Journal of Archaeological Science 57 (2015) 130–141

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Focus article

Artificial patination in Early Iron Age Europe: an analytical case study of a unique bronze artefact

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A R T I C L E I N F O

Article history:
Received 14 April 2014
Received in revised form
19 January 2015
Accepted 24 January 2015
Available online 17 February 2015

Keywords:
Artificial patination
Tenorite
Early Iron Age
Bronze axe
X-ray diffraction analysis
Micro Raman spectroscopy
FT-IR spectroscopy

A B S T R A C T

Direct evidence for the intentional patination of metal objects is difficult to ascertain and therefore studies concerning this technique are controversial. Only a couple of objects with artificially patinated surfaces have been positively identified, ranging in date from the early 2nd millennium BC to Roman and medieval times. In this paper a skillfully crafted and coloured Early Iron Age bronze axe belonging to the Villanova culture of ancient Italy was selected for examination. Optical microscopy and multiple mineralogical analyses of the surface of this object demonstrate that it was patinated deliberately by a thermal treatment technology (thermal patination). So far, this Iron Age axe is the oldest European object where this technology had been applied.

1. Introduction

The seminal research of Giumlía-Mair and Craddock (1993) provided empirical evidence that ancient metal craft specialists intentionally manipulated the colourful appearance of metal through various chemical treatments. In particular, metal objects from the Mediterranean region with metallic inlays – sometimes referred to as damascenings made of alloys named *corinthium aes*, *kuwano* or *ḥmty km* – are often quoted to have been patinated artificially. This is suggested because of their dark surface layers and the rather weak colour contrasts between the metal bases and inlays. The most prominent examples having artificial surface layers are the Bronze Age daggers and vessels from the Mycenaean shaft graves and other Greek locations. In addition, a large corpus of Egyptian and Roman artefacts with metal inlays has been identified as intentionally patinated in the last decades (Craddock, 1982; Giumlía-Mair and Craddock, 1993; Giumlía-Mair, 1996a; 1996b; Giumlía-Mair and Riederer, 1998; Mathis et al. 2007, 2009; Aucouturier et al. 2010; Giumlía-Mair, 2012).

Besides their characteristic patinas, the copper alloys of these objects have distinct compositions. Often the metal inlays or bases contain appreciable amounts of gold and silver (from 0.5 up to 3 wt.%) which in case of gold clearly exceed natural impurities of copper. In fact, it has been shown that copper–gold (-silver) alloys readily develop dark purple or blue to nearly black corrosion crusts of cuprite (Cu_2O) with a high lustre and adherence when treated with chemical solutions (*e.g.* acetic solutions with copper salts) or simply when held in hand for some time (Giumlía-Mair and Lehr, 1998, 2003; van Bellegem et al. 2007; Craddock et al. 2009; O'Dubhghaill and Jones, 2009). Since minor gold concentrations neither change the colour of copper nor its casting and mechanical properties (Berger, 2012a, 24–26) this behaviour is taken as the main, yet not undisputed (*cf.* Jacobson and Weitzman, 1995) line of evidence to explain how past metal smiths used artificial patination technologies on these kinds of objects.

Less unambiguous are black coloured copper sulphide patinas. Well-known objects with this kind of patination are the Hellenistic bronze sculptures and pieces of furniture found off the coasts of Riace, Italy, and Mahdia, Tunisia. Their surface layers are smooth and blue black and consist of different sulphide minerals (Formigli, 1985; Willer, 1994; Eggert, 1994). Because of their appearance, composition as well as manufactural details some authors suggested that such patinas reflect deliberate colouring treatments (Zenghelis, 1930; Formigli, 1985; Willer, 1994; Garbassi and Mello, 1984, 176–179). Although it was easy for ancient people to

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http://dx.doi.org/10.1016/j.jas.2015.01.025
0305-4403/

achieve such sulphide containing patinas (*e.g.* with sulphur or egg yolk), there is still a controversy amongst scientists whether the surface layers developed from the intentional actions of past metal smiths or result from natural corrosion in anaerobic environments (Schwab et al. 2008, 20–21; Quaranta, 2009, 107–110). Such conditions are often observed in underwater sites and waterlogged soils (Tylecote, 1979, 352; MacLeod, 1991; Schweizer, 1994).

Similarly controversial is the intentional patination by thermal treatment. Several ancient metal objects from Egypt show characteristic patination patterns that were likely produced by controlled annealing in order to serve as aesthetic oxide layers. Mohamed and Darweesh (2012) assembled a group of Egyptian bronze artefacts without deliberate gold alloying, including statuettes, situlas and plaques, which possess superficial black patinas, too. The authors demonstrated that the patinas of many of these objects consist of black copper oxide tenorite (CuO) together with cuprite (Cu_2O) and secondary corrosion products which distinguish them from black patinated copper–gold alloys (Giumlía-Mair, 2000). The authors assumed that thermal patination (annealing with scale production) was the most likely colouring procedure in all cases because large quantities of tenorite almost exclusively develop during the heating of copper or copper base alloys (Mohamed and Darweesh, 2012, 184; Scott, 1997, 96–97). Natural corrosion in soils seldom produces traces of this mineral under highly alkaline conditions (Nord et al. 1998). Without knowing the details of the depositional context, the site formation processes and the object's life history, it is, however, impossible to rule out accidental events. For example, site conflagration or cremation could also theoretically stimulate the formation of tenorite. Despite this possibility it is more likely that the patinas on the Egyptian examples are the result of intentional application.

Currently no other Bronze or Iron Age object outside Egypt has been identified with similar patination treatments. However, there are two black patinated examples from the Roman Empire with tenorite. They have initially been investigated by Mathis (2005, Fig. 72, 163–164), but later on Aucouturier et al. (2010) confirmed them to be treated thermally deliberately at around 600 °C. In contrast to the Egyptian items, one of the two Roman objects has copper inlays in a bronze base. This appears fairly unusual because during prolonged heating at temperatures of 500 °C or above the alloying elements from the metal base (especially tin) might migrate into the copper inlays and potentially cause the formation of irregular and undesired seams. Therefore, the reconstruction is somewhat doubtful in this case, even though deliberate thermal treatment was also suspected on an inlayed antique bronze mask in the British Museum (Jenkins, 1993, 299).

The above examples demonstrate the difficulties associated with determining the original surface colour on ancient metal artefacts. On the one hand, it is all but impossible to identify exactly those objects amongst the large quantity of prehistoric metal finds that were actually deliberately patinated. In many cases green coloured natural corrosion crusts conceal original produced patinas lying underneath. In addition, present patinas, especially on older finds, may be inauthentic and merely the product of modern restoration. On the other hand, artificially grown mineral phases often cannot be distinguished from natural corrosion products because almost the same species form during intentional patination and long-time burial. One important exception is the black copper mineral tenorite that rarely occurs under burial conditions because its formation is kinetically impeded relative to the ubiquitous cuprite (Scott, 2002, 95; Quaranta, 2009, 19). If circumstances like conflagration can be ruled out, the presence of tenorite thus appears to be a good indicator for the deliberate colouring of metal surfaces by thermal treatment. This paper utilises this framework to examine in detail a conspicuously coloured Early Iron Age winged axe from the collection of the Museum für Vor- und

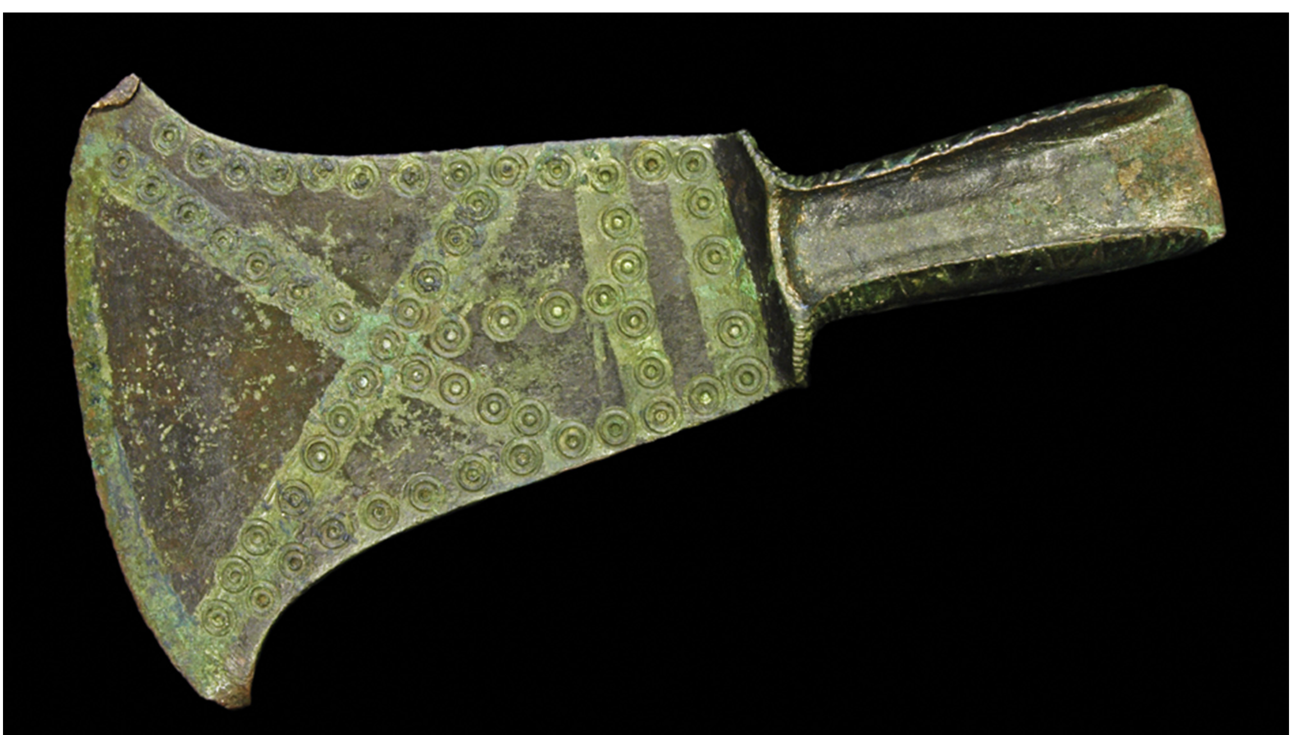

Fig. 1. Front face of the winged axe from the Museum für Vor-und Frühgeschichte Berlin, Germany. The back face is decorated in almost the same way. Total length 178 mm (photo: D. Berger).