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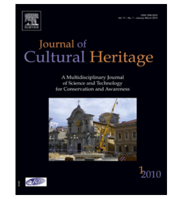

Original article

Meteoritic origin and manufacturing process of iron blades in two Bronze Age bimetallic objects from China

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ABSTRACT

It is widely accepted that meteoritic iron was the first iron alloy used by mankind, however, the manufacturing processes of the earliest iron artefacts remain uncertain and sometimes disputed. Here, we present both chemical and microanalytical results of samples from two bimetallic objects from Bronze Age central China. It is confirmed that the blades were made of meteoritic iron. In-situ photomicrograph and detailed microanalysis provides solid evidence for the cast-on and hot-work processes. We also demonstrate that significant information can be extracted through multiple analyses despite the severely corroded condition of ancient iron objects.

1. Introduction

Notable numbers of early iron objects have been reported from Bronze Age contexts in the Near East, Egypt and the Eurasian Steppe prior to the appearance of iron smelting in these regions [1–4]. Meteoritic origin is generally suggested for the iron used, especially when the artefacts contain nickel, despite the alternative possibilities of telluric native iron, the by-product of copper smelting, and smelting of nickeliferous ores [2,5,6]. The sporadic occurrence of iron blades on bronze weapons during the late 2nd millennium BCE in central China was identified as early use of meteoritic iron [7–9]; this bimetallic technology persisted with the replacement of meteoritic by smelted bloomery iron once iron smelting started in central China around the 8th century BCE [10–12].

Discriminating criteria combining both chemical composition and microstructure for the identification of meteoritic iron in archaeology have been proposed by Photos [5]; and recent non-invasive analyses of several famous items from ancient Egypt have revealed valuable information regarding their material nature and manufacturing technology [13–15]. It was proposed that the experience of hot-working meteoritic iron was essential for the development of iron metallurgy, which produced metal in a solid-state [14]. This seems even more plausible in the context of Bronze Age China given the long-standing tradition of cast bronze. Due to the scarcity and inevitable corrosion of ancient meteoritic artefacts, however, robust data, especially metallographic information reflecting their manufacturing history, are still limited. The manufacturing techniques of ancient meteoritic iron artefacts have therefore remained uncertain and sometimes disputed [13,14]. On the basis of detailed scientific analytical results, this paper confirms the meteoritic origin of two bimetallic artefacts' iron blades; and also sheds new light on the perception of hot-work processing of similar ancient meteoritic iron items.

2. Material and methods

Located at a loess mound named Shangcunling, about 600 meters from the northern bank of the Yellow River in Sanmenxia city, Henan province, the Guo State cemetery is one of the most important Zhou sites in China [16,17]. Among numerous objects recovered during the excavation in the 1990s, a total of twelve bimetallic weapons and tools were unearthed from two well-preserved very large tombs containing bronze ritual vessels. Two of the twelve were retrieved from tomb number M2001 and the other ten from M2009. These two tombs were assigned to *Guo Ji* (M2001) and *Guo Zhong* (M2009) according to the inscriptions found on the bronze vessels; both were kings of the Guo State, and lived in the Western-Eastern Zhou transition period around the 9th to 8th centuries BCE [17]. Previous research on six bimetallic

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Fig. 1. Photograph of bimetallic knife (upper) and *Ge* blade (bottom).

items had revealed that both meteoritic iron and smelted bloomery iron were used to produce the iron blades, indicating their particular significance for research on the beginnings of iron metallurgy in central China [18]. Recently, corrosion fragments from two bimetallic objects, a knife and a *Ge* blade (Fig. 1, Supplementary material, Fig. S.1) in M2009 were collected and scientifically analysed, revealing crucial information about their material nature and manufacturing technology.

The samples, which had notable magnetism despite of their severely corroded condition, were mounted and polished to a 1.0 μm finish. Metallographic observation was carried out on a Leica DM4000M optical microscope. Samples were then carbon coated and examined using scanning electron microscopes (SEM, Hitachi S3600N and FEI Quanta 250 equipped with Bruker XFlash6) and an electron probe microanalyser (EPMA, JEOL JXA-8230) in wavelength-dispersive mode for high quality electron imaging and chemical composition. Operating conditions for SEM-EDS were an accelerating voltage of 20 kV and a work distance around 10 to 15 mm. For EPMA, the conditions of an accelerating voltage of 20 kV, an absorbed electron current of approximately 1×10^{-8} A and a spot beam diameter of 1 μm were used. The measured intensities were quantified against pure metal/alloys or compounds using JEOL's ZAF correction procedure. Chemical compositions presented are normalized to 100%.

3. Results

The photomicrograph of sample SGT002 from the knife (M2009:710-2, Fig. 1, Supplementary material, Fig. S.1) shows clearly the conjunction of two materials (Fig. 2a). While the metallographic structure of the embraced iron is severely distorted by corrosion, the surrounding bronze part is properly preserved. The remnant α solid solution dendrite matrix together with interspersed (α + δ) eutectoid display a typical metallographic structure of as-cast bronze (Fig. 2b), being consistent with its chemical composition derived by EDS analysis, which shows a relatively high tin concentration due to the selective corrosion and dissolution of copper.

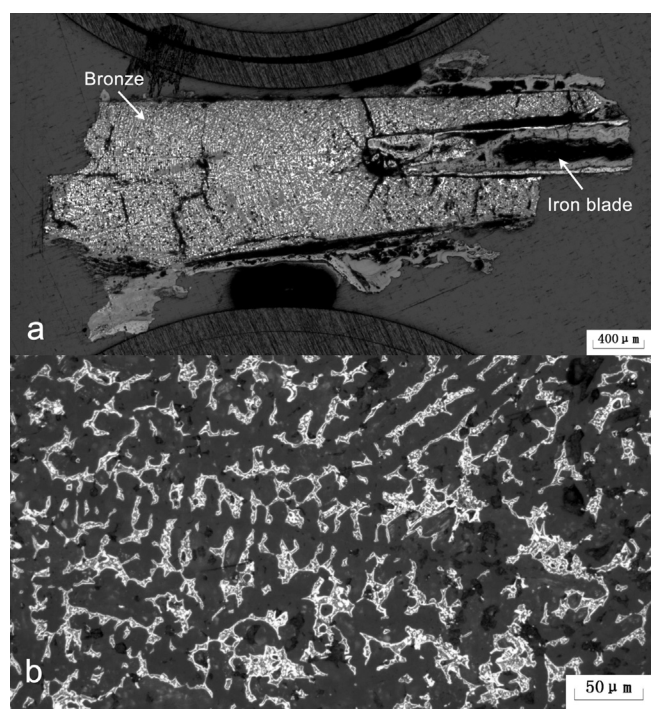

Fig. 2. Photomicrograph of sample SGT002 showing the conjunction of iron blade and bronze handle (a), which retains an as-cast metallographic structure (b).

The iron part of SGT002 is substantially corroded with numerous particles of remnant metal displaying bright twists and kneaded belts in a dark matrix of weathering products in a backscattered