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UNDERSTANDING ALLOY DESIGN PRINCIPLES AND CAST METAL TECHNOLOGY IN HOT MOLDS FOR MEDIEVAL BENGAL

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Two beautiful bronze images of medieval period unearthed in South Bengal have been investigated. After laser cleaning, material characterization was undertaken to reconstruct the technology as well as the knowledge base of metal workers. The bronze items were found to be cast product whose chemistry belongs to copper – zinc – lead system with small addition of tin. The use of copper-zinc alloy in place of copper-tin with addition of lead becomes quite significant in this respect and points towards developing a working knowledge for copper-alloy design. The analysis of microstructures signifies towards a casting technology, where, hot molds were used. For confirmation of the molds, some tribal metal casting operations were also investigated. The technology was then reconstructed in the laboratory and some casting as the facts were produced. Microstructures of all three types look almost similar leading to the conclusion that coppersmiths used hot clay molds for bronze production.

Key words: Alloy-design, Bronze casting, Hot molds, Laser cleaning

INTRODUCTION

East Indian subcontinent has got a long history of using different metals from ancient time and a number of archaeological sites have been

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excavated which produced a large number of metal images used by the ancient population. From the days of Pāṇḍu Rājār Dhibi[1] to the recent excavation of Tilpi in South Bengal it proves the occurrence of the metal artefacts in continuum.

Two copper- alloy images one of *Rādhā* and *Kṛṣṇa* (referred here as bronzes) were locally (Baruipur) collected by a Museum, Sundarban Āñchalik Saṅgrahaśālā, Baruipur, South 24-Parganas, West Bengal, India, for conservation. Bronzes had been in heavily corroded state and needed restoration for display at the museum gallery of Sundarban Āñchalik Saṅgrahaśālā. Both the metal images incidentally do not hold any stele behind them. As per conventional museum practice, normal cleaning work was attempted but failed to provide desired result. Jadavpur University was requested to help in the restoration work of these specimens.

For preservation, the bronze items were cleaned by application of a Q-switched Nd: YAG laser keeping the patina, as intact as possible, for making them ready as exhibits. Small metal segments were made available by the permission of the Museum authority for metallurgical investigation using common metallurgical tools. The material investigation reveals the bronze items as cast product and the casting technology as well as alloy design of the metals yielded valuable information about medieval metal forming technology of Bengal.

1. History And Cleaning Of Bronzes

1.1. History of Metal Icons

Metal images of *Kṛṣṇa* (Fig.1) (Ht. 145 mm and Wt. 378 gm) and *Rādhā* (Fig.2) (Ht. 150 mm and Wt. 716 gm) were recovered from the area of Karergaṅgā, Rajpur Bāzār near Baruipur which falls on the Eastern side of dried up Ādigaṅgā (later down South became a part of Mani-river), along with archaeological debris of bricks, stone artefacts, *Śivaliṅga*, coins, etc. This South Western Sundarban area holds a number of important archaeological sites of Buddhist, Jain and Brāhmanical origins at Boral[2], Sitakunda – Atghora, Deulpota, Harinaryanpur, Nalgora, Kankandighi, Jatar Deul, Baishhata and others. Close to Baruipur at Ramnagar many Brāhmanical images of *Mahiṣāsurmardinī*, *Gaṇeśā*, *Sūrya* and at Baishhata *Viṣṇumūrti* images are hallmark of a new style of bronzes for Bengal art[3].

Fig. 1. Icon *Kṛṣṇa*

Fig. 2. Icon *Rādhā*

A prolific number of East Indian bronzes, were recovered from different sites of Bengal and Bangladesh, and some even were found in hoards. Mitra and Bhattarcharya[4], Neogi and Schroeder, Sahai and Manowar Jahan, Datta and Chattopadhyay, and others analyzed some of these images. A part of that booty, a large number of metal images were also unearthed in 24-Parganas, in South Bengal in those areas mentioned in earlier paragraph. S. K. Saraswasti[5] recorded a few of them which were found at Manir Tat (a *mariaci* image) and Nalgora (an *Ambikā* image), near Baruipur. As recent as 2006, new finds in 24-Parganas, of South Bengal were excavated by Directorate of Archaeology, Government of West Bengal at a village Dhosa, near Jaynagar close to District headquarter Baruipur. Structural evidences were exposed at that site and there was suggestion of existence of *stupa* during 1st and 2nd century BC. Close to that site lies Tilpi[6] (22°15′ N, 88°38′ N), in 24-Parganas, where bronze ingot, crucibles, hearth, slag were excavated and that indicates continuous metal production and human habitation near and adjacent regions of South Bengal, throughout historical periods - though ravaged or washed away, by flood, or nor-wester and changing courses of rivers. So is there, the recovery of metal images, on a regular basis in this area of 24-Parganas, from different periods of history, be it Gupta or Pāla-

Sena or Medieval or pre-modern ages. In close proximity, also inhabit a large number of famous archaeological sites of Chandraketugarh, Balaidhap (near Mahasthan), Śāgardīghi, etc.

The excavated materials proved to be remnants of a lost civil society of this area. From the iconographic angle, Sri Hemen Majumdar, Secretary of the Museum, suggested in consultation with many art historians, that the excavated images represent icons of *Rādhā* and *Kṛṣṇa*, following *Vaiṣnavaite* tradition of Madanapāla (12th century) period.

Those two metal images are of very miniature form[7]. The images also do not belong to the same pair, because *Rādhā* stands taller than *Kṛṣṇa*, which is most unlikely from the iconographic angle. Probably, the images were worshipped in separate enclosures, following *Śaivate* tradition of Pāla-Sena period like *Kevalacandraśekhara*[8] fashion. The probable reasons of small sizes of icons may be explained as follows. South Bengal ran a vibrant economy of trade and agriculture in historical periods and produced enough surpluses to indulge in costly metal culture. But, being deltaic and fragmented hinterland, the area (*maṇḍala*) never had a large political hegemony of a kingdom and was only capable of supporting little affluence of producing tiny metal images for village temples as *iṣṭadevatā*. So, Bengal bronzes, in comparison with South Indian bronzes predominantly are small in size.

These bronzes from stylistic angle followed the proto-Australoid anatomy of round geometry as generally depicted by Jamini Roy's folk women or Konarak's dancers. As per physiognomy, *Rādhā* looks with wide open eyes made by incision in the shape of angular ends (*paṭalcerā cokh*) with a plump face of Pāla-Sena female icons. She possesses features of an ideal Bengali woman, having short stature, voluptuous breast, and plump hip, supported by heavy buttocks, round hands and legs. Similar to *Hara Pārvati* – bronze at Nalgora (7th - 8th century AD)[9], a *tṛratha* pedestal of a full blown lotus, a derivative of Pāla-Sena period, carry the image. She stretches out her palms probably to hold a lotus or a flower. Conversely, *Kṛṣṇa* has a chiseled frame, almost lifted from the figure of *Cola* bronze, with *tṛbhaṅga* pose, playing his flute. He wears a pointed crown over his head and postures close to a *nṛtya mūrti* (dancing pose), exposing graceful radiance of romance, unlike soft Buddha image of Pāla-Sena style. His exuberant mood was further enriched by a flat lotus at his knee with flying robes at his belt with a full-blown lotus pedestal under his feet, where petals are projected outside at second layer of *tri-ratha* foundation. *Kṛṣṇa* image again was better crafted and fashioned with sleek physique having sunken eyes, and can pose a challenge to earlier Pāla-Sena bronzes in beauty. All these iconographic features, with a free-wheeling style of over-flowing emotions, after Buddhist period of Pāla-Sena age, hold many sharp features of earlier bronzes acquired through generations.

Samatat area or Mani-river basin are dated between 8th - 12th century AD and many areas are variously dated from as early as Kuṣāṇa period (Kuṣāṇa coins at Jatardeul)[10] to as late as 13th century AD. Considering Brāhmanical nature of icons, those two images could be placed between 13th -14th century AD.

1.2. Laser Cleaning Operation of Bronzes

Both the bronzes before cleaning had hard dark corrosion coating over the surface. The dark coating was removed by laser cleaning method with Q-switched Nd:YAG laser. Bronzes were not subjected to chemical cleaning rather laser cleaning were adopted with a very slow removal rate, by Quanta System Laser (Model: PALLADIO, Serial No. PLLOOI-0207). During laser treatment bronzes got overheated which was countered by cooling the items under water. It was also observed during Laser treatment, that cleaning of the artefacts under wet condition yield better contaminant removal rate than dry condition. By repeated laser cleaning for two hrs per seating it took 4 to 5 seating, for arriving at a dull but clear appearance. The dull appearance comes from the presence of a thin layer of patina. The patina is deliberately left on the artefacts as it helps in protecting the substrate against further degradation. Details are shown in Table - I. After removal of the coating, Bronze castings showed dull yellow color with shallow irregular poke marks over some areas.

The cleaning sequence had been documented with photographs (Fig. 3 and Fig. 4) after each stage for the items of *Kṛṣṇa* and *Rādhā*, respectively.

2. Results Of The Laboratory Analyses

Two smaller inner fragments of the bronzes were collected and then were investigated using common metallurgical tools for Microstructure study, Scanning Electron Microscopy with EDX and X-Ray Diffraction Analyses.

Table 1: Details of the Laser Cleaning Operation by Q-switched Nd: YAG Laser

Experimental Run No.	Sample	Time (Second)	Frequency(Hz)	Energy(m J)
1.	Bronze*	30	10	155
2.	Bronze	5	10	151
3.	Bronze	60	10	157
4.	Bronze	30	10	155
5.	Bronze	60	10	156
6.	Bronze	30	10	154
7.	Bronze	30	10	152
8.	Bronze	30	10	151

*****Bronze here signifies copper-alloy items as is the convention of archaeologists and does not represent the scientific copper-tin alloy understood by metallurgists.

Fig. 3. Icon *Kṛṣṇa* (as received)

Fig. 3(a) Half Cleaned

Fig. 3(b). Totally Cleaned

Fig. 4. Icon *Rādhā* (as received)

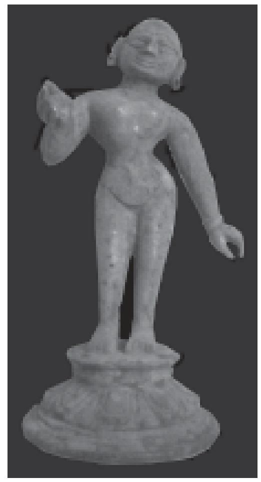


Fig. 4 (a) Half Cleaned

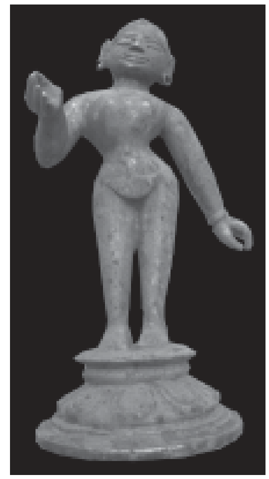


Fig. 4 (b) Totally Cleaned

2.1. Chemical Compositions by SEM-EDX

The average chemical composition analyzed using Energy Dispersive X-Ray Analysis (EDX) of Scanning Electron Microscopy has been given in Table-II. From the given compositions, bronzes *Rādhā* and *Kṛṣṇa* are found to belong to Cu-Zn system and can be termed as Leaded-Brass**.** Art historians generally call all copper alloy artefacts as bronzes but in actual metallurgical terminology Cu-Zn alloys are called as brass. When brass contains up to 30 wt. % Zn, the brass is called α-Brass or 70/30 brass as per British practice[11]. In American practice[12] when brass contains good percentage of zinc and low amount of tin and lead, those are called Leaded Semi-Red Brass.

Table II: Chemical Compositions of Bronzes

Elements (Weight%)	*Rādhā*	*Kṛṣṇa*
Zn	16.89	20.76
Pb	6.16	9.75
Sn	3.85	1.86
As	0.81	0.95
Sb	0.87	-
Fe	-	2.55
Cu	71.43	64.13

Considering,

(i) Lead is soluble in copper at higher temperature having monotectic $\alpha + L_1$,

(ii) But, lead is insoluble in copper at room temperature and get precipitated beyond the Cu-Zn system,

(iii) Although, lead forms eutectics with tin [13] at 183°C and so,

Lead becomes sparingly soluble in Cu-Zn-Sn system and let us assume, 80 % of the lead, to be out of the alloy system. Therefore, 20% lead will be soluble in the Cu-Zn-Sn system.

For example, in icon *Rādhā*, percentage of Lead insoluble and outside the system: 6.16 x 0.8 = 4.93 wt.%, percentage of Lead: 6.16 x 0.2 = 1.23 wt. % soluble in the system.

- Total elements remaining in the solid

  Cu + Zn + Sn + As + Sb + Pb = 71.43 + 16.89 + 3.85 + 0.81 + 0.87 + 1.23 = 95.08 wt.%

- In weight percentage, the actual composition achieved by the alloy is,

$$\text{Cu} = \frac{71.43}{0.9508} = 75.13\ \%,\ \text{Zn} = \frac{16.89}{0.9508} = 17.76\ \%,\ \text{Sn} = \frac{3.85}{0.9508} = 4.04\%,$$

$$\text{As} = \frac{0.81}{0.9508} = 0.85\ \%,\ \text{Sb} = \frac{0.87}{0.9508} = 0.92\ \%,\ \text{Pb} = \frac{1.23}{0.9508} = 1.29\ \%.$$

- With this alloy for calculation* of Zn-Equivalent[14], the zinc will be,

  17.76 (Zn) + 2 x 4.04 (Sn) + 1 x 0.85 (As) + 1 x 0.92 (Sb) + 1 x 1.29 (Pb) = 28.9 %

- For Zn-Equivalent calculation the total comes to

  28.9 + 75.13 (Cu) = 104.03

* The equivalents, due to Guillet,

Element	Sn	Pb	Fe
Equivalent Zn	2	1	0.9

- Zn-Equivalent will be $\frac{28.9}{104.03}$ = 27.78 wt.% and Cu – will be $\frac{75.13}{104.03}$ = 72.29 wt.%.

  Similarly, in icon *Kṛṣṇa*, percentage of lead insoluble and outside the system: 9.75 x 0.8 = 7.8 wt.%, percentage of lead: 9.75 x 0.2 = 1.95 wt.% soluble in the system.

- Total elements remaining in the solid

  Cu + Zn + Sn + As + Fe + Pb = 64.13 + 20.76 + 1.86 + 0.95 + 2.55 + 1.95 = 92.2 wt.%

- In weight percentage, the actual composition achieved by the alloy is,

  Cu = $\frac{64.13}{0.922}$ = 69.55 %, Zn = $\frac{20.76}{0.922}$ = 22.52 %, Sn = $\frac{1.86}{0.922}$ = 2.02 %,

  As = $\frac{0.95}{0.922}$ = 1.03 %, Fe = $\frac{2.55}{0.922}$ = 2.76 %, Pb = $\frac{1.95}{0.922}$ = 2.11 %.

- With this alloy for calculation* of Zn-Equivalent, the zinc will be,

  22.52 (Zn) + 2 x 2.02 (Sn) + 1 x 1.03 (As) + 0.9 x 2.76 (Fe) + 1 x 2.11 (Pb) = 32.18 %

- For Zn-Equivalent calculation the total comes to 32.18 + 69.55 (Cu) = 101.73

- Zn-Equivalent will be $\frac{32.18}{101.73}$ = 31.63 wt.%. and Cu – will be $\frac{69.55}{101.73}$ = 68.37 wt.%.

Therefore, taking the composition as binary Cu-Zn system, the bronze items can be approximated as α-brass from calculation of Zn-equivalent in copper as shown in Table - III. According to that convention, both *Rādhā* and *Kṛṣṇa* icons can be termed as α-brass, having constitutionally a single phase structure, as shown in copper-zinc phase diagram.

Following American convention both can be termed as Leaded semi-red brass having small percentage of tin in both bronzes. Those can be

Table III: Calculated Zn-Equivalent of Bronzes (wt.%) (excluding undissolved Lead)

	Radha	*Kṛṣṇa*
Zn Equivalent	27.78 wt.%	31.63 wt.%
Cu	72.29 wt.%	68.37 wt.%
(Pb)	(+ 4.93 wt.%)	(+ 7.8 wt.%)

further classified as Naval brass or a variety of Gunmetal where the basic alloy constituents are Copper-Zinc-Tin-Lead system, as per British practice.

Further to note that Bengal copper smiths introduced tin and lead into low zinc brasses (zinc content, 17-20 wt.%). Metallurgically, the use of Cu-Zn system with large amount of lead and low amount of tin though is not very conventional, but this complex combination of alloying elements are something notable for Bengal copper smiths. This may be due to non-availability of Tin in lower Bengal region or may be a borrowed practice from itinerant metal workers of copper hoard culture. Some of them still exist as migratory *Dokrās* at present. The similarity of metal culture between the coppersmiths of Bengal and migratory *Dokrās* is noteworthy.

On the basis of this discussion, it is well understood that Bengal metal smiths probably had thoughtfully designed the alloy of bronzes. Therefore, the alloy designs of the two bronzes signify many notable metallurgical understanding.

2.2. Microstructure of Bronze Icon *Rādhā*

2.2.1. Optical Microscopy

The microstructure of bronze (Fig.5) *Rādha,* in chemical composition, can be pronounced as a Leaded semi-red brass, Cu-Zn-Sn-Pb system, and shows typical cast brass structure with clear copper rich dendrites arranged in fir-tree pattern (white areas) as α-Cu phase. Black areas remain as last-to-freeze solute Zn-Sn rich β-Cu phase. Black round spots, in between dendrite, or sometime within dendrites indicate low melting point insoluble Lead[15], which does not dissolve in copper and present itself dispersed as uniformly distributed globules in the matrix and some time occupy the spaces of micro-voids or simply get entrapped. In such castings, lead effectively

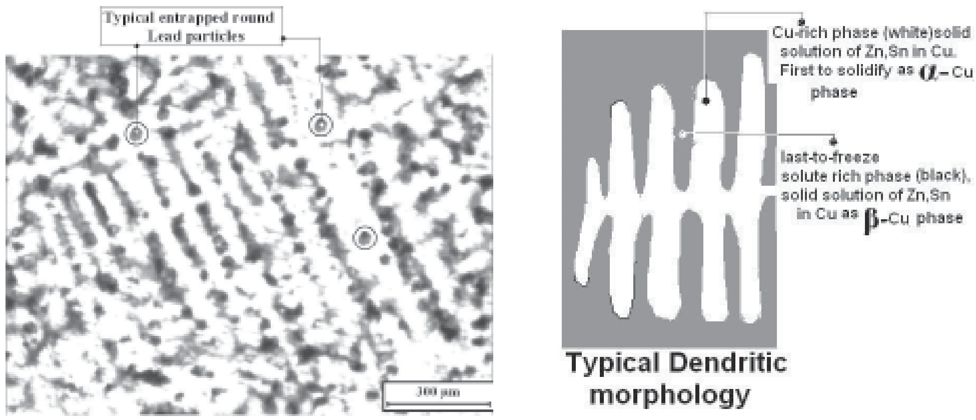


Fig. 5. Magnification: 50 X; Etchant: $FeCl_3$ in HCl. For icon *Rādhā*, white areas show Copper rich dendrites. Dark areas indicate solute rich (Sn, Zn etc.) last solidified β-Cu phase. Round spots reveal Lead. (R.H.S. in Fig. 5.a) The morphology of dendrites has been shown schematically.

seals the pores and helps to produce castings without micro-porosity. The typical Cast structure proves conclusively that the icon *Rādhā* had been produced by metal casting process in a foundry.

2.2.2. Scanning Electron Microscopy

For understanding distribution of elements, the specimen was further investigated by SEM & EDX method. From the results of the Scanning Electron Microscopy the structure (Fig. 6) clearly reveals serial orientation of Cu-rich α-phase dendrites (black) as matrix. Last-to-freeze solute rich, β-phase can be seen as shaded areas (white to grey). Lead particles are shown as white round or roundish spots. The typical cast single phase, the microstructure of Gunmetal, showing dendritic morphology predominates the photograph. The composition analyses of many areas conclusively prove the above observation. The chemical analysis of matrix α-phase (black) proves Cu-rich primary grains of dendrite. The round spots analyzed show the presence of lead as major constituent (white). Also the presence of (Zn, Sn, Pb, Cu) S – sulphide (2^{nd} left, Fig.6) concentration points towards the origin of copper as sulphide ore like copper pyrites, sourced from Singhbhum copper belt.

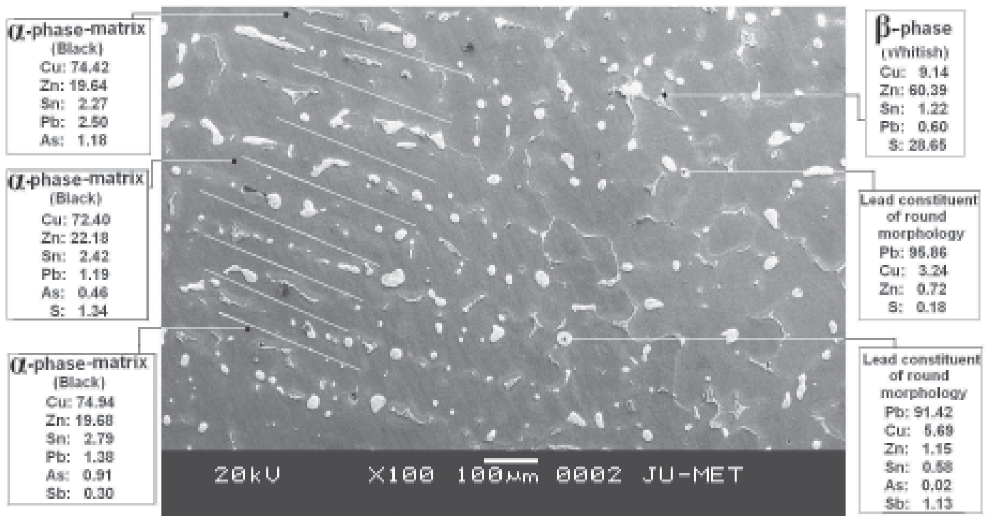


Fig. 6. Magnification: 100 X, Etchant: $FeCl_3$ in HCl, all compositions are given above **in wt.%**. The microstructure is of same material as of Fig. 5, but the contrast is different to indicate the matrix of α-Cu phase. β-Cu phase is white and round insoluble Pb particles are of the same color. The minor phases obviously contain less volume fraction. Note the serial nature of dendrites at the left hand portion shown by parallel (Q%) lines, with sectional cut-off polygonal rounds at the right hand side (schematically later shown in Fig. 10). SEM-EDX analyses the material compositions of respective phases.

During non-equilibrium cooling[16], segregation ratios *k*,

$$k = \frac{C_S}{C_L} \qquad \ldots(1)$$

calculated by the minimum solute composition to the maximum solute composition, gives the idea of non-equilibrium cooling, during solidification. C_S = Concentration of solute (Zinc) in solid phase, wt.% (First to solidify), C_L = Concentration of solute in liquid phase, wt.% (Last-to-solidify) (see Fig. 7).

For icon *Rādhā*, Zn: 19.64 : 60.39 = 0.32, which is different form, equilibrium diagram values of, $k = \frac{C_S}{C_L} = \frac{16.5 wt.\% Zn}{20 wt.\% Zn}$ = 0.83 obtained from Cu-Zn phase diagram. [Taken @ 1000ºC, C_S = 16.5wt.% Zn , C_L = 20wt.%Zn].

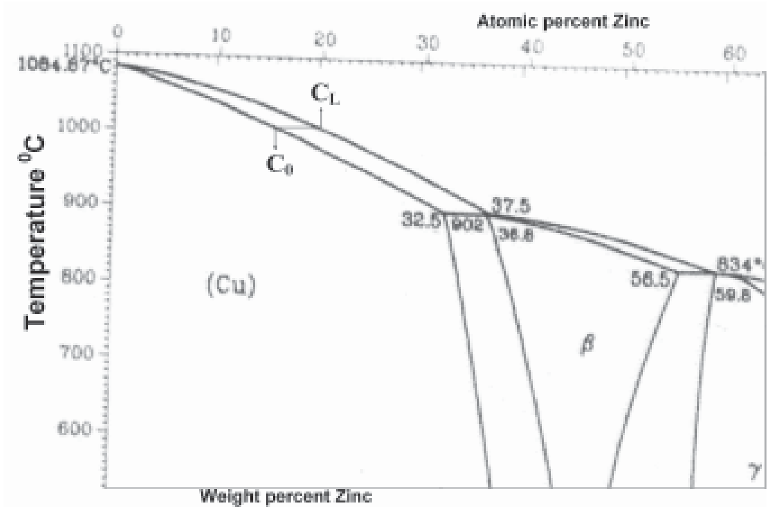


Fig. 7. A part of Cu-Zn phase Diagram[17]

This indicates deviation from phase diagram compositions and occurrence of the non-equilibrium cooling of liquid metal. In case of cellular dendrites Segregation ratios (k) generally change significantly[18]. The cellular dendrites and Segregation Ratio (C_S:C_L), also provide information about slow cooling rate of the casting where, as only low liquid temperature gradient can exist at that condition.

From the classical solidification condition for plane front solidification[19],

$$\frac{G}{R} \geq - \frac{mC_0(1-k)}{Dk} \qquad \ldots(2)$$

Where,

G = Temperature gradient of cooling liquid metal, K/cm,

R = Rate of solidification front advancement, cm/sec,

m = Slope of the liquidus line in Cu-Zn Phase Diagram,

k = Partition coefficient of solute in solid and liquid phase = $\frac{C_S}{C_L}$,

C_0 = Average composition of solute (Zinc) of the liquid metal,

D = Diffusivity of Zinc in Copper, during solidification.

In this case the values for Cu-Zn system of the liquidus line,

$$m = -\frac{(1083.6 - 902)}{37.6} = -\frac{181.6}{37.6} = -4.83 \text{ K/ wt. \% Zinc,}$$

$$k = \frac{C_S^{\;*}}{C_L} = \frac{16.5}{20} = 0.83 \approx 0.8, \text{ *from Cu-Zn phase diagram.}$$

D = Diffusivity[19] of zinc in copper @ 727 - 955°C, $D = D_0 e^{-(\frac{Q}{R_0 T})}$ ...(3)

Substituting values of, @ 1000°C, D_0 = 3.2 x 10^{-3} cm^2/sec, Q = 18.5 kcal / g. atom,

R_0 = 1.98 cal /mole/K, T = (1000 + 273)K = 1273 K, D = 2.9735 x 10^{-3} cm^2/sec (calculated).

For icon *Rādhā*, Zn content, C_0 = 16.89 wt.%

Therefore, Putting values, $-\frac{mC_0(1-k)}{Dk}$ = 6858 K. sec/ cm^2,

$$\Rightarrow \frac{G}{R} \geq 6858 \text{ for plane front solidification.}$$

Assume, for G = 10 K/cm, and G = 5 K/cm,

$\Rightarrow$ R = 1.46 x 10^{-3} cm/sec $\Rightarrow$R = 7.29 x 10^{-4} cm/sec.

For thin section in Fig. 8 of icon *Rādhā*, the rim thickness is 2 mm, with 1 mm is the depth of solidification front from both ends for plate casting. The local solidification times come approximately, 1/R or 68 sec and 137 sec, respectively.

This first solidification time is much less than expected in actual practice of investment casting. So, the actual temperature gradient of cooling liquid metal is much lower and suggests the application of hot molds which can only actuate low heat flux (transfer) rate $q = k_1 \frac{dT}{dx}$, with subsequent long solidification time.

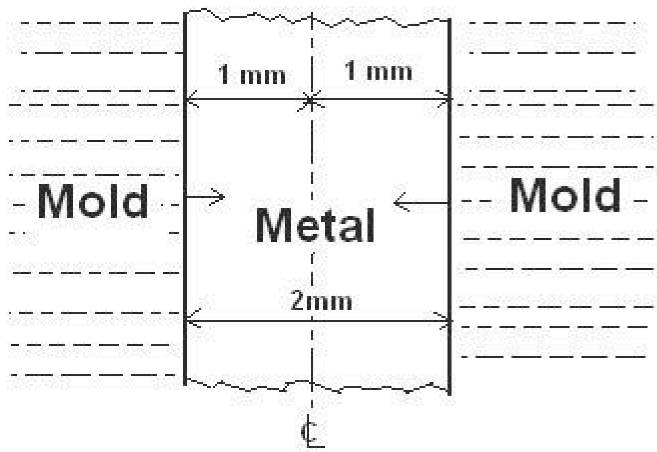


Fig.8. Thin section of the icon *Rādhā*

2.2.3. X-Ray Diffraction (XRD) Analysis of Icon *Rādhā*

Analyzing the X- Ray diffraction data for icon *Rādhā* (Table IV) a number of phases have been identified[21]. The important phases are located in Fig. 9. From the X-Ray Diffractogram, the presence of dominant α-Cu phase (solid solution of Zn, Sn in Cu), FCC is confirmed. Some minor β-phase (solid solution of Sn, Zn in Cu), BCC are also present. Insoluble Lead as separate phase can be found in the analyses.

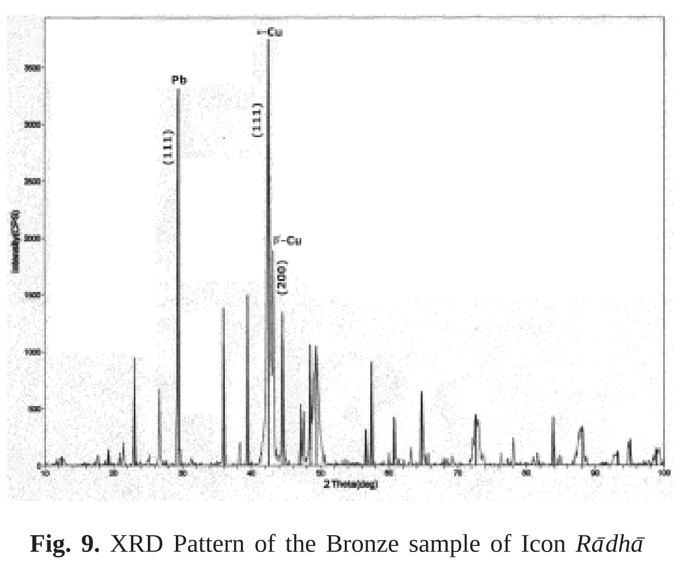


Fig. 9. XRD Pattern of the Bronze sample of Icon *Rādhā*

Table IV: Details of X-Ray Diffractogram of Bronze sample *Rādhā*

No.	Angle(2θ)	d_{space}	I / I_0	Identified Phase	Diffracting Plane (hkl)
1.	29.400	3.0355	87	Pb	(111)
2.	39.400	2.2851	36	Pb	(200)
3.	42.500	2.1253	100	α-Cu	(111)
4.	43.200	2.0924	41	β''– Cu phase	(200)
5.	44.600	2.0300	12	β_1– Cu phase	(110)
6.	47.100	1.9279	17	β_1– Cu phase	(011)
7.	47.500	1.9126	16	β''– Cu phase	(210)
10.	48.500	1.8754	26	α-Cu	(200)

2.3. Microstructure of Bronze Icon *Kṛṣṇa*

2.3.1. Optical Microscopy

The optical micrograph (Fig. 10) shows equiaxed dendrites or cellular dendrites, with grey Lead particles all around. Dendrites are the signature of casting process and that vindicates the metal forming technology of Bronze *Kṛṣṇa* as casting.

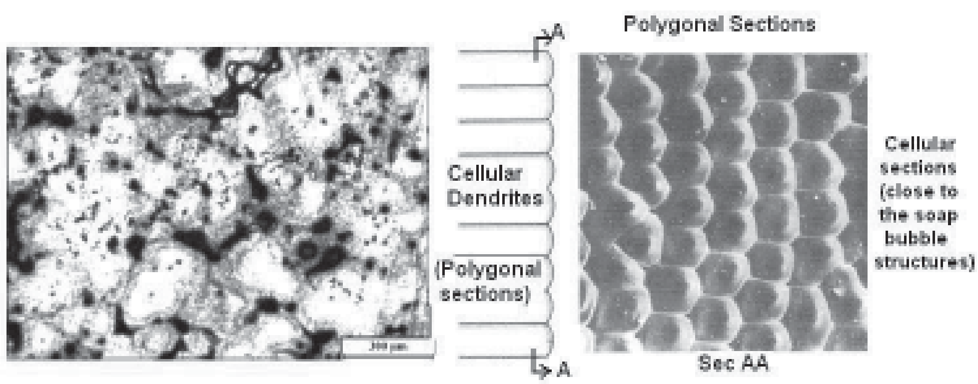


Fig. 10. Magnification: 100 X; Etchant: $FeCl_3$ in HCl. The optical microstructure of icon *Kṛṣṇa* reveals the impression of a highly distinctive cellular structure formed by α-phase (white round areas). Surrounding the cluster of polygonal rods (dendrites) solute rich second phase grow (grey areas) in the intermediate region. Some globules of Lead (black rounds) can be seen on and outside the dendrites. (R.H.S.) Schematically, the cellular dendrite morphology with cross sectional view has been shown. Cellular dendrite sections commonly called 'soap bubble structure'[22]

The formation of distinctive cellular structure is significant, which needed a certain level of under cooling, obtained only in a slow solidification process, like sand molding or investment molding.

2.3.2. Scanning Electron Microscopy

Under SEM the sample was further investigated and micro-analyzed by EDX method. The microstructure (Fig. 11) of Bronze *Kṛṣṇa* reveals coarse dendrites with lots and lots of Lead precipitated within or around dendrites. Coarseness of dendrites leads to the conclusion that the castings were produced in hot molds. Due to the low temperature gradient $\left(\frac{dT}{dx}\right)$ between cooling liquid metal and hot (heated) mold, the heat transfer rate becomes very small and solidification takes long time, when adequate diffusion of atoms allow growth (G) of dendrites or grains and the coarseness of dendrites develop.

With respect to bronze *Rādhā*, the amount of lead can be seen significantly higher. The chemical compositions of α-Cu and β-Cu (black areas) show (Fig.11) Cu-rich and solute rich elements respectively. Last-to-

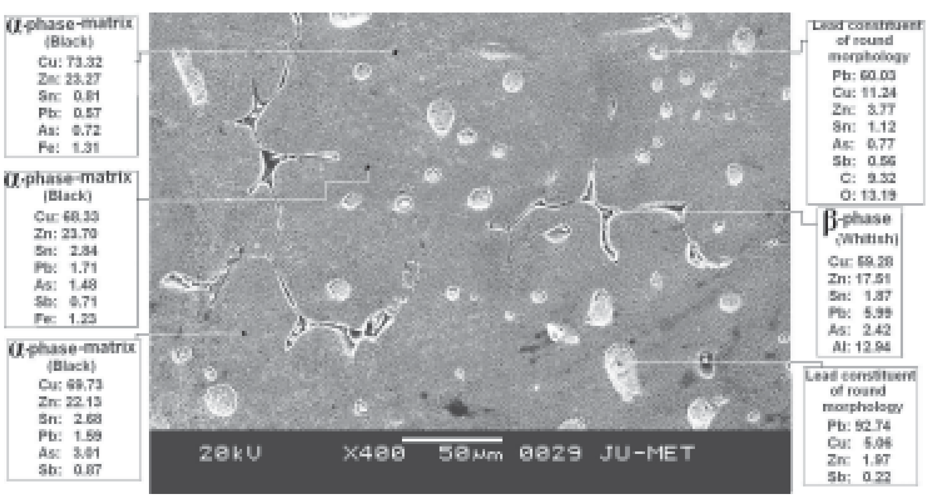


Fig. 11. Magnification: 400 X; Etchant: $FeCl_3$ in HCl, all compositions are given above in wt.% (Material same as Fig.10). The coarse microstructure of icon *Kṛṣṇa* has been depicted in the SEM photograph. The structure is single phase of α-Cu with very little β-phase (black colored) within it. Dendrites are very coarse indicating very slow rate of solidification. The round phases are insoluble Lead constituents. The compositions of matrix α-phase and minor β-phase in the inter-dendritic region have been marked.

freeze Lead constituent was also analyzed. The insoluble Lead effectively fills up pores between dendrites and makes the casting more sound. During non-equilibrium cooling[23], segregation ratios, calculated by the minimum solute composition to the maximum solute composition, during solidification as follows:

Zn: 17.51 : 23.70 = 0.74.

Under formation of cellular dendrites SR generally increases significantly, with respect to equilibrium partition ratio, *k*.

2.3.3. X-Ray Diffraction (XRD) Analysis of Icon *Kṛṣṇa*

In case of *Kṛṣṇa* all the comments about the bronze *Rādhā* are valid — that is the major phase is α-Cu phase and minor phase is β-Cu phase which are shown in Fig. 12 and Table - V. Only exception is the peak of lead[24] which is substantially higher with respect to that of *Rādhā*, indicating higher amount of Lead is present in this sample.

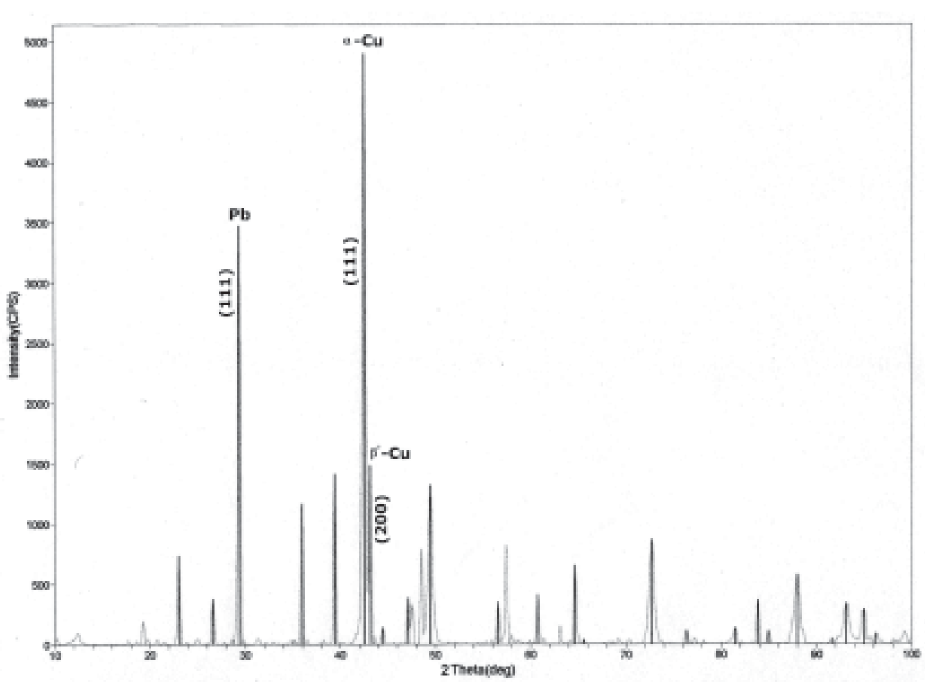


Fig.12. XRD Pattern of the Bronze sample of Icon *Kṛṣṇa*

Table V: Details of X-Ray Diffractogram of Bronze sample, *Kṛṣṇa*

No.	Angle(2θ)	d_{space}	I / I_0	Identified Phase	Diffracting Plane (hkl)
1.	29.500	3.0254	88	Pb	(111)
2.	36.000	2.4927	43	Pb	(200)
3.	39.500	2.2795	47	Undefined	Undefined
4.	42.500	2.1253	100	α-Cu	(111)
5.	43.200	2.0924	57	β''– Cu phase	(200)
6.	44.600	2.0300	44	β_1– Cu phase	(110)
7.	47.200	1.9240	26	β_1– Cu phase	(011)
8.	47.600	1.9088	24	β''– Cu phase	(210)
9.	48.600	1.8718	38	α-Cu	(200)

3. Technology and Type of Molds Used for Production of Bronze Images

Primary investigation so far discussed conclusively proves the metal forming technology of bronze icons follows metal casting route. To find out further the type of the casting process, let us consider the parameter of Secondary Dendritic Arm Spacing, which can provide us the types of casting process used by the metal workers.

According to Beeley[25], the Arm spacing of Secondary dendrites confirms to the relation $\lambda\ r^{a} = B$ where, 'a' and 'B' are constant and λ = Secondary Dendritic Arm Spacing in µm, r = Cooling Rate in K/sec. The relationship signifies refining effect due to increasing cooling rate, as the Secondary Dendritic Arm Spacing (SDAS) is inversely proportional to the cooling rate. Also this represents coarsening of dendrites due to decreasing the cooling rate, i.e. the slower the cooling rate wider is the Dendritic Arm Spacing. In this particular case of hot molds, the cooling rate of the castings would be slower and thereby, the Dendritic Arm Spacing would be larger. According to Hwang[26], for Tin-Bronze, the Secondary Dendritic Arm Spacing follows the relationship of

$$\lambda = 101 \times r^{-0.42} \qquad \ldots(4)$$

Using this relationship, the Dendritic Arm Spacing of both bronzes, *Rādhā* and *Kṛṣṇa*, have been measured from microstructures (ref. Figs. 5, 6, 10, 11) and their cooling rates calculated using equation (4), have been given in Table VI.

Table VI: Secondary Dendritic Arm Spacing and Cooling Rates of Bronzes

Specimen	Secondary Dendritic Arm Spacing (λ), μm	Cooling Rate (r), K/sec.
Bronze *Rādhā*	59.50	3.522
	78.57	1.818
	66.66	2.687
	54.56	4.333
	47.62	5.990
Bronze *Kṛṣṇa*	60.00	3.45
	125.00	0.60
	80.00	1.74
	50.00	5.33
	70.00	2.39

The cooling rates of both bronzes show very slow cooling rate during solidification. The question arises what type of molds produced this slow cooling rates.

Molds of the Archaeological period as quoted in the text[27] refer to Clay Molded process. The clay molds consist of clay, sand, charred Rice-husk and other cotton fabrics bound together to produce a highly non-conductive, ceramic material of poor heat conductance (k_1) comparable to silica sand (k_1 = 6.0 w/m.K)[28]. On heated condition, the molds were dewaxed and the red hot molds were supposed to be used for copper-alloy castings as mentioned in the text. If hot molds are used, then conductive heat flux, through mold for removal of heat energy of solidification during phase transformation would be less as the temperature gradient between copper-alloy and the hot mold would be very low and the ceramic heat conductance, k_1 would be very poor. The poor heat transfer rate or the heat extraction rate through the mold will cause the solidification to take place for long time and there will be ample time (t) and sufficient temperature (T), when diffusion of atoms could take place. Increased diffusion rate as well as high temperature of the liquid metal would produce low nucleation rate[29] (n) and comparatively high growth rate, and ultimately coarse dendrites will result. Due to high local solidification time, Secondary Dendritic Arm Spacing will also be wider. Therefore, the slow cooling rate of the order of single digit cooling rate (K/sec.), confirms red-hot condition as well as ceramic clay molds used during casting.

4. Context of Relationship of the Traditional Castings with Dhokra Castings

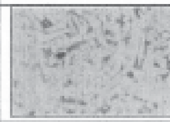
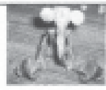
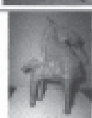
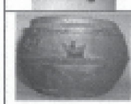
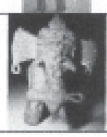
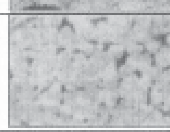
Eastern India, in particular Bengal region has been fortunate enough to have various types of metal workers from pre-historic time, due to the presence of abundant mines, thick forest and heterogeneous populations, expert in many trades. Over and above natural resources, there is a zigzag corridor of continuous tribal path, down the lower Vindya region, from the extreme West coast of Dang district of Gujrat, through Nimar in Maharastra, Bastar, in Chhattisgarh, Hazaribagh- Ranchi, in Jharkhand up to the foothills of Rajmahal hills in the West of Bankura. The forested area remained unaffected almost in post-Harappa period, over two millennia from the bloody upheavals of Gangetic civilization. Thereby a tremendous inter-mixing of technology took place from the pushes of Southern Dravidians, Western Marathas or Gujratis or Eastern Mongols towards the wooded plains of riverine East India. Thankfully medieval Bengal was privy to these histories. There is a record of eight types of metal workers (*Aṣṭakāmār*)[30] that originated in Bengal- probably those were *Svarṇakāmār* (Goldsmith), *Cāndkāmār* (Silversmith), *Tāmrakāmār* (Coppersmith), *Kānsakāmār* (Bronzesmith), *Dokrākāmār* (Tinsmith or Brazier or Lost-wax Caster), *Pitulikāmār* (Brass smith), *Lauhakāmār* (Ironsmith), and *Ghaṭakāmār* (*Ghaṭi*» *Ghaṭ* = Pot = maker or Sand-clay casting smith or Impact loader or Sheet metal worker). There might be intra- or inter-caste rivalry or conflicts of smithy communities and interchanging of job work, still they shared their knowledgebase and contributed heavily to the up-gradation of technology. In every trade this was true. Most of the Tamil or Austro-Dravidian dialects of indigenous tribes, which contributed generously to modern Bengali or Oriya, have got excellent glossary of technical terms and rules, which are used by workers even to-day, through out the East, be it casting, forging, carpentry or boat making. The ancestors of modern *Dokrās* or some such tribes[31] might be the originators of Copper-Hoard Cultures who carried their brilliant casting technology of hot-molds and profound knowledge of strong Copper-Zinc alloys, known as Brass (*Pit-tal* = Yellow colored metal) to the East, in Bengal. Incidentally, Brasses are famous for low melting points and so were very easy for melting or liquefaction during casting. The irony is that Zinc was being produced in the Western India by people of Rajputana or Rajasthan, thousands of kilometers away from Bengal, from the first half of 1st millennium BC by the famous Distillation Process[32], unknown any where in the world, but the metal became popular in Bengal in the East. Bengal artisans mastered the art of Brass casting in most of icon making, unlike other major areas of India, where mainly bronze (Copper-Tin alloy) were used in icon making. In this case, icons of *Rādhā* and *Kṛṣṇa* have become the embodiment of that culture. Naturally tribal *Dokrās* acted as conduit in transferring the Brass technology to *Kāmārs* of *Rāhṛ* Bengal (South Western Bengal), though the technology is not exactly the same photocopy, rather it was the opposite. *Dhokras* use bees-wax patterns, whereas, Bengal artisans used a replica to build piece-molds, which were assembled together like Far Eastern *Mongol* artisans of China. Again, while Chinese artisans used bronzes (Copper-Tin alloys), it is already mentioned that Bengal casters used Brass and hot-molds like *Dokrās*. It seems that technology respects no boundary or barrier, through out history, unlike boundary of a kingdom made by ethnic domination of majority community or powerful community. Thus a close synergy exists between traditional Bengal casters and tribal casters, like *Dokrās*.

4.1. Comparison with Present Tribal Metal Castings

Tribals (*Dokrās*) also use hot molds of clay molded investment material in their casting production. Some of those castings were collected and the microstructures of those castings were developed. Then Secondary Dendritic Arm Spacing of those castings was measured and cooling rates were calculated. The results have been tabulated in table –VII. The observation on the chemical compositions of Tribal castings informs that Tribals are still using a kind of α-Brass (Cu + low Zn %) containing some amount of Lead and Tin, to get low melting copper-alloys. So, a comparison has been made of the archaeo-bronzes so far discussed with the Tribal castings traditionally produced. Microstructures found in this type of castings consist of coarse grained dendrites, which can only be possible if castings are produced in hot molds.

A comparison of the cooling rates of tribal castings with that of investigated bronzes indicates that, in both cases those are below or around 10 K/sec, which vindicates a very slow cooling rate, possible only in case of hot clay molds.

Table VII: Details of sources, metallographic study and cooling rates of Tribal Castings

Item	Source	Microstructure	Chemical Composition (wt.%)	Secondary Dendritic Arm Spacing (λ), μm	Cooling Rate (r), K/sec.
	Kuliana, Mayurbhanj, Orissa		Cu:62.97 Pb:1.52 Zn:28.46 Ni:1.24 Sn:4.66 Fe:1.15	85	1.5
	Bastar, Kondagaon, Chatishgarh		Cu:65.07 Ni:1.15 Zn:30.45 Fe:1.40 Sn:1.92	60	3.5
	Jhigiri,Raygada, Near Bisam Cuttock		Cu:62.22 Pb:0.80 Zn:36.15 Fe:0.83	55	4.3
	Bikna, Bankura, West Bengal		Cu:62.63 Pb:2.06 Zn:31.57 Ni:0.59 Sn:2.05 Fe:1.10	61	3.3
	Jhimripali, Orissa		Cu:68.16 Pb:1.08 Zn:24.39 Ni:0.70 Sn:4.64 Fe:1.03	62	3.2
	Sadaibhirini, Orissa		Cu:59.11 Pb:6.13 Zn:31.72 Sn:3.04	54	4.4
	Dariapur, Bardhaman, West Bengal		Cu:59.61 Pb:5.20 Zn:23.40 Ni:5.14 Sn:4.18 Fe:2.47	53	4.6

5. Reconstruction of The Casting Technology in Laboratory

For further confirmation of metal technology, a reconstruction of the metal casting process was simulated in Rural Casting Laboratory of Jadavpur University. Some castings of brasses were produced in moderately hot clay molds as follows:

Stage 1: Core Making: A clay-core was made up of appropriate form, using a mixture of alluvial, rice-husk and coarse silica sand (40-60 AFS No.) in the ratio of 4: 1: 1, with sufficient moisture so as to develop enough flowability suitable for making their form.

Stage 2: Polishing, Drying and Wax Making: The top surface was polished and the core was dried slowly. A wax recipe of 20:80 of Sal-dammer resin (*dhuna*): Bees wax was prepared.

Stage 3: Wax Pattern Making: Waxing was done over the dried core, along with suitable runners and gates, made of the same wax.

Investment Shell Molding

Stage 4: (Facing) Shell Molding: A 3-5 mm. thick investment shell of fine clay (Bentonite) and cow-dung mixture was pasted over the wax pattern and was slowly dried.

Stage 5: Back-up Shell Molding: Covering the investment shell, another back-up layer of the clay-sand-rice husk aggregate (used earlier in the core) of generous thickness (minimum 6 mm) was applied, with the making of a funnel at the gate, to hold the metal.

Stage 6: Metal Charging, Firing & De-waxing: After complete drying, the investment mold was transferred to a furnace and gradually heated for de-waxing and casting.

Stage 7: Melting and Pouring: Metal was melted in a graphite crucible in a muffle-furnace and then the hot metal was poured uninterrupted into the pre-heated dewaxed investment clay mold, like any other casting process.

Stage 8: Fettling: When the casting cooled, after usual fettling, brushing was done. For reference a sample casting with gates and riser has been shown in Fig. 13.

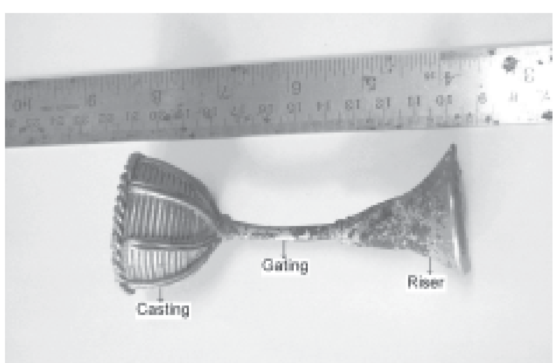


Fig. 13. A casting sample produced in Jadavpur University

A small portion of the castings was cut for metallographic investigation.

The microstructure of one brass sample (Fig.14) produces an ingot structure (Dendritic Structure) and reveals that the α-Cu phase predominates. This structure also shows micro-voids in the inter-dendritic region (black encircled portion). Whitish dots of Pb analyzed by EDX in Pb-Zn form are also present sealing the micro-voids in the inter-dendritic region. The chemical composition analyzed by SEM-EDX method is given by Cu: 58.68 wt.%, Zn: 33.69 wt.%, Sn: 1.27 wt.%, Pb: 4.85 wt.% and Fe: 1.50 wt.%.

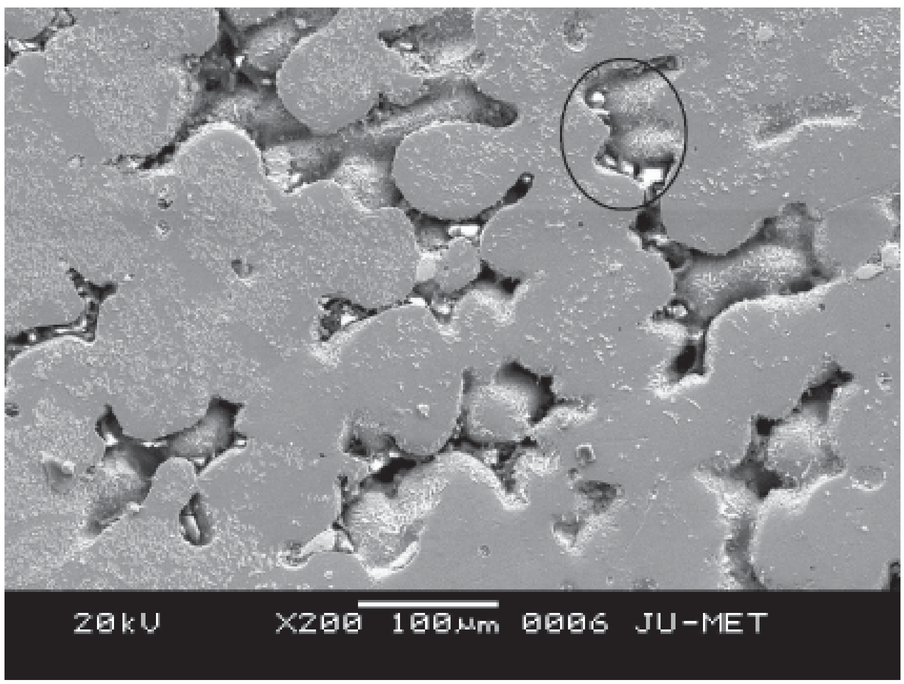


Fig. 14. Magnification: 200X, Etchant: $FeCl_3$ in HCl

Another microstructure (Fig.15) of a cast brass sample depicts that the α-Cu phase is again dominant. The chemical composition is given by Cu: 66.13 wt.%, Zn: 32.57 wt.%, Sn: 0.18 wt.%, Pb: 0.41 wt.%, Ni: 0.13 wt.% and Fe: 0.57 wt.%.

The microstructures of the Brass casting samples, produced in laboratory of Jadavpur University made by investment casting process in hot

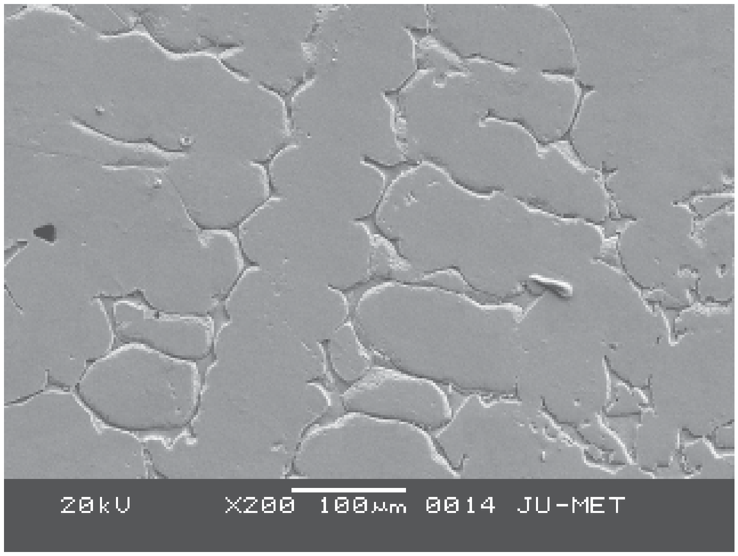


Fig. 15. Magnification: 200X

Table VIII: Secondary Dendrite Arms Spacing and Cooling Rates of Brass Casting produced in Hot Molds of Laboratory

Specimen	Secondary Dendritic Arm Spacing (λ), µm	Cooling Rate (r), K/sec.
1.	63.0	3.07
2.	54.0	4.44
3.	53.0	4.64
4.	81.0	1.69
5.	64.0	2.96
6.	62.0	3.19

molds. The predominant α-Cu phase dendrites with few amount of β-Cu phase in the inter-dendritic region can be seen.

Secondary Dendrite Arm Spacings of those castings are also tabulated in Table-VIII. The investigation reveals slow cooling rates of the brass castings, likely to be found in cast metals produced in hot clay molds.

The reconstructed casting schedule provides much information, which could help us to understand the cast technology of medieval Bengal.

6. Discussion on Alloy Design

The analyses of the two bronzes raise some metallurgical principles which indicate working knowledge of metallurgy for Bengal metal workers. These metallurgical principles are being elaborated as follows:-

6.1. Hume-Rothery Rules for Solid Solubility of Alloying

Both the alloys can be termed metallurgically as α-Brass of Cu-Zn system with additions of significant quantity of primary lead and secondary tin. According to Hume-Rothery's principles, the formation of alloying, depends on the various parameters, in which the atomic size of elements is the most important factor. The atomic radius of Cu is 0.128 nm and so the alloying elements of Cu should have as per H-R rule, atomic size within $\pm$ 15% of its atomic size. This is solubility limit of Cu shown by Fig. 16. The common soluble elements in copper[33] like As, Zn, Sn, Au, Ag, Sb, Al have atomic radii 0.125 nm, 0.133 nm, 0.141 nm, 0.144 nm, 0.144 nm, 0.145 nm, 0.143 nm, respectively and fall within $\pm$ 15%. Accordingly, the common alloying elements of Cu are As, Zn, Sn, Au, Ag, Sb and Al. In this regard

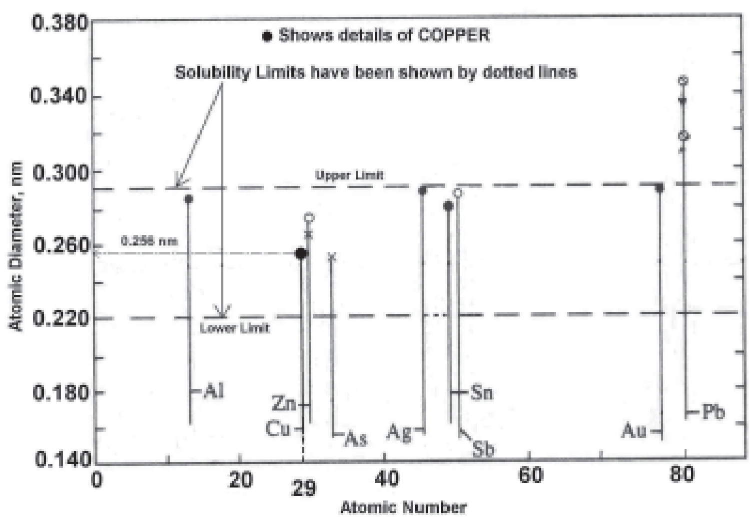


Fig. 16. According to atomic size parameter of Hume-Rothery Rule, upper and lower limits of atomic size of alloying elements of Copper[34] are given by the horizontal dotted lines. Atomic sizes of elements have been shown by circles. The atomic size of copper is given by dark circle. Except Lead most of the common elements are coming within the dotted lines

Pb has atomic radius over Cu as 36.72%. It means that Pb becomes insoluble in copper alloys. Bengal Smiths had definitely an understanding on this respect and visualized some effects due to alloying.

6.2. Alloy Hardening due to Solid Solubility

Alloying makes a metal stronger[35] and harder known as solid solution hardening. It is already stated that Zn addition made the metal a Cu-Zn alloy. Zn – equivalents of *Rādhā* (27.78 wt.%) and *Kṛṣṇa* (31.63 wt.%) show that the bronzes belong to α-brass group of alloys. β-brass also have ductile material characteristics[36] and well known for its resistance to fracture. Therefore, the choice of the metal composition, by Zn – alloying provided strong material for icon durability.

6.3. Melting Point Depression due to Alloying

The addition of Zn lowers the melting point of the alloy by 4.6 K per 1 wt.% Zn[37] from the melting point of pure copper (m.p. of Cu 1356 K). Sn and Pb addition also lower the melting point of the alloy by 11 K per 1 wt.% Sn[38] and 2.6 K per 1 wt.% Pb[39], respectively. So, the melting point of the alloy substantially gets lowered due to alloy additions. Additions of As, Sb also lower the melting point. The addition of all alloying elements so far discussed from Zn to Sb depresses substantially the melting point of the alloy thermodynamically much more than the arithmetically calculated melting point. For an example, an American specification CDA 544 alloy[40] having composition of Zn: 3.96 wt.%, Sn: 3.92 wt.%, Pb: 3.20 wt.% and base metal Cu: 88.92 wt.%, the lowering of m.p. due to Zn, Sn, and Pb are 18 K, 43 K and 8 K, respectively. So, total lowering of melting point is 69 K of this alloy. In actual practice, thermodynamically, the melting of this multi-component alloy starts much lower than the calculated melting point of the alloy, 1356 K – 69 K = 1287 K (1014ºC). Therefore, the melting of the multi-component alloy becomes easier for the metal smiths and Bengal metal workers probably had a notion about this melting point phenomenon.

6.4. Removal of Primary Pipes due to Multiple Alloying

Cu-Zn alloys generally fall in Group – I cast alloys[41] which have a narrow freezing range (about 50 K), that is a range of 50 K between liquidus and solidus temperature. These alloys can be directionally solidified and the central pipes or volume shrinkages occur in the last solidified thick section, where risers are to be placed for feeding the volume shrinkage. But in the case of *Rādhā* and *Kṛṣṇa* bronzes, the situation is different. The addition of zinc and tin extend the freezing range of the alloy and those are grouped as Group – III alloys having a wide freezing range. These alloys have a freezing range well over 110 K and generally Leaded Red Brass, Leaded Semi-Red Brass, Tin bronzes fall into this group. These alloys are very difficult to feed as volume shrinkages are widely distributed, but risers cannot be placed in every location of castings and thereby, render it difficult to feed the castings. This makes the castings unsound, but allows the foundrymen to avoid the problem of compensating the volume shrinkage by placing a heavy riser at the last solidified region of the castings. In Ancient or Medieval time, the distributed voids or shrinkages within the metal allowed the metal smiths to have castings devoid of any major shrinkage though the metal might be of poorer mechanical property. It is observed that the distributed porosity in casting[42] increases heavily when (Zinc + Tin) content exceeds 10% and feeding of the castings become very difficult. But the avoidance of central pipes makes the foundrymen feel happy as no apparent contraction or shrinkage on outside casting surface is observed. The case looks like rimming steel, — full of sub-surface blow-holes and porosity, where central pipes are very shallow comparatively to killed steel ingot, having very large pipes, where the top end of the metal ingot is rejected. So, the output of rimming steel is always good with respect to killed steel ingot as the total pipe is to be eliminated for the later. Therefore, the addition of multiple alloying helped metal workers to *get apparently good outside casting surface, but inside unsound metal*, although this was not fully recognized or comprehended by the metal smiths.

6.5. Fluidity Improvement due to Alloying of Zinc and Tin

The addition of Zn[43] upto 20 wt.% Zn lowers the viscosity of Cu – alloy (Fig. 17). Similarly, the small addition of Sn lowers the viscosity[44] (Fig.18) and increase the flow of the liquid alloy into the mold (Fig.19). The addition of Tin also lowers substantially the surface tension of copper-alloy[45] (Fig.20). Surface tension, of liquid alloy is also an important characteristic and with a decreased surface tension the alloys becomes more fluid and

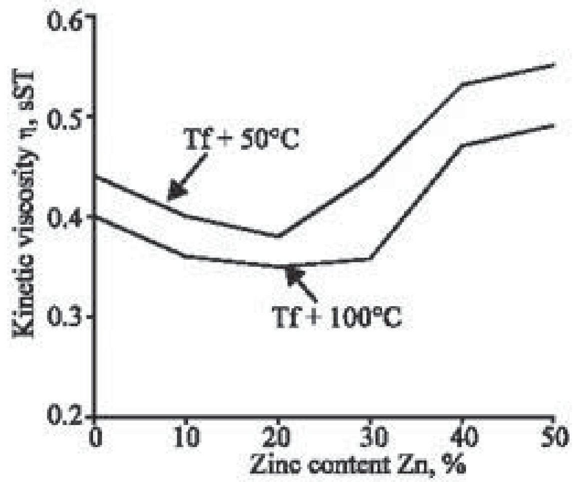


Fig. 17. Viscosity of liquid Cu-Zn alloys at 50ºC and 100ºC over melting points

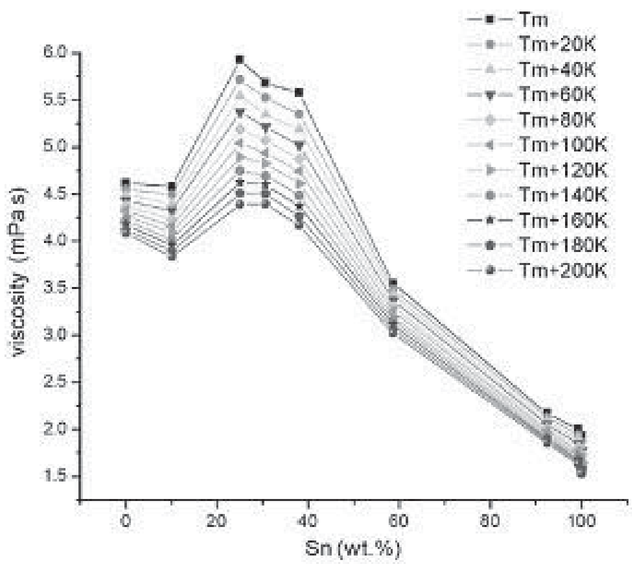


Fig. 18. Comparison of viscosities of liquid Cu-Sn alloys at different temperatures

efficiently fill thin channels[46]. So, the castability of the alloy increases due to additions of Zn and Sn.

Due to lower viscosity[47] (2.65 mPa.s.) and melting point of Pb (~ 594 K) further improvement is expected in case of Lead addition to Copper-alloy. All this is given by the alloy of American specification CDA 544

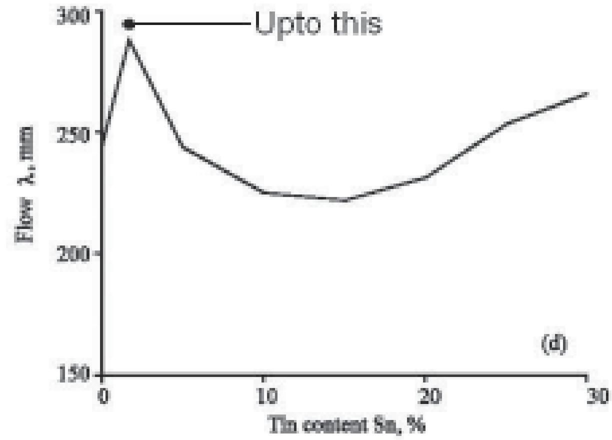


Fig. 19. Maximum flow of Cu-Sn alloys

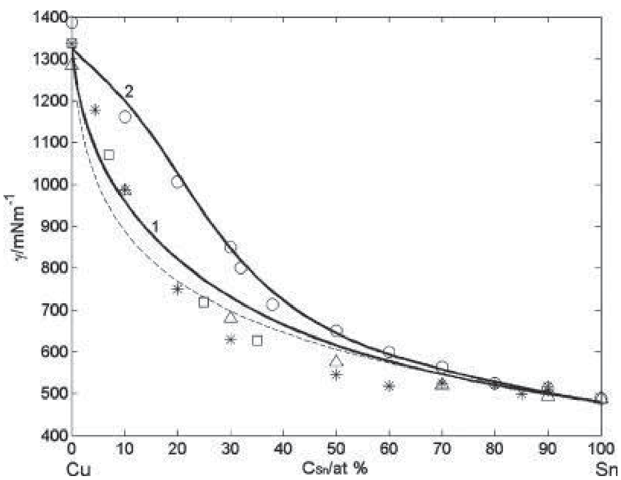


Fig. 20. Surface tension isotherms of liquid Cu-Sn alloys at T = 1423 K. 1, calculated curve by QCA for regular solution model; 2, calculated curve by CFM, calculated curve by the ideal solution Model

alloy[48] (mentioned earlier) which shows a viscosity of 3.8 mPa.s. whereas pure copper[49] has a viscosity of 4.38 mPa.s. at its melting point. From the liquid metal characteristics viscosity of a liquid metal is a reciprocal of fluidity. So, a lower viscosity alloy generates easier metal flow in the mold and the flowability of the alloy improves. Therefore, additions of Zn, Sn and Pb improve the castability of the alloy. Actually, the Cu-Zn-Sn-Pb system is a modern variation of Gun-Metal composition. Gunmetal is comparatively more fluid than copper and the metal smiths had probably good perception about the right type of copper alloy composition to achieve fluid metal. A similar comparison can be made with Roman Bronzes[50] where the similar Cu-Zn-Sn-Pb system was vigorously used for production of castings.

6.6. Cleansing of Liquid Metal from Dissolved Oxygen [O] by Alloying with Zinc, Tin and Lead

Zinc has a low vaporization point at 1179 K and vaporizes easily during melting of Cu-Zn alloys producing zinc oxide. The phenomenon is known as Zinc-flaring[51] and very much utilized by foundry men to remove dissolved oxygen in copper alloy, which is known as deoxidation practice. Copper – Zinc[52] alloys rarely have problems associated with gas porosity, primarily because zinc deoxidizes the metal. Zinc may also remove dissolved gases because of its high vapor pressure, which results in the zinc vapor flushing hydrogen out of the melt. According to Ellingham Diagram[53] (Fig.21) of oxides, thermodynamically Zn, Sn, Pb, Ni have lower oxygen potential

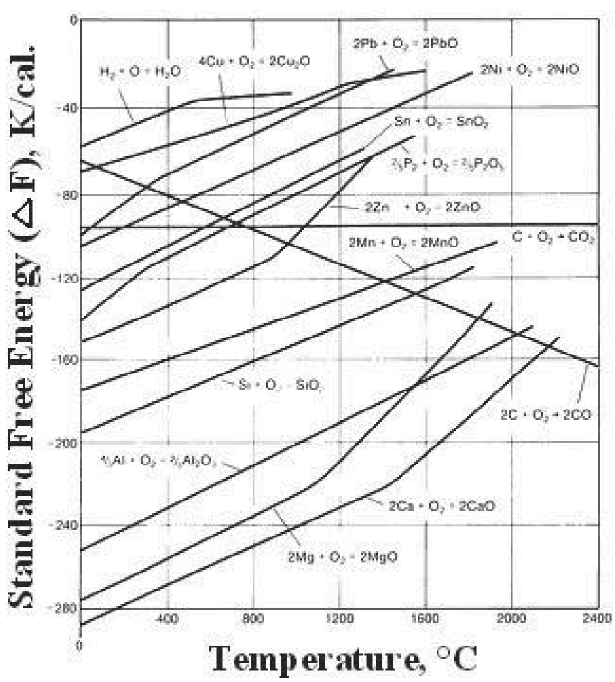


Fig. 21. Free energy changes for various metal oxidation reaction

than Cu in standard state. Though Zn is the most efficient deoxidizer, Sn and Pb also helps in removing dissolved gases like oxygen. According to Ricci[54], ‘from the thermodynamic point of view, Sn segregates over the whole composition range, and it should be more oxidizable than Cu, as the saturation pressure of Sn is some orders of magnitude lower than that of Cu. On the other hand, the vapor pressure of CuO is extremely lower than the vapor pressure of the volatile oxide of Sn (i.e., SnO). In fact, Cu can be mentioned among those metals for which the effective oxygen pressure coincides with the saturation pressure. So, only the evaporation of the tin volatile oxide, SnO, maintains the cleanness of the liquid alloy surface.’ Therefore, high Zn addition and small addition of Sn and Pb produced a liquid Cu-alloy very low in dissolved oxygen, and conducive for quality castings.

This deoxidized alloy free of oxygen further improves the mechanical properties of the cast metal, which was actively noticed by Bengal metal smiths.

6.7. Cleansing from Dissolved Hydrogen [H] in Copper

Tin reduces the solubility of hydrogen in Cu-alloy. As per observation (Fig. 22), more is the addition of Sn in Cu- alloy[55], less is the dissolved hydrogen, [H] in the alloy. Thus, both Zn & Sn help reducing dissolved gases like [O] (text in above) & [H] in Cu alloy and improves soundness of Cu- alloys. All these ultimately improve the mechanical properties, when Zn and Sn join the liquid Cu-system.

The addition of Sn in Cu also makes the alloy stronger and harder than alloying with Zn[56]. Therefore, little addition of Sn made the discussed Cu-Zn alloy better in mechanical properties. Further to note that small addition of Sn improves the corrosion resistance of Cu-Zn alloys[57] known as Naval Brass and Admiralty Brass. So, the corrosion resistance improvement due to Sn addition may be another impetus of Bengal metal workers.

6.8. Addition of Arsenic

Both *Rādhā* and *Kṛṣṇa* bronzes also contain small amount of arsenic. Arsenic is also a very efficient deoxidizer as arsenic oxide having gaseous phase at the melting temperature, leaves no residue, while removing oxygen, unlike other metals. So, arsenic addition indicates a significant improvement

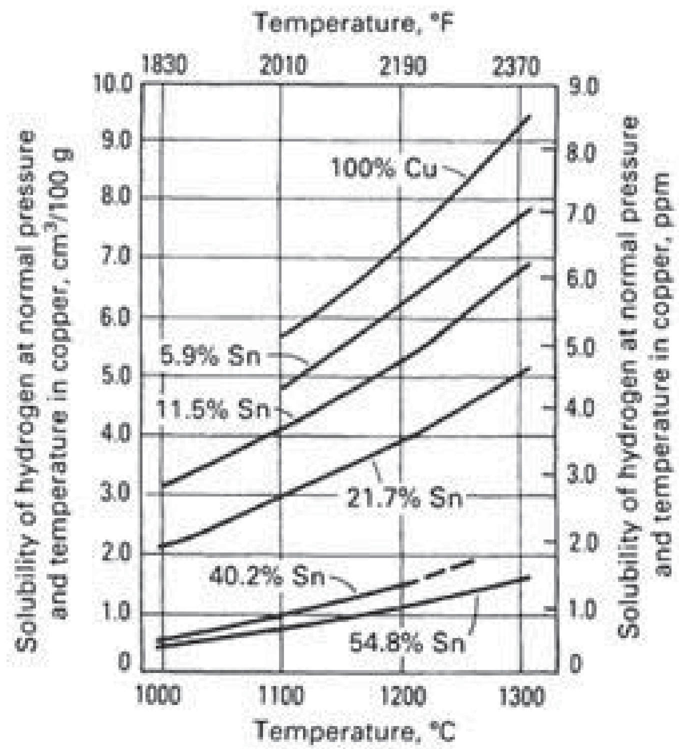


Fig. 22. Most common alloying element Sn decreases the solubility of hydrogen

in metal technology for Bengal artisans like other copper smiths of ancient India.

6.9. Casting Soundness by Alloying with Lead

From Physical metallurgy and the alloy solidification mechanism, it is known that during Liquid ’! Solid phase change, dendritic formation[58] produces micro-shrinkages between dendrites. This is very difficult to feed - riser problem[59] (already discussed in art. 6.4). Low melting point Pb remains liquid during solidification of primary dendrites and squeezes into the micro-voids acting as filler material and thereby seals the micro-porosity. The sealing improves fracture toughness or water tightness of the cast metal, in which way we may look at. So, Pb addition definitely imparted positive improvement in mechanical property (strength) into the cast metals and must be applauded by customers. This point definitely was noted by metal smiths of Bengal, as it can be seen also in many Pāla-Sena Bronzes[60], where foundrymen used Pb as an alloying element. Chinese bronze[61] makers also noted the effect of Pb and many Chinese bronzes possessed basically Cu-Sn-Pb ternary composition. Ancient Chinese bronze makers adopted Pb as a principle alloying element in bronzes. The tradition of Pb addition may be the influence of Far Eastern Chinese technology from which many other technologies were probably adopted in Bengal.

6.10. Corrosion Resistance due to Addition of Lead

Lead physically forms solid solution with Tin and Pb-Sn alloy having eutectics further strengthens the system. Most of the Cu-Sn alloys are resistant to acid and lead further assist in increasing the resistance. Lead (E°= – 0.126 V) is electro-chemically as per e.m.f. series[62] is very close to tin (E°= – 0.136 V) and so, from corrosion protection concept lead can replace a percentage of tin by forming protective oxides. Probably this phenomenon vaguely impressed Bengal metal workers. Otherwise, so much Pb addition (?) around 7 – 10% cannot be explained as incidental, and must have been intentional for those metal smiths.

6.11. Iconographic Effect of Lead Addition

Kṛṣṇa in local dialect means black or *kālo*, and as such is a Black Prince (God). Bengal people being too much infatuated with that Black God must have appreciated the black colored metal, Lead. So, metalsmiths added generous amount of Lead for winning the inclination of the customers as well as economizing the cost of the alloy (Pb must have cost less than Sn and Zn).

All the above discussions based on chemical compositions of the bronzes as well as these interpretations lead us to conclude that Bengal coppersmiths attained a high proficiency of alloy design for copper metals in medieval period.

Conclusion

The investigation about the bronze samples of *Rādhā* and *Kṛṣṇa* throws some important light on metal technology of Bengal smiths and it centered on technical aspect only and no iconographic discussion was attempted. The metal technology covered non-ferrous system only.

To appreciate the technology of casting process, microstructures were further analyzed by measuring Secondary Dendritic Arm Spacings which showed slower cooling rates for solidification of castings. As slower cooling rates mark the possibility of hot molds, therefore, in all probability, Bengal coppersmiths used hot molds during casting. This technique was compared with the hot clay molds operations for brass casting of the tribal metal workers which establish that this casting technology was reconstructed in Rural Metal Casting Laboratory of Jadavpur University and the cooling rates were again compared. The cooling rates are slow and similar and thereby, proving that the medieval bronzes were cast in hot clay molds.

Bengal metalsmiths developed a good grasp of alloy design of copper also. This was known that the metals:

- Zn, As, Sn, Au, Ag, Sb are soluble in Copper, except Lead which is insoluble.
- Alloying with zinc or tin makes a material stronger.
- The addition of alloying elements lowers down the melting point of the Copper-alloy and makes melting of copper alloys easier.
- Multiple alloying by additions of tin, antimony, etc. removes primary pipes or shrinkages, by producing distributed porosity within castings in the inter-dendritic region. This phenomenon helps to get good outer surface of bronzes, though mechanically the castings become weaker.
- Small addition of tin and large amount of lead improves fluidity of the liquid alloy and makes the castability better. So, easy flowability of liquid metals within narrow mold channels ensures proper filling of thin sections.
- Due to low vaporization point of zinc, 'flaring of zinc' occurs, in brass and deoxidizes liquid Cu-alloy. The addition of Tin also removes Hydrogen and degasses the same alloy, making the alloy gas-free and produces sound castings also.
- Arsenic in Copper-alloy also deoxidizes and removes the deoxidation product - oxide as a gaseous phase, so, cleaner casting quality results.
- Lead has low melting point and insoluble in copper at low temperature. So, it is last to solidify during copper-alloy solidification. Last-to-freeze liquid lead diffuses into micro-porosities at inter-dendritic region and seals the micro-voids and therefore, countering the effect of the problem of multiple alloying for production of sound metals.
- Lead helps better corrosion protection of copper-alloy and probably the knowledge was borrowed from an ancient Chinese technique.

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Nomenclature

Ag: Silver
Al: Aluminum
As: Arsenic
Au: Gold
B: Constant
C: Carbon
Cu: Copper
C_0: Average composition of solute (Zinc) of the liquid metal
C_L: Concentration of solute in liquid phase
C_S: Concentration of solute in solid phase
D: Diffusivity
D_0: Diffusivity constant
E°: Standard Electrode Potential, Volt
Fe: Iron
G: Temperature gradient of cooling liquid metal K/cm
H: Hydrogen
L_1: Liquid phase
Ni: Nickel
O: Oxygen
Pb: Lead
Q: Activation energy
R_0: Gas constant
R: Rate of solidification cm/sec.
S: Sulphur
Sb: Antimony
Sn: Tin
T: Absolute Temperature
Zn: Zinc
a: Constant
k: Partition coefficient
k_1: Thermal conductivity, w/m.K
m: Slope of the liquidus line
n: Nucleation Rate
q: Heat Flux
r: Cooling Rate, K/sec
t: Time, sec
ë: Dendritic Arm Spacing, µm

$\frac{dT}{dx}$: Temperature gradient

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