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STUDIES ON ANCIENT INDIAN OCP PERIOD COPPER

R. BALASUBRAMANIAM*, M.N. MUNGOLE*, V.N. PRABHAKAR**
D.V. SHARMA** AND D. BANERJEE**

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The material of construction of an ancient Indian ochre colored pottery (OCP) period (2650BC - 800BC) anthropomorphic figure has been characterized by optical and scanning electron microscopy, and microhardness measurements. The green surface patina was analysed by X-ray diffraction as a mixture composed mainly of cuprite and minor amounts of malachite and brochantite. The copper possessed a highly heterogeneous grain structure consisting of equiaxed grains (of size 30-40 μm) and entrapped second phase particles of spherical shape. The identification of equiaxed grains with straight annealing twins, coring and the spherical shape of the inclusions indicated that the anthropomorphic figure has been cast to shape without any further working operation. The relatively low microhardness (65 to 80 kg/mm^2) of the sample further confirmed that the sample was a cast structure. Local compositions from several different locations in the metallic matrix and the entrapped inclusions were obtained using an electron probe microanalyzer. The composition of the metal was almost pure Cu, with minor impurities of C and Sb. The major elements identified in the second phase particles were Cu, Pb and S, which indicated that these particles were sulphides. The presence of these sulphides has been discussed in with respect to the Cu extraction process.

Key words : Anthropomorphic figure; composition, copper; microstructural characterization; OCP period; patina.

* Department of Materials and Metallurgical Engineering, Indian Institute of Technology, Kanpur 208 016.

** Archaeological Survey of India, Agra Circle, Mall Road, Agra 282 001.

INTRODUCTION

The copper hoard implements have been discovered all over India over a fairly wide area, the concentration of these are of course found in Bihar and western Uttar Pradesh[1]. Ochre colored pottery (OCP), first identified by Lal during his excavations at Hastinapur[1], has been found in the same stratification as the copper hoards[2], thereby placing these copper hoards with the OCP period. Bharadwaj places this period between 1100-800 BC[3], while thermoluminescent dates on several OCP sites indicated a time bracket from 2650 BC to 1180 BC[4]. The copper hoards usually contain implements like celts, hatchets, harpoons, spearheads, antennae swords, rings, anthropomorphic figures, etc. Of the numerous copper hoard objects recovered from different North Indian sites, the so-called anthropomorphic figures are more distinctive and significant[5]. An analysis of the discoveries indicate that copper anthropomorphic figures along with harpoons occur in western Uttar Pradesh only.

The identification of copper hoard implements to a distinct group or tribe or community is still elusive. There are several theories associating these copper hoards to traces of Indo-Aryan migration, to refugees of the Harappan civilization, Central Indian tribes, hoards originated in Bihar and then spread to the west, etc.[1,6,7]. Although the weapons and implements found in these hoards could be explained based on their functional aspect, the proper identification of antropomorphic figures has been difficult due to the limited number of such figures discovered. Before the discovery of anthropomorphic figures reported in the present study, only fourteen copper anthropomorphic figures were known to the scholarly world[5], of which two were mere fragments. Therefore, the discovery of 31 anthropomorphic figures in 2000 AD from an agricultural field near Madarpur village, Thakurdvara tehsil, Moradabad district in Uttar Pradesh assumes enormous significance. The photographs of six of of these anthropomorphic figures are provided in Fig. 1 (a) (three are currently at the National Museum). The leg portion of the figures was less conspicuous. The leg portion has been indicated stylistically and only two projections were seen at the base with a concave formation in between. This could be

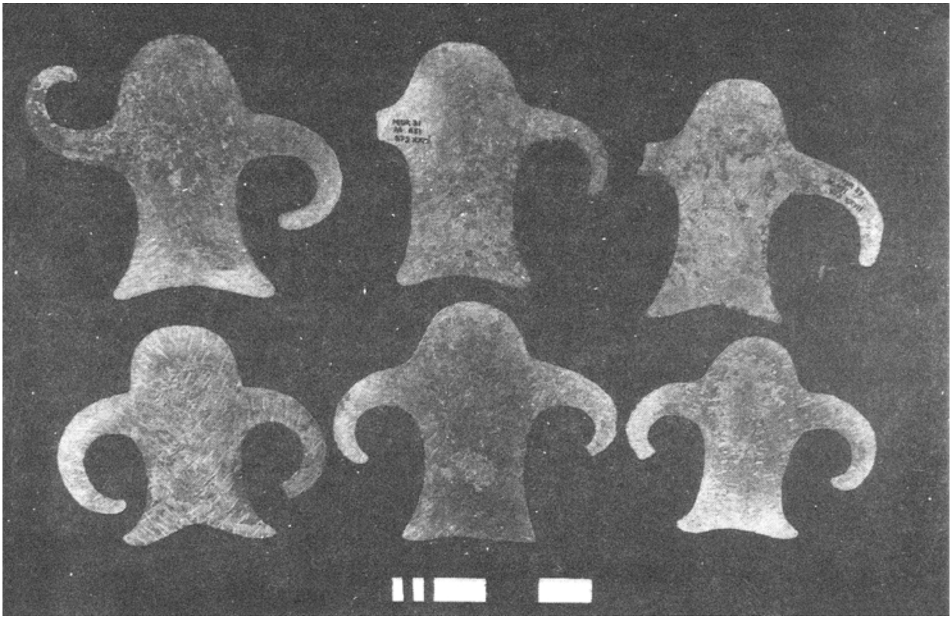

Fig. 1 Photographs of six of the 31 discovered anthropomorphic figures.

the representations to indicate a seated cross-legged human. All the 31 anthropomorphic figures are shown in a similar seated posture. Two of the figures were found with their right hand raised above, the posture indicating *abhaya-mudrā* in which Hindu deities are generally depicted. The present discovery was also the first instance that only anthropomorphic figures in such large number were found in a single spot.

Two of the authors (VNP and DVS) also examined the find spot of the discovery of the copper figures. OCP could be collected from an area of nearly 200m x 200m. A small trial pit, in an area of 2m x 2m, was dug adjoining the find spot. The trial dig also revealed the presence of OCP in a thin layer of nearly 5 cm in thickness. Moreover, considerable amount of OCP could be collected from all the exposed area of the field. The OCP compared well with that from other sites in terms of color, fabric, nature and peeling of color from the surface. The discovery of the 31 copper anthropomorphic figures has provided scope for study of OCP and copper hoards afresh. The aim of the present study is to characterize the material of construction of one of the anthropomorphic figures and to obtain insights on its processing methodology, from a metallurgical viewpoint.

EXPERIMENTAL PROCEDURE

A broken arm of one of the figures was utilized for the analysis, Fig. 1(b). The object (broken arm) was curved and the thickness was approximately 3 mm. The object was covered with a relatively thin light green scale. In order to understand the nature of the scale, X-ray diffraction (XRD) patterns were obtained from the surface in a Rich Seifert X-ray diffractometer using Cu Kα radiation. The pattern were analyzed in order to obtain insights on the surface scale nature.

A small portion of material was sectioned from one corner of the specimen (Fig. 1b) and two sections were prepared from the sectioned material for metallographic analysis, one parallel to the surface and another per-

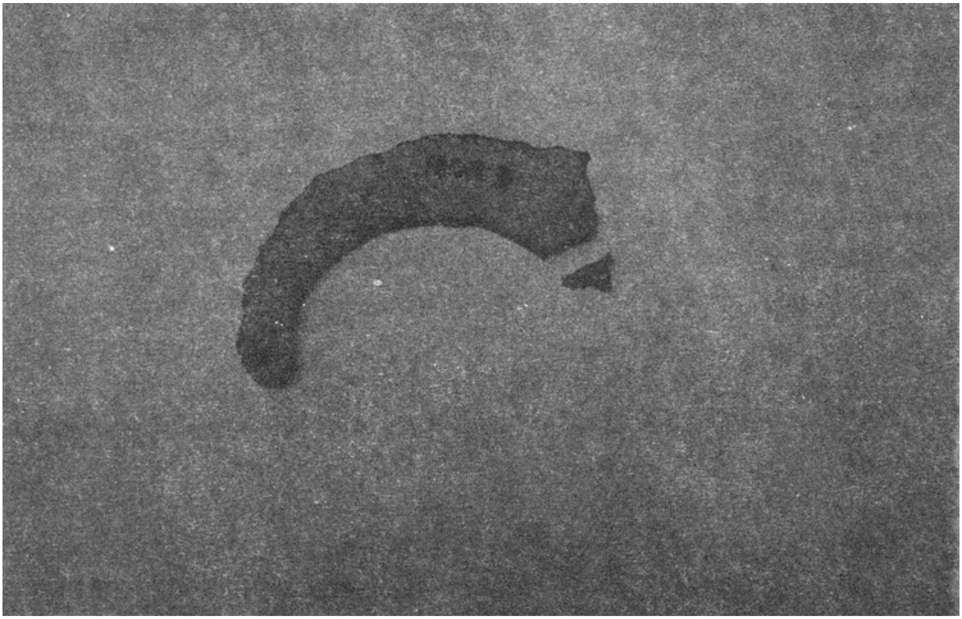

Fig. 1(b) Macroscopic view of broken arm of one of the figures that was utilized for the present analysis pendicular to the surface. They were mounted and prepared for metallographic observations by initial polishing on emery paper in dry condition and finally with alumina (1 μm) in water suspension. The polished samples were etched with ferric chloride at room temperature to reveal the microstructural features. The microstructures were observed in an optical microscope and a JEOL 840A scanning electron microscope (SEM). Elemental analyses were obtained at several different locations in the sample using a JEOL 8000 JXA electron probe microanalyzer (EPMA). The microhardness variation across several sections were measured using a Carl Zeiss Jena 160 microhardness tester with a 40 gm load.

Results and Discussion

The results of the present study will be presented and discussed in the following sections.

X-ray Diffraction Analysis

The X-ray diffraction pattern obtained from the surface scale of the object is presented in Fig. 2. The peaks were compared with that of the common corrosion products of Cu using JCPDS[8] files. Apart from peaks due to the substrate Cu, the peaks could be indexed to the corrosion products, identified in Fig. 2. Based on the peak intensities, it can be concluded that the major corrosion product was cuprite (Cu_2O, JCPDF[8] 34-1354), while the minor corrosion products were malachite [$Cu_2CO_3(OH)_2$ JCPDF 41-1390 and 10-0399] and brochantite [$Cu_4SO_4(OH)_6$, JCPDF 43-1458]. The occurrence of cuprite as the major corrosion product is reasonable as the specimens were not exposed to the atmospheric environment. Therefore, the known end corrosion products of Cu on atmospheric corrosion (namely, strandbergite, posnjakite, langite, antlerite, brochantite, nantokite and atacamite[9]) were not observed in significant proportions in the patina. The identification of minor amounts of malachite and brochantite is indicative of soil corrosion of the anthropomorphic object. It is interesting to note that malachite is not a common atmospheric corrosion product of Cu and is sometimes found as a patina constituent of ancient statues[9].

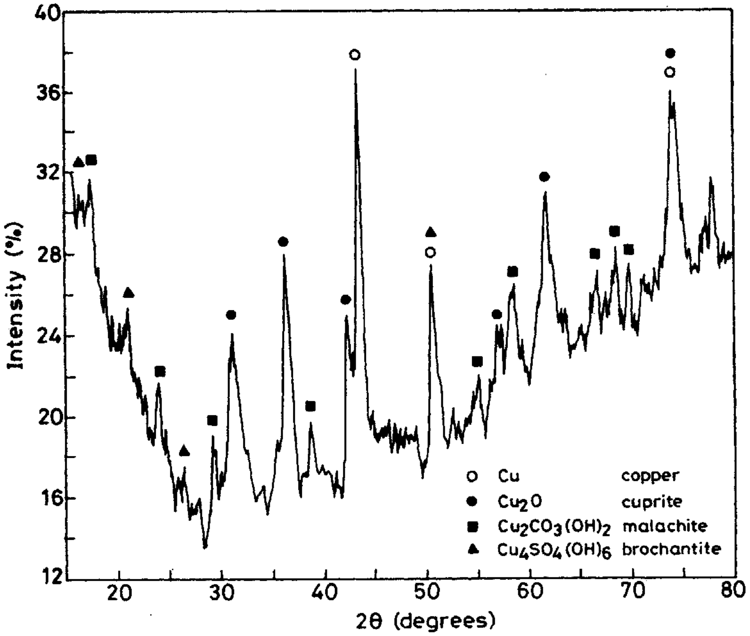

Fig. 2 : X-ray diffraction pattern from the surface of the Cu anthropomorphic figure. The peaks corresponding to the identified phases have been marked.

Microstructural Analysis

Optical microscopy indicated several macrodefects in the cross section of the specimen, like wide cracks (Fig. 3a). The grain structure was equiaxed and a non-uniform distribution of second phase particles was observed in the matrix (Fig. 3b). There were several grains in the structure where straight annealing twins were present. This indicated that the structure had not been deformation processed because annealing twins were straight and not bent[10]. Secondly, the second phase particles were rounded and spherical in shape and not elongated, further proving the absence of the any deformation processing[10]. The equiaxed grains further did not exhibit any indications of deformation (Fig. 3b). The equiaxed structure was revealed in both the sections (parallel and perpendicular to the surface), which strongly suggested the casting route for the manufacture of the object. The grain size was not strictly uniform and a detailed analysis of the grain sizes (in the microstructures) indicated that they were in the range of 30 to 40 μm.

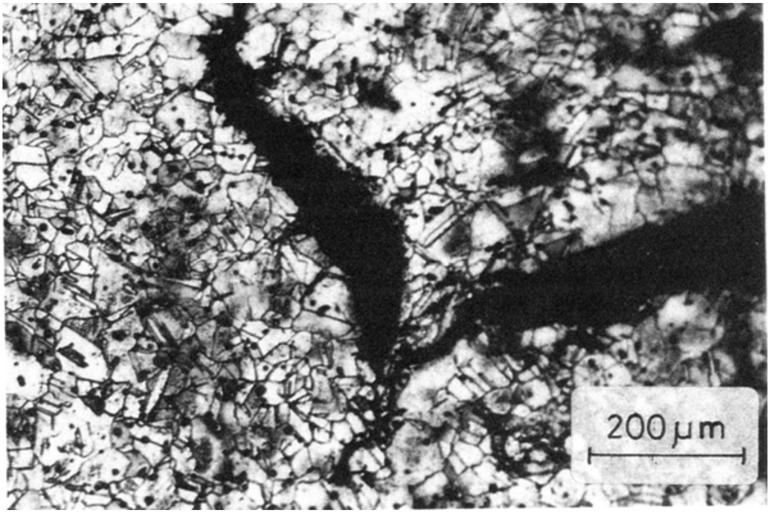

Fig. 3(a) : Optical micrograph of the sample showing presence of a macrodefect (crack.) Notice the relatively uniform grain structure.

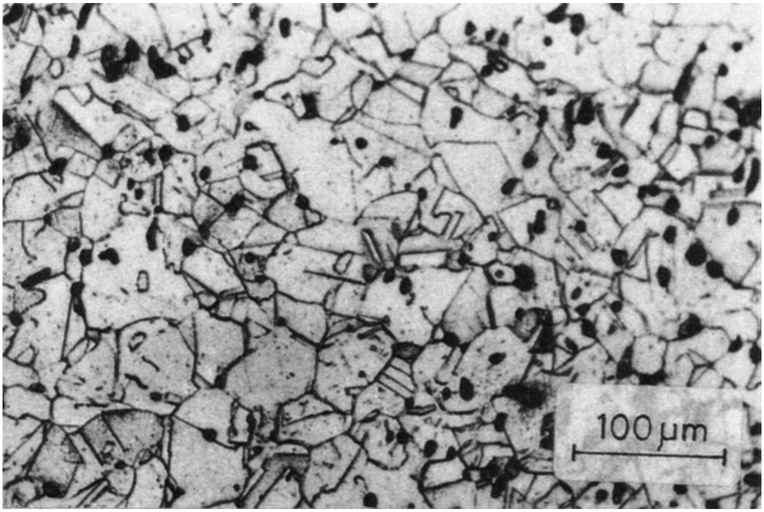

Fig. 3(b) : Optical micrograph showing equiaxed grains and entrapped slag inclusions of spherical shape. The presence of straight annealing twins in some of the grains can be noticed. The microstructure represents a typical cast structure.

Scanning electron microscopy of the polished and etched sections also revealed similar features (Fig. 4). Coarse dendritic structures (fernlike growth) were noticed in some of the grains. As faster cooling results in finer dendrites, the presence of relatively coarser dendrites indicated the relatively lower cooling rates after the casting process. Features indicative of coring (and the presence of dendrites) confirmed that the object was a cast structure. There was no preferential grain growth, like columnar growth, thereby eliminating chill casting of the object. Moreover, the presence of dendrites negates annealing[10] and therefore, the objects were cast structures. The second phase particles were nearly rounded in most of the cases (see Figs. 3b and 4), thereby indicating that the material was molten and then cast into moulds. In the process, the second phase particles assume spherical shapes based on surface energy considerations. This aspect of coagulated second phase particles in ancient Cu objects indicating casting of Cu object has also been addressed elsewhere in detail[11]. The results of the present study are in conformity with a detailed study of copper hoard implements by Agrawal *et al*[12], who had concluded that the objects were cast in closed moulds. They also noted the skill of the metal casters be-

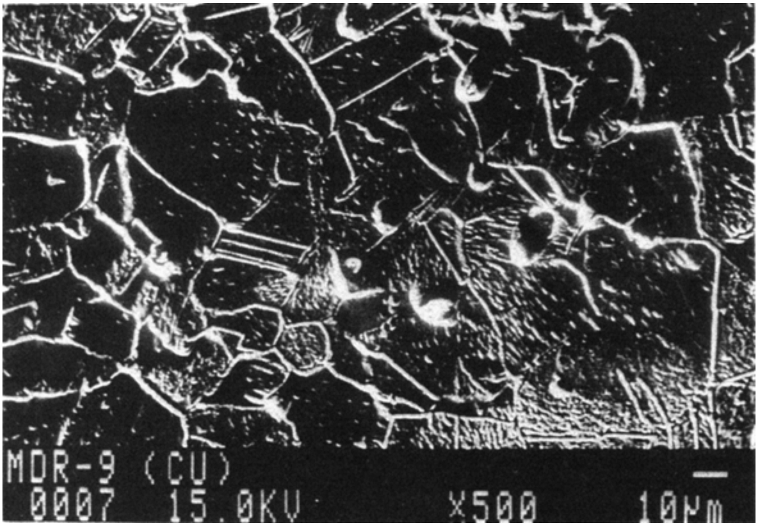

Fig. 4 : SEM micrograph of structure showing spherical-shaped sulphide inclusions in almost pure copper matrix. Coring can be observed in some grains.

cause casting of pure Cu is a difficult process. Finally, it was confirmed in the present study that the objects were manufactured by the casting process by visual observation of depressions on the surface of the objects, indicative of shrinkage of the material after they were cast into shape.

Another significant feature that was observed in some of the discovered anthropomorphic figures were the presence of gouging of chevron markings on the flat surface (for example, see bottom left figure in Fig. 1a) This indicates that secondary operations (smoothening, gouging, etc.) were performed on the initially cast objects. The functional and religious aspects of chevron markings (and also other features) of anthropomorphic figures have been discribed in detail elsewhere[5]. It is interesting to note that seven copper anthropomorphic figures discovered at Bankot were found systematically arranged one over other and all of them did not show signs of chevron marking. This seem to suggest that the figures were manufactured locally and then they were carried to other places where the secondary works were performed[5].

Composition

Compositions from select locations in the material were obtained qualitatively in the EPMA. Quantitative EPMA could not be performed due to the non-availability of some metals and non-metal standards. Several analyses from the matrix locations provided that the major element constituting the material was Cu and the major impurities were C and Sb. Analyses from the second phase particles revealed that the major elements were Cu, Pb and S, while the minor elements were C and As. Therefore, it was confirmed that the material of constrution of the anthropomorphic figure, that was studied was almost pure containing entrapped sulphides. Detailed chemical analyses of all the discovered Cu anthropomorphic figures have to be conducted in order to obtain further insights on the compositional differences, if any, between the figures.

In the copper hoard implements discovered from Uttar Pradesh and Bihar, alloying of arsenic (upto 8%) has been reported[12,13]. As arsenic was not detected in the matrix of the anthropomorphic figure in the present study, it is reasonable to conclude that As alloying was not resorted to in case of the anthropomorphic figures because they merely served as cult objects or images.

The presence of C in the metal and in the entrapped sulfide inclusions, in the present case, indicates the possible use of charcoal for reducing the ore to metal. The presence of a significant amount of sulfide inclusions indicates that the material (Cu) was produced from the ore rather than being obtained in the native state. The presence of the sulphide inclusions alludes to the use of sulphide ores for producing the metal. The sulphide ore must have been rich in Cu and Pb, as indicated by the analysis of the entrapped sulphides in the copper matrix. As the sulphides could not be completely removed from the metal, this probably indicates absence of stirring of the melt and/or the relatively short time the metal must have been molten. Therefore, a small amount of these unreduced ores must have been invariably left behind. It is also possible to hypothesize that the ancient people did not know the art of refining Cu metal to a higher degree than the people of later period, thereby explaining the relatively high amount of second phase sulphide inclusions in the metal.

Lead presence in ancient Cu is an impurity from the ore itself. It is supposed to be a persistent impurity. Its removal is favored by acidic slags and therefore, its absence in the metal may indicate the possible use of acidic slags (ex. fayalitic or silicate) during the extraction process. However, it must be noted that this is highly speculative and detailed analysis of second phase particles in several other samples needs to be conducted to understand if fluxes (and the resulting slags) were used or not. As regards Sb, it partly volatilizes during smelting but not eliminated completely. The amount of Sb depends upon the atmosphere used for roasting. During roasting, they volatilize as Sb_2O_3 but some get converted to less volatile Sb_2O_5 and form antimonate with Cu. Usually, Sb is associated with As and therefore, the identification of As in the second phase particles indicates that the original ore contained both As and Sb. However, as pointed out earlier, there has been no intentional alloying of As, unlike in the case of copper hoard implements[12,13].

Copper Extraction Process

In general, the procedure adopted to extract copper from sulphide ore in medieval India was a follows. The ore was first roasted to remove the bulk of S. The roasted ore was smelted to remove the gangue material to produce Cu matte (copper iron sulphide). The copper matte was roasted and subsequently smelted with charcoal and flux, wherein S was oxidized to SO_2 and Fe to FeO, which was fluxed by silica (flux) to form the slag. This was strained off from the surface of the metal. The blister Cu, which was thus produced, was further refined. The copper-extraction furnace was generally built with refractory clay or was simply a deep hole in the ground with a clay rim at the sides and front[14]. The insides were plastered with refractory clay. Clay tuyeres in the bottom of the furnace provided the forced draught. The furnaces were filled with lighted charcoal and raised to full heat by working of the bellows attached to the tuyeres. After furnace was lit and well heated, the material was gradually introduced alternately with charcoal.

Primitive Cu-making methodologies could have certainly not have been the same[15]. Generally two methods are discussed with reference to copper extraction in ancient India[14,15]. In one method, copper sulphide ore along with silica was powdered and mixed with dung and made into lumps. These were roasted in a hearth to convert them to oxide, in order to remove the bulk of S. The roasted ore was gradually introduced alternately with charcoal and flux (called *reet*, which was essentially slag from iron making furnace). The ore was also sprinkled from time to time. It has been mentioned that the relative proportions of materials roasted was 5 parts ore, 4 parts charcoal and 5 parts *reet* [16]. After this operation, the slag was removed from the top, leaving the heavier metal behind. When the heavier metal had solidified, it was taken out, pounded and kneaded with dung and made into balls. These balls were dried in the sun and then roasted with free access of air in shallow furnaces. The last process of refining consisted of treating the powder produced from these roasted balls in the same furnace and in precisely the same manner as the original ore, the result being a fluid mass of copper was found at the bottom of the furnace which on cooling was removed. It was sometimes further refined before being utilized in useful product forms. It is unlikely that this method was utilized for extracting the copper that has been analysed in the present study because iron making was not established in ancient India during the OCP period.

In the second method, sulfide ore was washed and smelted in furnace to separate gangue and CuS[14,15]. The sulfide ore did not undergo any change in this operation and was left as a cake in th bottom of the furnace. The slag was run off and copper sulphide cake allowed to cool. These cooled cakes were broken, made into balls and roasted to oxide. The oxide was later smelted in the original furnace with charcoal and reduced to metallic state. In the present case of the Cu anthropomorphic figures, this would have been the likely process to extract the copper because of the presence of a significant amount of sulphides in the metallic matrix.

Source of Copper Ore

The possible source of ore for making the copper object is briefly discussed. The sulphide inclusions, being rich in Cu and Pb, indicates that the mineral source was a supplied ore. Copper metallurgy in ancient India has been reviewed extensively by Bharadwaj[16]. Copper ore was obtained from Rajasthan (Khetri belt) during the Harappan and Chalcolithic period, while by the time of the copper hoard culture, newer areas of mining were exploited in Bihar (Singhbhum copper belt)[16]. The mining areas of Bihar appear to be the likely source for the material analyzed in the present study. Mineralogical examination of ores in the Singhbhum area indicated the availability of a wide variety of minerals (chalcopyrite, pyrrhotite, pyrite, pentlandite, magnetite, ilemenite, goethite, covelite, malachite, azurite, chrysocolla, cuprite, chalcocite)[17]. Evidence further suggests that Cu smelting started in Singhbhum area by the copper hoard period[16]. The exploitation of the rich ores of Singhbhum is evidenced by the discovery of copper hoards in the nearby districts of Manbhum, Karahari, Hazaribagh and Ranchi[18]. In fact, it has been rightly stated that copper metallurgy in India took rebirth in this area during the copper hoard period[16,19]. A detailed spectroscopic examination of the specimen is required to understand the possible trace impurities and based on this, obtain deeper insights on the possible source of ore from which the Cu, used for making the figures, was extracted[12,13].

Microhardness Meaurements

Microhardness readings were obtained from several locations in the matrix and the results indicated a relatively soft matrix (hardness in the range 65 to 80 kgŪmm^2). The relationship of microhardness and grain size with the possible temperature range of working for the case of Cu has been addressed in detail, recently[11]. In the present case, grain sizes in the range of 30 to 40 mm and hardness in the range of 65 to 80 kgŪmm^2 were obtained. These specifications are well within the range for cast structures[11]. Earlier, based on microstructural analysis, several arguments were provided for the material being a cast structure. Microhardness measurements further confirmed that the discovered anthropomorphic figures were made by the casting process.

CONCLUSIONS

The material of construction of an OCP period (2650 BC-800 BC) copper object has been characterized by optical and scanning electron microscopy and microhardness measurements. The major constituent of the green-colored surface patina was cuprite, while the minor constituents were malachite and brochantite. The specimen exhibited an equiaxed structure with grain size in the range of 30 to 40 μm and hardness in the range of 65 to 80 kg/mm^2. Microstructural evidences (straight annealing twins, coring and rounded second phase particles) point to the anthropomorphic object being a cast structure. The composition of the metal was almost pure Cu, with minor impurities of C and Sb. The major elements identified in the second phase particles were Cu, Pb and S, which indicated that these particles were sulphides. The presenece of these sulphides has been related to the probable Cu extraction process.

REFERENCES

1. Lal, B.B. "Futher copper hoards from Gangetic basin and a review of the problem," *Ancient India,* 7 (1951) 20-39.

2. Lal, B.B. "A note on the excavation at Saipai," *Puratattva,* 5 (1971-72) 46-49.

3. Bharadwaj, H.C. *Aspects of Ancient Indian Technology,* Motilal Banarsidass, New Delhi, 1979, pp. 1-23.

4. Dikshit, K.N. "The Ochre Coloured Ware Settlements in Ganga-Yamuna Doab," In: D.P. Agarwal and D.K. Chakraborty (ed), *Essays in Indian Protohistory,* New Delhi, 1979, pp 285-299.

5. Kumar, K. "The Beginnings of the Brahmanical Iconography in the Ganga Valley," *Journal of the Indian Society of Oriental Art, New Series,* XXII and XXIII (2000) 27-68.

6. Piggot, S. *Prehistoric India,* Harmonodsworth, Lodon, 1950, p. 238.

7. Ghosh, A. (ed), Copper Hoard, *Encyclopedia of Indian Archaeology,* Vol 1, New Delhi, 1989, p, 92.

8 JCPDS Powder Diffraction Files, *PCPDFWIN Software,* Joint Committee on Powder Diffraction Standards - International Centre for Diffraction Data, Swarthmore, USA, 1996.

9. Leygraf, C. and Graedel, T. *Atmospheric Corrosion,* Wiley-Interscience, New York, 2000, pp. 140-148.

10. Scott, D.A. *Metallography and Microstructures of Ancient and Historic Metals,* Archetype Books, London, 1991, pp 5-10.

11. Ryndina, N.V. and Ravich, I.J. "Determination of Temperature Ranges of Copper Heating after of during Forging in terms of its Hardness Values and Grain Size," *Bulletin of the Metals Museum,* 34 (2001) 16-21.

12. Agrawal, D.P., Krishnamurthy, R.V. and Kusumgar, S. "New Data on the Copper Hoards and the Daimabad Bronzes," *Man and Environment,* 2 (1978) 41-46.

13. Nautiyal, V., Agrawal D.P. and Krishnamurthy, R.V. "Some New Analysis on the Protohistoric Copper Arts," *Man and Environment,* 5 (1981) 48-51.

14. Shrivastava, R., "Smelting Furnances in Ancient India," *IJHS*,34 (1999) 33-46.

15. Tylecote, R.F. *Matallurgy in Archaeology,* The Metals Society, London, 1962, pp. 27-28.

16. Bharadwaj, H.C., *Aspects of Ancient Indian Technology,* Motilal Banarsidass, Delhi, 1979, pp. 75-106.

17. Ball, V. "On the Ancient Copper Mines of Singhbhum," *Proceedings of the Asiatic Society of Bengal,* (1869) 170-175.

18. Ray, P. *History of Chemistry in Ancient and Medieval India,* Munshiram Manoharlal, New Delhi, 1956, p. 32.

19. Agrawal, D.P., *The Copper Bronze Age in India,* Mushiram Manoharlal, New Delhi, 1971, p. 197.