mimicking that occuring in Wadi Natron. It was never pure, but included NaCl+ sodium sulphate and sodium carbonate. The analyzed sample (Alloy 7) is pictured next to it.

Pure natron was ineffective. Publication planned in 2017.

The produced alloys

Out of the total of 8 alloys, 4 were created based on results from published archaeometric analyses of archaeological objects. 3 alloys were copies of these omitting the arsenic and 1 alloy was based on previous experiment (Giumlia-Mair & Lehr 1998, Giumlia-Mair & Lehr 2003.)

The recipes approximating the archaeometric results of Mycenean Dagger (Alloy 7, Ogden 1993, 42; Giumlia-Mair 2013, 100) and the Balâța-Sichem sword(Alloy 1, Giumlia-Mair 1996, 340) are as follows:

Alloy 1: 91,8% Cu, 0,5 % Au, 0,2% Ag, 0,5% Fe, 0,5 % Pb, 3,1% As, 3% Sn, 0,1% Zn, 0,1% Ni, 0,15% Bi, 0,05% Co.

Alloy 7: 92,5% Cu, 2% Au, 0,5% Ag, 5% Sn.

* The chemical agent seems to be more important than the composition of the alloy to promote the growth and density of cuprite crystals - smaller crystals = darker colour, bigger crystals = purple /violet. Different results with similar temperature and time duration, but different patination recipes

* Some of the samples containing arsenic and iron were iridescent, but some weren't: it's possible that contamination creates iridescence

* Thermal experiments not conclusive, more testing merited - tenorite layer unstable, perhaps due to inexperience? Perhaps better adhesion with oil

* The regeneration seems slower for Bronze Age alloys than Shakudo - more testing!

* Supports observations of the effect of salts in Corinth (Caley 1941), and merit more investigation and experimentation (*N.B. objects in that paper contained no Au/Ag)

The author thinks collaboration to be most productive and seeks to work with goldsmiths, material scientists, and those active in experimental archaeology and metallurgy.

An example of the Japanese Mokume Gane technique with the black Shakudo alloy (96%cu, 4% Au). (made by author in 2005)

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