Archaeo-metallurgical analysis: metallurgy in the early medieval societies of Moghalmari, West Bengal, India

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Archaeo-metallurgical studies on early medieval Bengal trace, the history and development of metalwork. West Bengal, as an integral part of eastern India, has an ancient tradition of iron technology, as indicated by the metal objects obtained from various archaeological sites. All materials collected from these archaeological sites in West Bengal prove that the ancient alchemy and metallurgical science practised in the region were vast and rich. The detailed description of metallurgical processes and intricate properties of minerals and chemicals in the 10th-11th century alchemy-text, Rasaratna Samuchchava, is yet another proof of the high level of knowledge on metallurgy. Metals have a close relationship with human civilization, and the phases attributed to different stages of cultural growth are dominated by the metals being used at a particular period. Metal objects found in various early medieval sites of West Bengal provide a unique opportunity to study the development of metalworking fashion and technology. Several excavations and explorations have been conducted to study the societal structure and material culture of this period. The study of metal technology also provides information on cultural development and craftsmanship. The present study involves scientific analysis of metal objects (bronze) obtained from the culturally rich archaeological site of Moghalmari in West Bengal. X-ray diffractogram which revealed the composition of the materials. Scanning electron microscopy was used to analyse the microstructure of the sample. The results provide information regarding the purity and composition of the metal.

Keywords: Ancient metals, archaeo-metallurgy, early medieval sites, human civilization, scientific analysis.

ARCHAEO-METALLURGICAL analysis is associated with materials science and metallurgical engineering studies. It deals with copper smelting, bronze crafts, copper–bronze alloying technology, as well as metal and mineral transaction. In the present study, from the site of Moghalmari, West Bengal, India, several artefacts have been excavated like pottery, stucco images, terracotta objects, stone objects and bronze objects, which reveal the human activities and culture of ancient times. This study focuses on bronze content, aiming to determine the material handling and processing techniques used in the ancient period¹.

Objective of this study

The key aim of this study was to analyse the materials using various techniques such as X-ray diffraction (XRD) to determine their structure. The microstructure of samples collected from excavated sites can also be examined using a scanning electron microscope (SEM). The results of numerous experiments on the extracted samples provide information on their purity and coherence.

Study area

This study was conducted at the excavated site of Moghalmari. The site was initially excavated by the Department of Archaeology, University of Calcutta, Kolkata and later by the Directorate of Archaeology and Museums, Government of West Bengal. The village of Moghalmari (21°57'N and 87°16'E) is located in the district of Paschim (West) Medinipur's Dantan police station. On national highway no. 60, the village is about 5.2 km north of Datan town and 46 km south of Kharagpur railway station. The Moghalmari archaeological site is on the left bank of the Suvarnarekha River, which now flows about 4.5 km west of Moghalmari. Bronze sculptures are one of the important types of artefacts which have been collected from this archaeological site. Figure 1 a shows the archaeological site of Moghalmari where excavations have been done and the sample collected².

Description of collected metal sample

The present analysis was conducted using a small portion cut-off from the corner of a collected bronze sculpture.

Initially, these were in a corroded condition. The bronze had been converted to oxide after coming in contact with the oxygen in the surrounding air, which was evident from the greenish colour of the sculpture. Due to heavy corrosion the sculpture had become brittle and required careful

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Figure 1. a, Archaeological site of Moghalmari, West Bengal, India. b, Excavated bronze sculpture from Moghalmari.



Figure 2. Sample collection process.

handling. Figure 1 b shows one of the bronze sculptures collected from the archaeological site at Moghalmari.

Methodology

The excavated bronze samples from Moghalmari were subjected to limited metallographic analysis. For the test, a small portion from the corner has been taken. For scientific analysis, XRD, optical microscopy (OM), SEM and SEMenergy dispersive X-ray analysis (EDX) were used.

Scientific analysis

A small portion of an excavated bronze sample was taken for limited metallographic analysis. Figure 2 shows the steps involved in the sample collection process.

The specimen was first subjected to XRD to ascertain the material composition. The experimental results confirmed that the metal was bronze composed of mostly copper (Cu)

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Figure 3. X-ray diffractogram results produced in the laboratory.



Figure 4. SEM-EDX results of bronze sample in etched condition.

and tin (Sn). The bronze sculpture was made by rural artisans of the early medieval period. The study revealed the presence of the Cu–Sn phase, but the exact identification of the particular phases needs to be done. Traces of copper oxide (Cu₂O) indicate the corroded natural element of the sample as well as the oxide slag of copper.

Figure 3 indicates the presence of Cu–Sn and Cu₂O. Since XRD analysis has certain limitations such as absence of standardized reference data set, SEM-EDX was used to better understand the structure of the sample. Figure 4 and

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Figure 5. Area implication for SEM-EDX analysis for (*a*) area 1 and (*b*) area 2.



Figure 6. Segregate presence of tin shown in SEM-EDX analysis.

Table 1. Weight percentage of composition	
Element	Weight (%)
Copper	79.8
Tin	9.07
Iron	3.16
Nickel	2.14

Table 1 show the elements present in the bronze sample. SEM-EDX sample revealed a small volume of iron and nickel in the sample, in addition to copper and tin. However, the SEM-EDX microchemical study revealed only limited information regarding the main element, i.e. copper and minor elements like tin, nickel and iron.

Composition

The SEM-EDX results suggested a copper alloy with only a small number of elements. The inclusion of nickel and iron in the specimen lent more weight to the bronze sculpture. Results showed that the wt% of copper was high, whereas it was low for iron and nickel. The latter two elements were doped in the parent material to give the sculpture more strength and stability. Figure 5a shows the area of the specimen on which SEM-EDX was done. In the second stage of analysis, another area was selected for another set of operations.

Figure 5 *b* shows the second area in which another set of analyses was done. SEM-EDX identified tin as a segregated element. This may be due to the presence of some extraction elements of residual material from the sample. It is well known that tin and nickel could have originated from the primary ore of Eastern Indian chalcopyrite. This is the most important copper ore, since it is a copper–iron sulphide mineral. The chemical formula of chalcopyrite is CuFeS₂ and it crystallizes in a tetragonal system. It is brassy to golden yellow in colour and has a Mohs hardness of 3.5-4. It also has a distinctive green-tinged black streak.

In the bronze sample, the limited amount of iron indicates a successful copper refining extraction technology, as the iron had been almost completely removed during freezing (Figure 6).

Cu–Sn phase diagram

Under slow heating or cooling, phase diagrams demonstrate the relationship between the existing phases, alloy structure and temperature. Slow heating or cooling causes the atoms inside a metal to move and achieve equilibrium, resulting in a stable alloy. The Cu-Sn alloy phase diagram gives the structural morphology of the material at a particular alloy percentage and a particular temperature. Figure 7 is a phase diagram indicating the percentage of Cu-Sn on the X-axis and the temperature at which casting was done on the Y-axis. The SEM-EDX results reveal that the weight percentage of Sn is 9.07, indicating a β -phase. In this β -phase, the metal structure of the element should be face-centred cubic (FCC). There are eight atoms at the corners of the unit cell and one atom centred at each of the faces of the FCC arrangement. The face atom is shared with the cell next to it. Four atoms make up an FCC unit cell, consisting of eight corners with 1/8th of an atom in each of its corners and

the six faces of the unit possessing half of an atom on each of its side.

Atomic packing factor

The atomic packing factor (APF), also known as packing efficiency or packing fraction in crystallography, is the fraction of volume in a crystal structure that is occupied by constituent particles³. It has a value of less than one. By convention, the APF of atomic structures is calculated by assuming that the atoms are solid spheres. The radius of the sphere is set to the highest value, which prevents the atoms from overlapping. The packing fraction of one-component crystals (those containing only one type of particle) is defined mathematically by







Figure 7. Phase diagram of Cu-Sn.



Figure 8. Cross-sectional image of face centred cubic structure.

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Figure 8 shows the position of atoms in the FCC structure. Bronze is a substitutional solid solution composed of copper and tin atoms. In this substitutional solid solution, copper is the solvent and tin is the solute (Figure 9).

A substitutional solid solution is a mixture of two kinds of atoms in which one type of atom can be substituted for the other. In this study, the copper atom can be substituted by tin atoms.

Optical microstructural image analysis

In next phase of analysis gives a clear idea about the microstructure of the specimen.

Figure 10 a shows the optical microstructural image in unetched conditions with equiaxed grains of copper alloy. Dendrite-like crystals can be seen that resemble a tree-like structure. This proves that the metal had been cast without further forging treatment, signifying the low efficiency of the casting process.

Figure 10 *b* shows an optical microstructural image in etched condition. The reddish (alpha) copper grains are found in primary metallography readings; Cu–Sn solid solutions are also seen with slag entering the grain. This slag makes the copper alloy weak.

Structural analysis using scanning electron microscopy

The optical microscope has a limitation for this reason SEM can be applied for the detailed analysis of the sample.

Figure 11 shows SEM images of the sample with a white zone present in the microstructure in etched condition. A rough dendritic pattern can also be discerned from the overall metallic component. However, there are too many non-metallic materials, which do not reveal much about casting process.

Conclusion

This study highlights the use and composition of bronze prevalent in the early medieval century. Alloy materials like bronze, which is a mixture of copper and tin, were preferred in ancient times. XRD analysis revealed the presence of



Figure 9. Position of atoms.

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Figure 10. *a*, Unetched condition of microstructure of the sample. *b*, Etched condition of microstructure of the sample.



Figure 11. SEM image of the sample.

both iron and nickel, which contributed to the strength of the structures. People were able to construct an FCC crystal structure even in the early era, as evident from the sample belonging to the site of Moghalmari. In the early medivel time, people, people not only knew how to melt metal objects, mould and cast them, but they were also quiet excellent at it⁴. The microstructural analysis indicates a dendrite-like crystal structure, suggesting that the casting process was less effective than modern technologies. SEM analysis showed the presence of non-metallic components in the sample, indicating that they lacked thorough casting process. The inefficient casting process and the presence of nonmetallic components led to the brittle nature of the metal⁵. It may be inferred from the present study that though people of the 9th-10th centuries were not skilled in the casting method, they could effectively make a sculpture using the casting process to achieve the perfect form and scale.

In conclusion, the present study has thrown a considerable amount of light on the culture of the early medieval era, with the scope significant for future research using archaeometallurgical analysis.

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ACKNOWLEDGEMENT. I thank Prof. (Dr) Durga Basu (formerly at Department of Archaeology, Calcutta University) for guidance and Dr Utpal Maity (Research Scholar, Jadavpur University) for providing vital information regarding this work.

Received 3 June 2021; revised accepted 2 September 2022

doi: 10.18520/cs/v124/i2/226-230