Hot mold casting process of ancient East India and Bangladesh

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Abstract: Ancient casting process for production of brass or bronze utensils and icons were made in hot molds using clay molded investment casting or piece mold process, as presumed by archaeologists. Piece mold process is still traditionally practiced in many parts of Eastern India and Bangladesh along with investment casting process. Incidentally, Bengal artisans are more accustomed to piece mold process unlike tribal artisans who practiced investment casting process. This piece mold casting process has been reconstructed to get the idea of metal characteristics in order to investigate ancient casting process of Bengal and Bangladesh. The characterization of ancient archaeo-metal products come to a type of cast Cu-Sn-Zn-Pb type quaternary alloy produced by a slow freezing process. Though these alloys physically differ from the traditional cast alloy of binary Cu-Zn type brass, the physical characteristics are similar to the binary cast alloy character. This investigation throws light on the similarity of the production processes by which ancient artisans probably produced cast metal products.

Key words: piece mold casting; characterization; hot-molds; copper-alloys
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Many metal icons of Pala – Sena or Mayurya or Gupta period or similar genre have been recovered[1] by archaeologists in Eastern India and Bangladesh. Those icons had got intricate shape, complex geometry of different sections with smooth surface finish. Most of the metal icons were made by a casting process. All of these castings were produced by either clay molded investment or piece mold process. The excellent surface finish and intricate shape of castings lead us to this conclusion as those castings are very very difficult to produce using sand mold process. Meera Mukherjee[2] has referred to the practice of investment mold and piece mold process in many places of India. Both casting processes conventionally use the red hot mold during casting.

Historically, China has a glorious past (1000 B.C.) of piece mold casting process of heavy sections of metal[3]. Eastern India and present Bangladesh being very close to South China via Burma (presently Myanmar) there remains a district possibility of historical connection on land route between India and China, with the seepage of metal casting technology to India.

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Technology knows no border, unlike administrative border, man knows. Therefore, this region of India developed an easy and cheap casting process of piece mold technology without wax, while continental India, including prosperous South India mastered clay molded investment casting process, using wax[4]. Clay molded investment casting process has already been discussed in some articles[5,6] and elsewhere, and hence the piece mold casting process has been discussed in this article. This casting process has been reconstructed in Rural Metal Casting Laboratory of Metallurgical & Material Engineering Department, Jadavpur University to understand the cast metal characteristics. A few brass castings produced by rural artisans of a district casting center was procured and tested in the laboratory. Both the castings then have been compared with the ancient metals of Bangladesh.

1 Reconstructed piece mold casting process

The piece mold process follows the following stages (Fig.1). Let us assume an example of casting a small flower vase.

A small flower vase casting [Fig. 2(a)] has been produced in Rural Metal Casting Laboratory of Metallurgical & Material Engineering Department, Jadavpur University using Cu 65/35 Zn brass. The mold-clay and core-clay were mixed in the form of dough as per flow sheet given in Fig.1. At first, green mold clay has been pasted over the pattern to get the initial piece mold. Grooves were made on the surface of the mold where next half of the mold would be fixed. When the initial piece mold developed handling strength, then the adjacent piece mold was worked out. Similarly, the top and the bottom

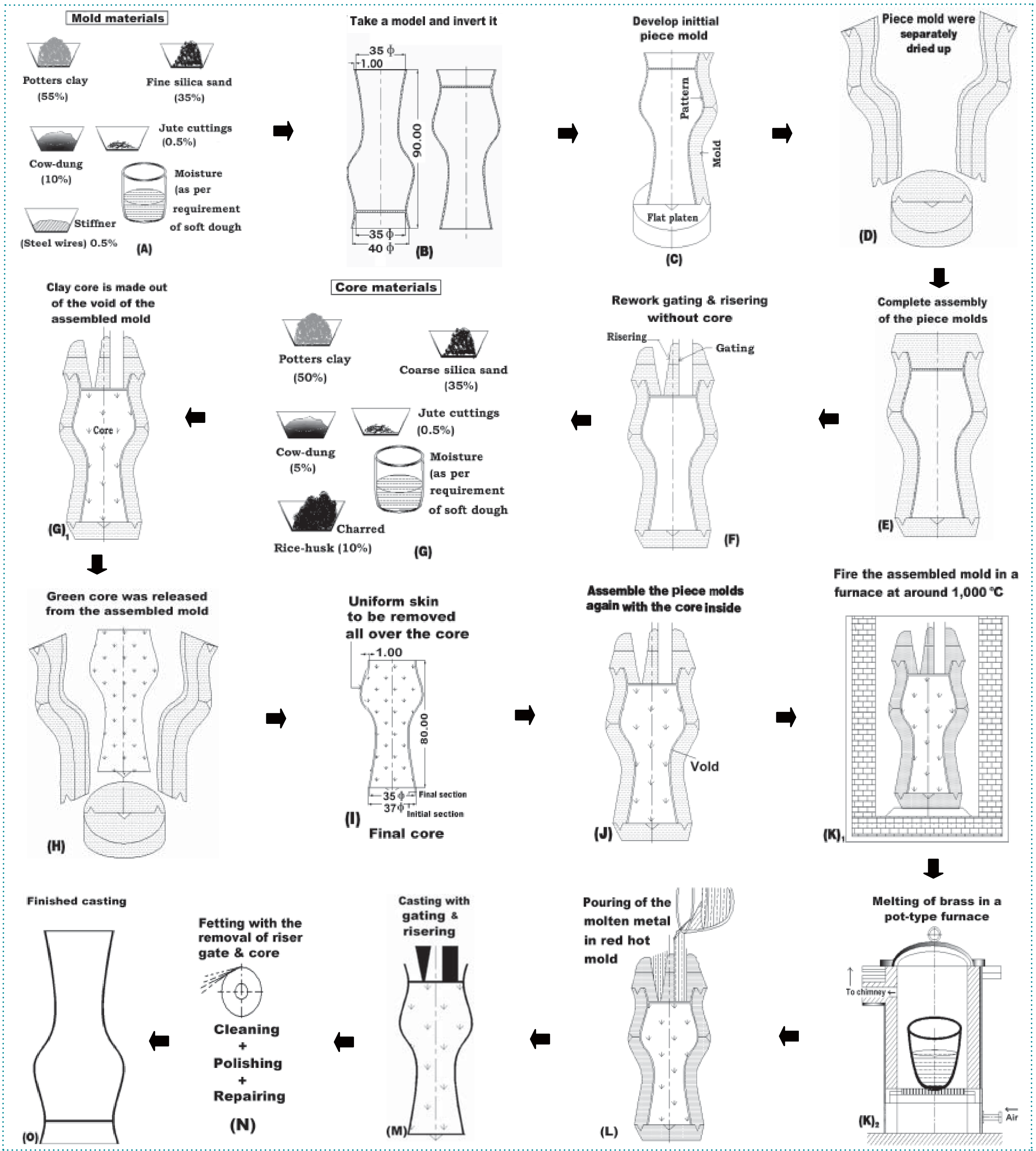

Fig. 1: Flow sheet of the complete piece mold casting process

piece molds were prepared. The complete piece molds were separately dried up and then the piece molds were assembled without pattern. The gating and the risering were reworked in the top piece mold. The void space of the assembled mold was packed with the core clay aggregate. The green core was released from the assembled mold and was dried up. An outside skin was removed from the core to get the casting thickness of the job. All these piece molds were assembled together with the core inside keeping uniform void-free the future metal thickness. The complete mold was heated in a pot furnace at a temperature of around 1,000 ℃ and brass was melted in a crucible within a pot furnace. The liquid metal was poured into the red hot mold. When the mold cooled, after usual fettling and finishing, the casting [Fig. 2(a)] became ready.

A utensil casting of a drinking water glass [Fig. 3(a)] made of brass was collected by one author from Nabadwip, district Nadia (23°25'0"N, 88°22' 0"E), West Bengal where the similar type of piece mold casting process is traditionally practiced.

(b) **Chemical analysis**
by wet method
(all are in wt.%)

Cu: 61.20	Fe: 0.76
Zn: 34.51	Al: 1.05
Sn: 0.48	Ni: 0.42
Pb: 0.32	Mn:1.26

(c) **Mechanical property**
Bulk hardness: 76.46 HV 5/10
(by Vickers hardness tester,
Model: VM50, SR. No 02/2006-815)
Micro-hardness of α-Cu phase: 136.26 HV 50/10
(by Vickers micro hardness tester,
Model: LEICA-VMHT, Serial. No. 518880)

Fig. 2: (a) The brass casting produced in Rural Metal Casting Laboratory; (b) Chemical analysis of the casting; (c) Hardness of the casting

(b) **Chemical analysis**
by wet method
(all are in wt.%)

Cu: 60.40	Fe: 0.52
Zn: 36.68	Al: 0.30
Sn: 0.20	Ni: 0.46
Pb: 0.42	Mn: 1.02

(c) **Mechanical property**
Bulk hardness: 87.24 HV 5/10
(by Vickers hardness tester,
Model: VM50, SR. No 02/2006-815)
Micro-hardness of α-Cu phase: 174.24 HV 50/10
(by Vickers micro hardness tester,
Model: LEICA-VMHT, Serial. No. 518880)

Fig. 3: (a) A glass of brass, produced by rural artisans of Nabadwip, West Bengal; (b) Chemical analysis of the collected sample; (c) Hardness of the sample

2 Characterizations of castings

Small fragments of the two casting specimens were taken for the metal characterization. Chemical analysis and hardness were measured [Fig. 2(b), 2(c) and Fig. 3(b), 3(c)] and both show Cu 65/35 Zn brass with minor impurities. Hardness of castings are comparable to sand cast brass, specification Nos. of C85700 and C85800 type alloys given by ASM handbook [7]. The chemical analyses of the brasses fall under the Group-I of short freezing range alloys (freezing range comes within 50 K)[8].

The SEM structure (OXFORD – JEOL JSM-6360 Scanning Electron Microscope) of the laboratory sample [Fig. 4 (a)] shows the single α-Cu phase of coarse dendrites as matrix (grey colored). Minor amount of β-Cu phase is visible within dendrites. The primary coarse dendrite sections as measured, vary from 80/120 – 60/100 μm. This α-Cu phase is the solid solution of Zn in Cu and predominates the structure. The white round particles [marked by circles in Fig. 4 (a)] exist throughout the microstructure, as lead-rich constituent.

The SEM structure of the collected brass sample [Fig. 4 (b)] depicts also the single α-Cu phase of coarse dendrites, as matrix. Some amounts of lead and β-Cu phase are present in the interdendritic region. The measured size of dendrites is similar to the laboratory sample as can be seen in the micrograph.

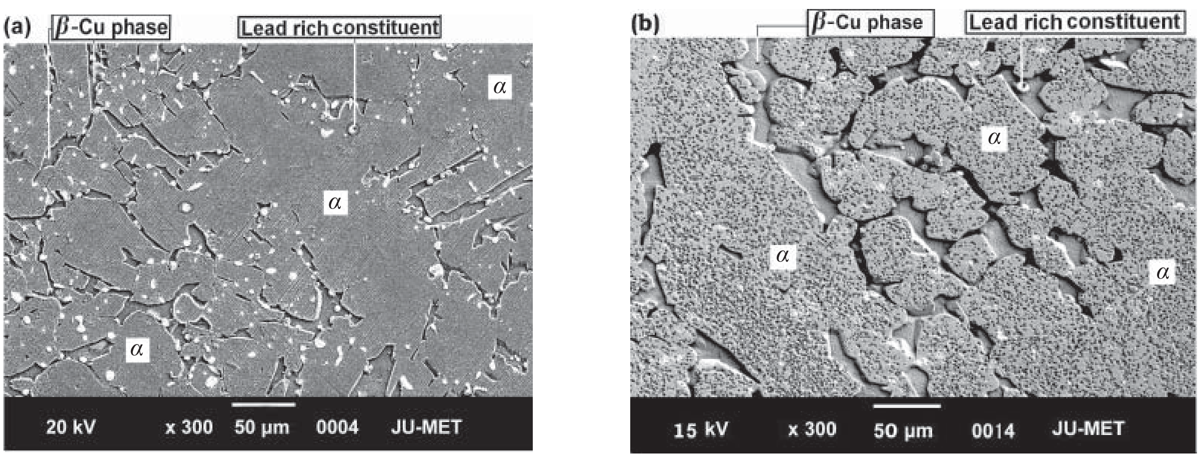

Fig. 4: (a) The single α-Cu ph e of heavily coarse dendrites (grey) dominate the total microstructure of the brass casting, produced by piece mold process in the red hot mold. Minor amount of β-Cu phase is present in the interdendritic region as a last-to-freeze constituent. Note the widely distributed lead bearing phase throughout the metallograph as white globules. (300 X) (Etchant: $FeCl_3$ in HCl);
(b) The single α-Cu phase of coarse dendrites again cover the whole structure of the brass casting produced by rural artisans. Small amount of lead and β-Cu phase in the interdendritic region can also be seen. (300 X) (Etchant: $FeCl_3$ in HCl)

For confirmation of phases, X-ray diffraction analysis (RIGAKU ULTIMA-III, make, Cu-target, Ni-absorber) using Debye - Scherrer method was used to test the metal specimens. The diffractogram of the laboratory casting specimen [Fig. 5(a)] confirms major phase as α-Cu phase (FCC) of Cu - Zn solid solution (Table 1). The minor phases are β-Cu phase (BCC) and small amount of insoluble lead (FCC) present in the system.

The XRD result of the collected brass sample (Fig. 5(b)) similarly identifies the major phase as α-Cu phase of Cu-Zn solid solution with minor β-Cu phase and insoluble lead as residuals (Table 2). All these phases mentioned have been compared and identified by JCPDS9 file Nos. 4-0686, 4-0836, 8-0349, 19-0179 and 25-322, respectively.

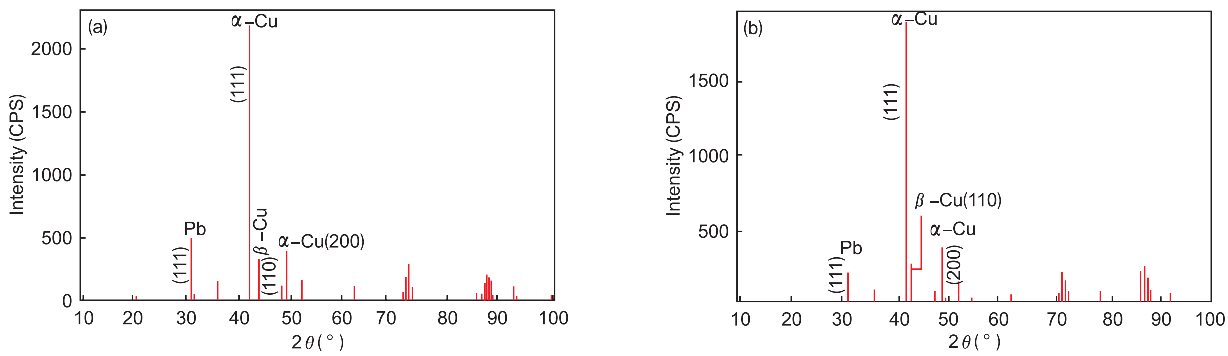

Fig. 5: (a) X-ray diffractogram of the brass specimen produced in the Laboratory. The major phase is α-Cu phase (FCC). (b) X-ray diffractogram of the collected brass sample produced by rural artisans. Similar to Fig. 5(a) the major α-Cu phase with the minor β-Cu phase and elemental lead, can be seen.

Table 1: Brief XRD data of the laboratory brass casting

Peak No.	Angle (2θ, Deg.)	d_{space} (Å)	I / I_0	Identified phase with plane (*hkl*)
1.	31.04	2.8788	26	Pb (111)
2.	36.04	2.4900	10	Pb (200)
3.	42.16	2.1416	100	α-Cu (111)
4.	44.42	2.0378	4	β-Cu (110)
5.	44.72	2.0248	4	β_1-Cu (110)
6.	48.92	1.8603	14	α-Cu (200)
7.	49.16	1.8518	15	---

Table 2: Brief XRD data of the collected brass casting

Peak No.	Angle (2θ, Deg.)	d_{space} (Å)	I / I_0	Identified phase with plane (*hkl*)
1.	31.200	2.8644	11	Pb (111)
2.	36.180	2.4807	6	Pb (200)
3.	42.220	2.1387	100	α-Cu (111)
4.	43.120	2.0961	4	β -Cu (110)
5.	46.260	1.9609	4	β_1 -Cu (110)
6.	48.860	1.8625	16	α-Cu (200)
7.	71.960	1.3111	12	α-Cu (220)

K. Hapkki and J. Miettinen[10] correlated the Secondary Dendritic Arm Spacing – SDAS (d, μm) of cast brass with the cooling rate ($\dot{T}$, K/s) of brass castings as:

$$d = 56\,(\dot{T})^{-0.33} \qquad (1)$$

The secondary dendritic arm spacings of both brasses, have been measured from microstructures and using this model, the cooling rates of those castings have been calculated (Table 3).

The average $\dot{T}$ (K/s) of both cast brass specimens of the order of single digit, vindicates a very slow solidification rate of castings, commonly expected of copper alloys being cooled in red hot clay molds[11]. The signature of the extremely slow cooling rate manifests in the very large secondary dendritic arm spacings (50–100 μm) of the microstructures.

Table 3: SDAS of brass castings and calculated cooling rates

Specimen	SDAS, d (μm)	Cooling rate, $\dot{T}$ (K/s)	Average cooling rate, $\dot{T}$ (K/s)
Brass casting (laboratory)	78.900	0.3540	0.4735
	56.250	0.9865	
	94.730	0.2030	
	92.105	0.2210	
	57.890	0.9040	
	100.00	0.1725	
Brass casting (collected)	50.000	1.4097	1.3278
	62.500	0.7169	
	40.000	2.7721	
	75.000	0.4126	

3 Characterizations of castings produced in archaeological period

The archaeological specimens investigated were obtained from the excavation at Mahasthan or Mahasthangarh, Bangladesh site in 2004 and 2005. The first specimen [Fig. 6(a)] is a metallic artefact of Gupta period 4th–5th century A.D. The second specimen, [Fig. 6(b)] a broken piece of the backrest of a metal image, was obtained from same site, of Pala-Sena period 10th –12th century A.D.

The chemical compositions [Figs. 6(a) & 6(b)] indicate the alloys as a Cu-Sn-Zn-Pb combination unlike Cu-Zn alloy being used in recent time by the artisans. The alloy

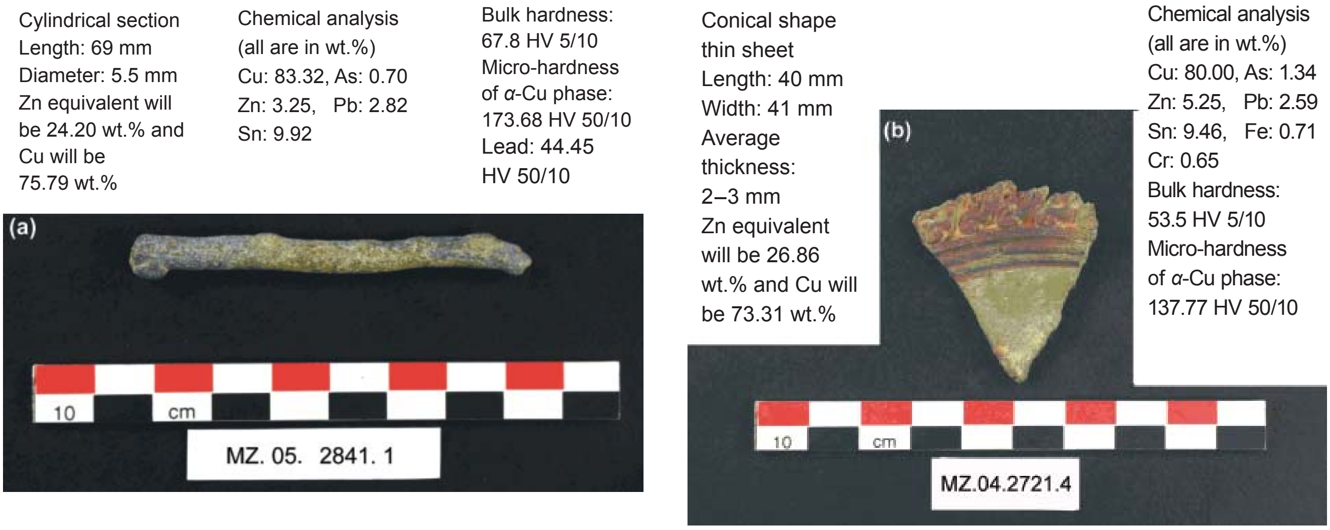

Fig. 6: (a) A metallic non-artefact of Gupta period. The chemical composition signifies a Cu-Sn bronze with addition of lead and zinc. The calculated Zn-equivalent [12] puts the material in α-brass category. Material hardness is comparable to sand cast bronze.
(b) A tiny fragment of broken circle of the backrest from Pala-Sena period. The chemical composition looks similar to the earlier artefact. Also the Zn-equivalent puts the material into α-brass category.

combination is a deviation of 90Cu-10Sn bronze where lead and zinc were added to mitigate the drawbacks of Cu-Sn cast alloys. As every one knows 90Cu-10Sn alloy is a long-freezing range alloy of Group-III cast alloy variety (mentioned in ASM specification[13]), having freezing range of 170 K[14], and suffers from huge micro-porosities and imposes difficulty in directional solidification due to the random dendritic solidification[15]. The low melting zinc and lead enters into the voids of the interdendritic region increasing the soundness and pressure tightness of the castings. Archaeologically, the combination of Cu-Sn with Zn and Pb can be found also in many Roman ancient castings[16]. The ancient East Indian casting workers adopted piece mold technology of the Far East from China and improved the bronze alloy by the addition of zinc and lead. From the SEM structure [Fig. 7(a)] of Gupta period casting, coarse dendrites of the single α-Cu phase (grey colored) can be seen. EDX analysis of the α-Cu phase, as matrix, determines the composition of Cu: 82.02, Zn: 4.35, Sn: 9.98, As: 0.86 and Pb: 2.79 (all are in wt.%) in the material. The EDX analysis of small globules confirm lead-rich constituent having composition of Pb: 71.19, Cu: 22.26, Sn: 3.40, As: 0.3 (all are in wt.%). The microstructure looks like a Gun-Metal metallograph of 85-5-5-5 (Cu-Sn-Zn-Pb) cast alloy[17]. Naturally the casting is heavily cored and the interdendritic regions are filled by globular lead, or residual zinc or tin rich last-to-freeze phases. The hardness of the material [Fig. 6(a)] comes very near to the C83600 alloy[18] specification and micro-hardness of α-Cu phase seems to be quite high as expected of Cu-Sn alloys.

The second sample of Pala-Sena period comes close to the sample of Gupta period in chemical composition [Fig. 6(b)]. EDX analysis determines the chemical composition of α-Cu phase as, Cu: 77.80, Zn: 9.22, Sn: 9.58, Al: 3.40 (all are in wt.%) and the interdendritic β-Cu phase as, Cu: 10.44, Zn: 4.47, Sn: 63.31, Pb: 10.55, Sb: 3.86, Ni: 2.83, As: 2.00, Al: 2.54 (all are in wt.%). The SEM structure of the sample [Fig. 7(b)] though contains the single α-Cu phase of coarse dendrites as matrix (of solid solution of Zn and Sn in Cu), but possess a distinct difference. The dendrites in this cast material look very distinct and grain boundaries are well delineated. Therefore, some kind of annealing or softening treatment was applied to the casting. This is confirmed by the hardness of the material as 53.5 HV 5/10 and shows some improvement of technology of cast metal production. This material though had a Gun-Metal character but was naturally much more ductile than the previous one of Gupta period.

XRD results of the Gupta period sample [Fig. 8(a)] shows major α-Cu (FCC) phase of Cu-Zn solid solution. The minor phases of β''-Cu, β_1-Cu and insoluble lead are also visible in the diffractogram (Table 4). The complexity of the minor phases arises due to quaternary system of the copper-alloys.

The X-Ray diffractogram of Pala-Sena period sample [Fig. 8(b)] similarly indicates the presence of dominant α-Cu phase. The minor phase is β''-Cu of Zn, Sn solid solution of Cu and insoluble lead can be found in the diffractogram (Table 5).

The Differential Thermal Analyses (DTA) were done in Pyris Diamond TG/DTA analyzer in the Metallurgical & Material Engineering Department, Jadavpur University, Kolkata. In Fig. 9(a) the DTA result of Gupta period specimen shows the presence of a number of endo peaks, which seems to be an indication of complex low-melting point constituents expected of a quaternary system. The DTA result of Pala-Sena period specimen indicates a phase change of 873 K (600 ℃) shown in Fig. 9(b). Most of the low-melting elements probably defused in the primary α-Cu phase during annealing and there may be probability of improving the alloy with elimination of low-melting point constituent.

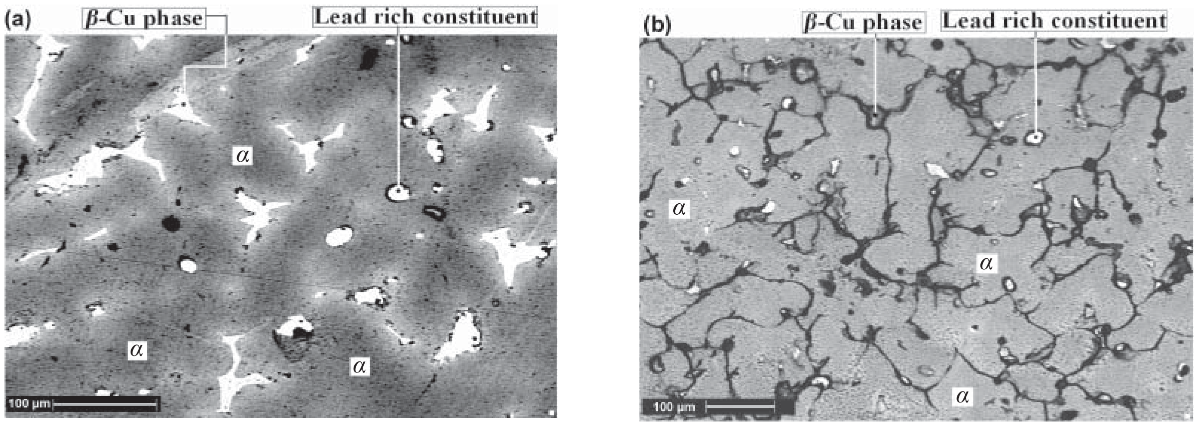

Fig. 7: (a) Coarse dendrites of *α*-Cu, as a major phase (grey areas) and minor amount of *β*-Cu phase (white patches) rich in Zn and Sn, are present in the micrograph. In some areas of the microstructure white globules of lead can be seen. Some dark black round patches of micro-porosities inhabit the structure. (450 X) (Etchant: $FeCl_3$ in HCl).
(b) Clearly visible dendrites with well marked grain boundaries can be observed in the microstructure. Dendrites consist of *α*-Cu phase (grey colored) as major phase. The clear grain boundaries and round nature of second phase, as *β*-Cu phase, provide information about post annealing treatment of this cast metal. The indication of diffusion is provided by the coalescence of grain boundary region in the form of roundish grains in many areas. (200 X) (Etchant: $FeCl_3$ in HCl).

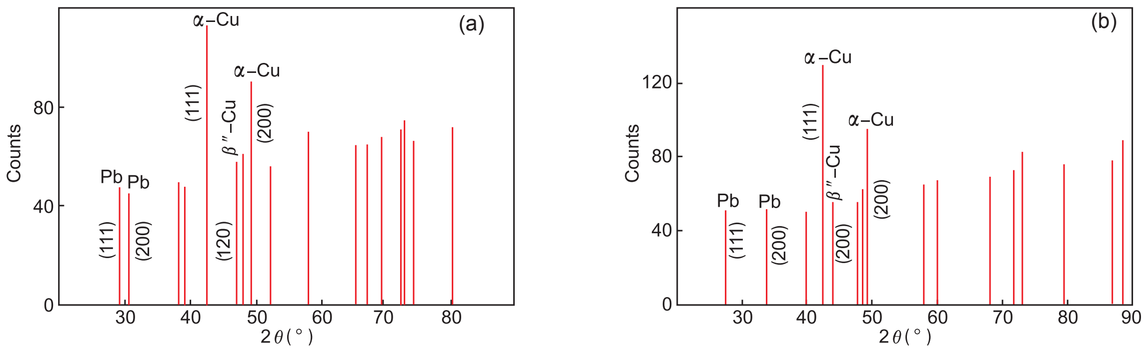

Fig. 8: (a) X-ray diffractogram of the sample of Gupta period. The major phase is *α*-Cu and the minor phases are *β*"-Cu, β_1-Cu, etc. Elemental lead is also present indicating insolubility of lead in Cu-alloys.
(b) X-ray diffractogram of the Pala-Sena image showing the major constituent as *α*-Cu phase and the minor constituent as *β*"-Cu, β_1-Cu phases. Peaks of insoluble lead are also visible.

Table 4: Brief XRD results of Gupta period casting specimen

Peak No.	Angle (2θ, Deg.)	d_{space} (Å)	I / I_0	Identified phase with plane (*hkl*)
1.	29.15	3.061	42	Pb (111)
2.	30.55	2.924	40	Pb (200)
3.	32.4	2.761	42	Pb (101)
4.	42.7	2.116	100	*α*-Cu (111)
5.	47.1	1.928	50	*β*"-Cu (120)
6.	49.5	1.84	79	*α*-Cu (200)
7.	58.3	1.581	61	*β*"-Cu (121)
8.	65.6	1.422	56	β_1-Cu (200)
9.	67.6	1.385	57	β_1-Cu (020)
10.	73.15	1.293	65	*α*-Cu (220)

Table 5: Brief XRD results of Pala-Sena period casting specimen

Peak No.	Angle (2θ, Deg.)	d_{space} (Å)	I / I_0	Identified phase with plane (*hkl*)
1.	27.7	3.218	40	Pb (111)
2.	33.7	2.657	40	Pb (200)
3.	42.8	2.111	100	*α*-Cu (111)
4.	44.1	2.052	43	*β*"-Cu (200)
5.	49.6	1.836	73	*α*-Cu (200)
6.	58.15	1.585	49	*β*"-Cu (121)
7.	60.05	1.539	50	*β*"-Cu (220)
8.	68.35	1.371	52	β_1-Cu (020)
9.	73.4	1.289	63	*α*-Cu (220)

According to Hwang[19], for tin-bronze, the Secondary Dendritic Arm Spacing (λ, μm) follows the relationship of

$$\lambda = 101 \times r^{-0.42} \quad (2)$$

Where, r is the cooling rate (K/s). Using this relationship, the dendritic arm spacings of both bronzes, have been measured from microstructures and their cooling rates calculated using equation (2), have been shown in Table 6.

The cooling rates of the castings are found to be very slow for both the process. The coarse dendrites indicate longer solidification time and this also identify the castings to have been produced in red hot molds.

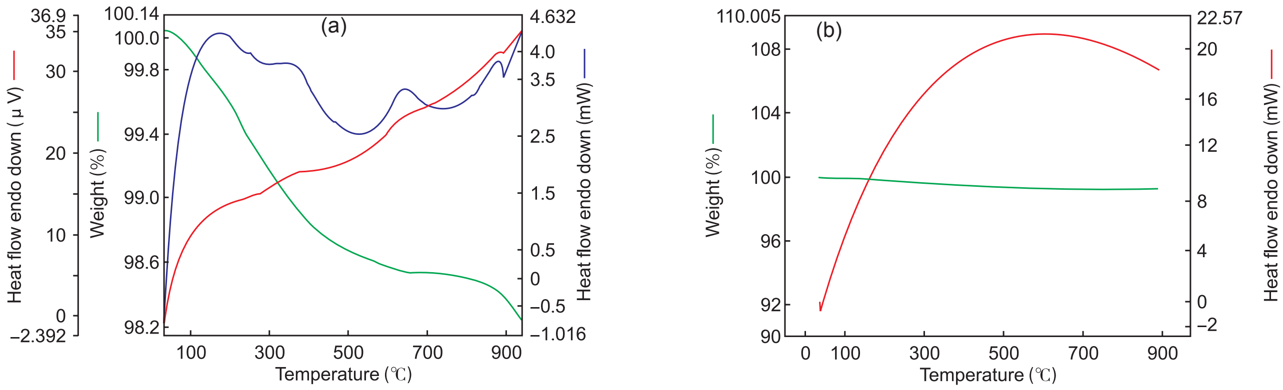

Fig. 9: (a) DTA analysis of the cast sample of Gupta period, (b) DTA analysis indicating improvement of the copper-alloy

Table 6: SDAS of cast archaeological specimens and calculated cooling rates

Specimen	SDAS, λ (μm)	Cooling rate, r (K/s)	Average cooling rate, r (K/s)
Gupta period casting fragment	59.52 61.90 57.00	3.522 3.208 3.904	3.544
Pala-Sena period casting	52.63 60.00 100.00	4.7208 3.455 1.0239	3.0665

4 Conclusions

At the beginning the piece mold process has been studied by visiting some rural production centers of West Bengal during field work. On that study it was found that the piece mold process uses clay mold and melt – an alloy of Cu-Zn system. After that the piece mold process has been reconstructed in Jadavpur University using modern materials and furnaces. Metal characteristics of cast metals produced in the laboratory as well as in the folk centers have been metallurgically analyzed.

Two available metal artefacts of one Gupta period and one of Pala-Sena period have also being metallurgical characterized. Metal characteristics of the ancient metal products and the recently produced cast products look very similar. From the similarity of the metal characteristics authors hold strong opinion that the ancient casting process for metal icons used hot molds during the casting process. Due to the ancient link between Eastern India and the Far East it can be presumed that a mutual transfer of technology occurred. Due to the technology transfer the piece mold process of Far East defused in Eastern India. Probably ancient Bengal artisans learnt the cheaper technique of producing copper alloy castings without wax and the process still continues in rural Bengal.

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