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LASER CLEANING AND METAL CHARACTERIZATION IN AID OF ARTEFACT PRESERVATION AND ARCHAEO-METAL TECHNOLOGY INVESTIGATION

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ABSTRACT

Two *bronze* icons, one *Radha* and one *Krishna*, were supplied by a West Bengal Museum for restoration and investigation of their manufacturing technology. After laser cleaning with Quanta system laser both the items recovered the dull initial appearance of yellowish brass metal. On material characterization of the metals it was established that the alloy used was leaded **α-**brass, cast possibly in hot clay molds. To understand that manufacturing process, a complete foundry design of one cast item *Radha* has been worked-out to reconstruct the probable methoding route followed by medieval Bengal workers.

Keywords: Laser Cleaning, Characterization, Methoding.

1. INTRODUCTION

Few years back some *bronze* artefacts were recovered by villagers in South 24-Paraganas District of West Bengal during excavation, as chance finds. Two of the artefacts were of *bronzes*, one *Radha* and one *Krishna*, and were in heavily corroded state, needing restoration for display at the museum gallery of Sundarban Anchalik Sangrahasala, Baruipur. Jadavpur University was approached to help in the restoration work and so, laser cleaning was applied to clean the surface of the items. Small fragments of each item were collected to undertake metallurgical characterization for investigation of metal technology. The investigation revealed cast metal technology in hot molds, and, on that basis a reconstructed methoding design for manufacturing the castings has been attempted.

2. LASER CLEANING 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. After removal of the coating, *bronze* castings showed dull yellow color with shallow irregular poke marks over few areas. A slow removal rate, by Quanta System Q-switched Nd:YAG Laser (Model: PALLADIO, Serial No. PLLOOI-0207) was used. The laser heating was countered by cooling under water. Under wet condition, laser cleaning yielded better contaminant removal rate than dry condition. By repeated laser cleaning for two hours per seating it took 4 to 5 seating, for arriving at a dull but clear appearance (Figs. 1, 2). 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 1.

Fig.1. *Krishna* (as received)

Fig.1(a). Laser Cleaned

Fig.2. *Radha* (as received)

Fig.2(a). Laser Cleaned

Table 1: Details of Laser Cleaning Operation.

Exp. No.	Sample	Time (sec.)	Frequency (Hz)	Energy (J)
1.	**Bronze*	30	10	0.155
2.	*Bronze*	5	10	0.151
3.	*Bronze*	60	10	0.157
4.	*Bronze*	30	10	0.155
5.	*Bronze*	60	10	0.156
6.	*Bronze*	30	10	0.154
7.	*Bronze*	30	10	0.152
8.	*Bronze*	30	10	0.151

**Bronze* here signifies Copper-Alloy items as is the convention of Archaeologists and does not represent the scientific Copper-Tin alloy understood by Metallurgists.

3. CHARACTERIZATION OF *BRONZES*

Two small inner fragments of the *bronzes* were collected and then investigated using common metallurgical tools like Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX), Hardness Measurement, X-Ray Diffraction Crystallography and Differential Thermal Analysis.

3.1 Chemical Composition by SEM-EDX

The average chemical composition analyzed using EDX of Scanning Electron Microscopy has been given in Table 2. Chemical compositions identify the *bronzes* as Copper-Zinc alloy, having **α**-brass signature coupled with generous amount of lead and a small bit of tin, arsenic, iron, etc. Might be it was the attempt of the medieval metal workers to reach the popular iconic, *Astadhat,* [1] Octo–alloy composition (Cu, Sn, Zn, Pb, Fe, As + [Au & Ag]). All these come close to modern Gun-Metal (Cu-Sn-Zn-Pb system). Bulk hardness values conform to cast leaded brass data [2]. The Bulk Hardness and Micro-Hardness of *bronze* icons, *Radha* and *Krishna* were obtained by Vickers' Macro Hardness Machine, Model no. HPO-250, 10 kgf, and Vickers' Micro Hardness Machine, Leica make, 15 gf load, respectively. The impressions of the bulk-hardness indentation of icon *Radha* are shown in Fig. 3.

3.2 Characterization of Icon *Radha*

The typical cast single phase, microstructure of **α**-brass, showing dendritic morphology produced in a casting process, predominates the photograph (Fig.4). Dendrites being the marker of a cast product, no doubt, the artefact was manufactured by a cast metal technology. The distribution of elements, when analyzed by SEM and EDX, shows clearly Cu-rich **α**-phase dendrites (black) as matrix. Last-to-freeze solute rich, Cu-lean **β**-phase can be seen as shaded areas (white to grey).

Lead particles are shown as white round or roundish spots. Micro-Hardness data of **α-** and **β**-phases show high HV values due to the high concentrations of many complex solutes.

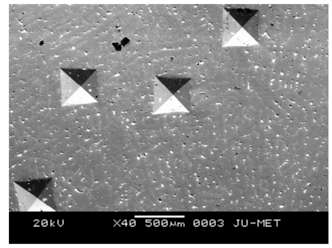


Fig.3. Vickers' Pyramidal Indentations of the Bulk-Hardness measurements show sinking-in effect of soft materials.

Table 2: Chemical Compositions and Bulk Hardness of *bronzes*.

Elements (Weight %)	***Radha***	***Krishna***
Copper (Cu)	69.45	64.13
Zinc (Zn)	19.08	20.76
Lead (Pb)	6.18	9.75
Tin (Sn)	3.60	1.86
Arsenic (As)	0.69	0.95
Antimony (Sb)	0.30	-
Iron (Fe)	0.34	2.55
Nickel (Ni)	0.36	-
Bulk Hardness (HV)	76.5	74.3

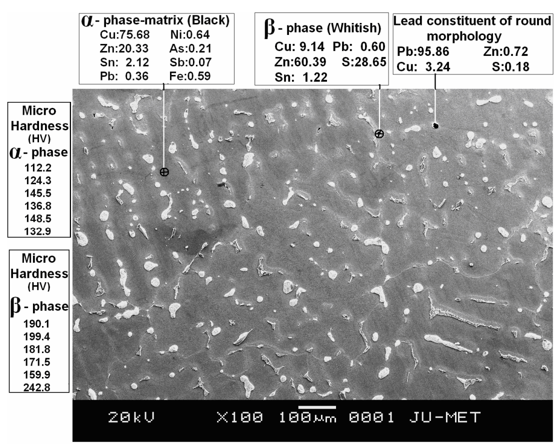


Fig. 4. Etchant: $FeCl_3$ in HCl. Compositions of **α, β** and lead constituents are given above **in wt.%**. Micro hardness of phases is shown in left hand side. The microstructure reveals typical serial grains, known as dendrites, commonly found in a cast product. This matrix is of **α** -phase (Black), while inter-dendritic regions (White) become solute rich **β**-phase. White round particles are mainly lead rich insoluble phase.

For clarification of uneven distribution of solute elements like zinc and tin in the given **α-** and **β**-phases further SEM-EDX analyses were undertaken as shown in Fig.5. The lower percentage of zinc and tin in primary **α**-phase and spike in percentages of solutes in last-to-freeze **β**-phase (Table 3), as expected in normal dendritic material, known as coring [3], are observed. So, the production process as casting is confirmed again.

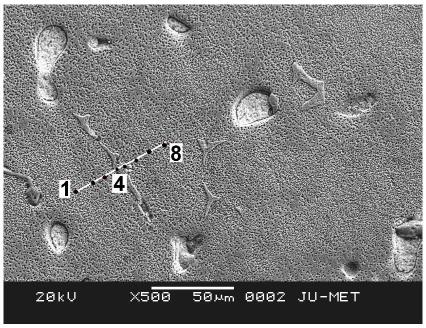


Fig.5. Marking points on the microstructure of icon *Radha*, where SEM-EDX analyzes were made to determine the distribution of percentages of Copper, Zinc and Tin. Markings 1-3 and 6-8 are in **α**-phase and 4, 5 are in **β**-phase.

Table 3: Chemical Compositions of icon *Radha* in the microstructure at points 1 to 8.

Pts.	**Phase**	**Copper** (Wt. %)	**Zinc** (Wt. %)	**Tin** (Wt. %)
1.	α	75.68	20.33	2.12
2.	α	75.50	19.88	2.50
3.	α	71.97	18.63	4.73
4.	β	59.95	8.38	29.31
5.	β	61.53	8.83	29.02
6.	α	72.09	18.29	5.03
7.	α	74.52	19.93	2.98
8.	α	75.40	19.32	2.63

Analyzing the X-Ray diffraction data for icon *Radha* (Table 4) a number of phases have been identified [4] by RIGAKU ULTIMA-III machine. From the X-Ray Diffractogram, (Fig.6) the presence of dominant **α**-Cu phase (solid solution of Zn, Sn in FCC Cu) is confirmed. Some minor **β**-phase (solid solution of Sn, Zn in BCC Cu) can also be seen. Insoluble lead as separate phase can be found in the analysis.

DTA analysis (Fig.7) was made in Pyris Diamond DTA instrument for icon *Radha*. Differential Thermal Analysis of the sample points towards the occurrence of early phase change. Obviously it vindicates the presence of low melting point elements (few are also insoluble) present in the alloy.

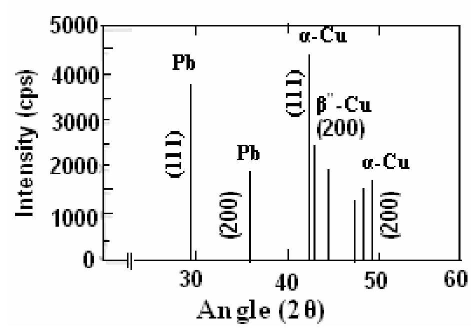


Fig.6. XRD Pattern of icon *Radha*, shows major constituents as **α**-Cu phase.

Table 4: Details of X-Ray Diffractogram of icon *Radha*.

Peak No.	**Angle** (2θ) (Deg)	$\mathbf{d_{space}}$ (Å)	$\mathbf{I / I_0}$	**Identified Phase and Plane** (*hkl*)
1.	29.40	3.0355	87	Pb (111)
2.	39.40	2.2851	36	Pb (200)
3.	42.50	2.1253	100	α-Cu (111)
4.	43.20	2.0924	41	β''–Cu (200)
5.	48.50	1.8754	26	α-Cu (200)

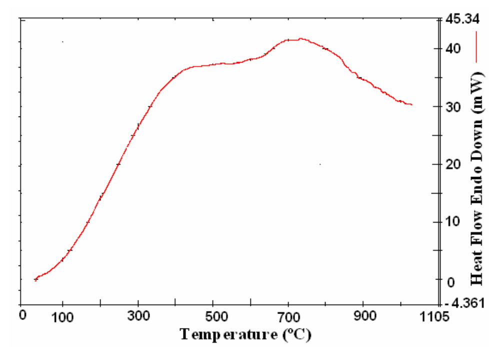


Fig.7. DTA analysis of icon *Radha*, points to an early phase change due to low melting constituents, lead & tin, etc.

3.3 Characterization of Icon *Krishna*

The microstructure (Fig.8) of *bronze* icon *Krishna* 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. The reason is poor heat dissipation rate can only provide long solidification time, necessary for grain growth. With respect to *bronze Radha*, the amount of lead can be seen to be significantly higher. The insoluble lead effectively fills up pores between dendrites and made the casting more sound.

The chemical compositions of **α**-Cu (black areas) and **β**-Cu phases show Cu-rich and solute rich elements respectively, as shown earlier. The insoluble lead constituent was also analyzed. The Micro-Hardness of **α**-and **β**-phases were measured and shown in Fig.8.

Though the hardness of the **α**-phase was similar to that of icon *Radha*, the hardness of **β**-phase is slightly higher than that of *Radha*. As usual lead constituent shows very low hardness values of soft lead.

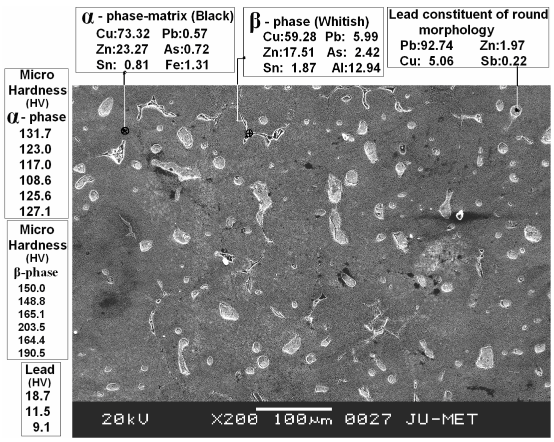


Fig.8. Etchant: $FeCl_3$ in HCl. All compositions of respective phases given above are **in wt.%**. Micro hardness of phases are shown in left hand column. Coarse dendrites (black area) engulf the microstructure, as major **α**-phase. Like earlier microstructure of icon *Radha*, white areas consist of lead bearing phase and minor **β** -phase, in which the former amount is large.

For X-ray Diffraction analysis (Table 5), in case of *Krishna*, (Fig.9) all the comments about the *bronze Radha* are valid — that is the major phase is **α** -Cu phase and minor phase is **β** -Cu phase.

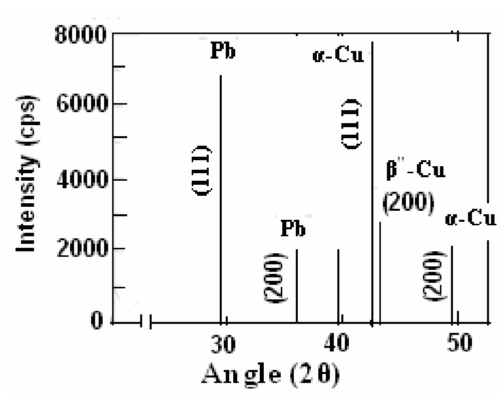


Fig.9. XRD Pattern of icon *Krishna* almost similar to earlier *Radha* sample.

DTA of *Krishna* is shown in Fig.10. The same comment mentioned in case of *Radha* is validated here also.

Table 5: Details of X-Ray Diffractogram of *Krishna*

Peak No.	Angle (2θ) (Deg)	d_{space} (Å)	I / I_0	Identified Phase and Plane (*hkl*)
1.	29.50	3.0254	88	Pb (111)
2.	36.00	2.4927	43	Pb (200)
3.	42.50	2.1253	100	α-Cu (111)
4.	43.20	2.0924	57	β''– Cu (200)
5.	48.60	1.8718	38	α-Cu (200)

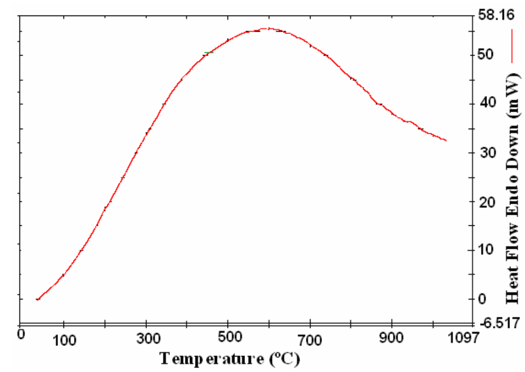


Fig.10. DTA analysis of icon *Krishna*, exhibits the early transformation of low melting constituents.

4. ARCHAEO-TECHNOLOGY CONSTRUCTION

Based on the characterization of metals, there is little doubt that *bronzes* were produced using Cast Metal Technology of hot molds. Following the medieval practice, the molds should be made of Silica sand with alluvial clay as binder, as reported in literature [5]. After joining those hard piece-molds together, liquid metal was poured in the hot assembly, through a gating system, and a riser was probably provided to compensate for the liquid-solid contraction during solidification. The total system of medieval foundry practice has been visualized here under.

The casting process starts with methoding in which pattern, core, gating and riser are designed in successive order. The reconstructed methoding for one casting, *Radha* has been described to get a glimpse of that technology.

5. METHODING DESIGN

Details of icon *Radha*, as received.

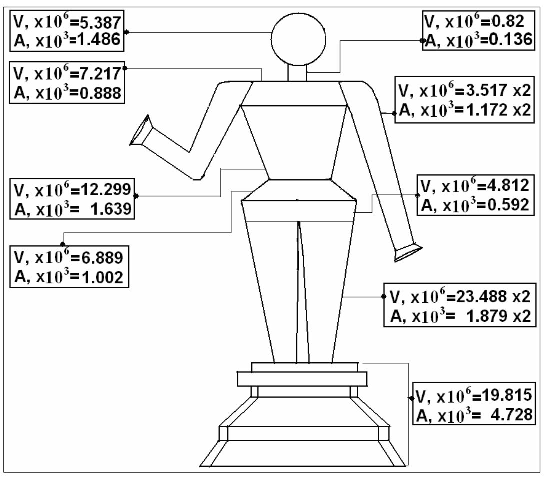
Weight of the Casting, x 10^3, kg = 716
Volume of the Casting, x 10^6, m^3 = 110
Height of the Casting, x 10^3, m = 150

On the basis of recovered casting, the pattern and core volumes with the associated heat dissipating areas have been estimated. Considering simple geometry the estimation has been made and these are totally approximate which is given in Fig.11.

(1) Pattern and Core parameters:

Height of the Pattern, x10^3, m = 155
(3% contraction allowance considered)
Volume of the Pattern, x10^6, m^3 = 111
Outside Area of the Pattern, x10^3, m^2 = 17
Volume of the Core, x10^6, m^3 = 24
Outside Area of the Core, x10^3, m^2 = 5

Heat dissipating area of the casting, $(A_c + A_{co})$ m^2= 22



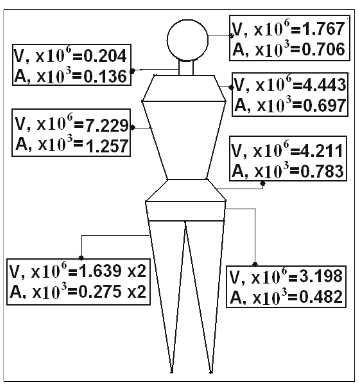


Fig.11. Calculated Volume (m^3) and Area (m^2) of the Pattern (top) and the Core (bottom) of reconstructed sample.

(2) Gating Design:

Assumptions: Top Gating
Sprue Diameter, x10^3, m = 4
Sprue Height, x10^3, m = 70
Cup Height, x10^3, m = 20
Discharge coefficient, = 0.9

For Bronze: Viscosity [6], mPa.s = 3.8
and Density [7], kg/m^3 = 7826

On the basis of above,
Sprue Area, x10^6, m^2 = 12.566

Velocity @ Sprue, v_s, m/sec, $= C\sqrt{2gh_s}$ = 1.0547

Liquid metal flow rate, $A_s\ v_s$, x10^6, m^3/sec = 13.2534

Time of filling, $t_f = \dfrac{V_c}{A_s v_s}$, sec, ≈ 8

Check by Reynolds's No., $R = \dfrac{v_s \rho d_s}{\mu} = 8688$

t_f is small and $R < 10{,}000$,

So,

Design satisfactory

(3) Sprue Design:

Aspiration Correction, $A_s\ /\ A_{cu} :: \sqrt{h_{cu}}\ /\sqrt{h_s}$

$$\Rightarrow \frac{d_s}{d_{cu}} = \sqrt[4]{\frac{h_{cu}}{h_s}}$$

⇨ Cup Diameter, d_{cu} , x10^3, m ≈ 6

(4) Riser Design:

Volume of the liquid Metal, $(V_c - V_{co})$, x 10^6, m^3 = 87

$$M_c = \text{Modulus of the Casting} = \frac{Volume}{Area} = \frac{V_c - V_{co}}{A_c + A_{co}}$$

⇨ M_c , x10^3, m = 3.954

Let, M_r = Modulus of Riser = 1.3 M_c

⇨ M_r, x10^3, m = 5.1402

Assume Cylindrical Riser, $d_r = h_r$

$$M_r = \frac{d_r}{4}$$

⇨ d_r, x10^3, m ≈ 20

Table 6: Design Summary (x 10^3, m)

Sprue diameter	Sprue height	Cup height	Cup diameter	Riser diameter
4	70	20	6	20

(5) Placement of Riser and Sprue:

The feeding distance (f_d, inch) is given by 5.61 $T^{0.53}$, when, T is the thickness of the casting in 'inch' [8].

Here, T_c , x10^3, m = 3

⇨ f_d, x 10^3, m = 46

The complete gating and riser dimensions with their placement position are shown in Fig.12.

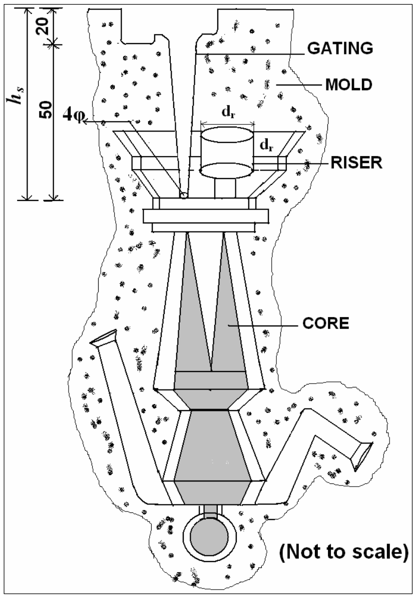


Fig.12. Gating and Riser dimensions are given with locations in the probable mold for *bronze* icon, *Radha.*

6. CONCLUSIONS

Laser cleaning using Nd:YAG laser has been successful in restoration of two museum *bronzes* in West Bengal and can be considered a viable alterative to chemical cleaning route.

Bronzes of medieval Bengal, in this case, constitute a copper alloy of primarily leaded **α**-brass composition, although coming close to modern Gun-Metal.

The metallurgical investigation further reveals a hot mold casting practice, probably executed by medieval Bengal metalworkers, to produce the artefacts. Using present knowledge, the prospective foundry design of the castings has been reconstructed to understand the manufacturing process, practiced in archaeological period.

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8. NOMENCLATURE

Symbol	Meaning	Unit
V_c	Volume of the Pattern	(m^3)
A_c	Outside Area of the Pattern	(m^2)
V_{co}	Volume of the Core	(m^3)
A_{co}	Outside Area of the Core	(m^2)
d_s	Sprue Diameter	(m)
A_s	Sprue Area	(m^2)
h_s	Sprue Height	(m)
h_{cu}	Cup Height	(m)
C	Discharge coefficient	(-)
μ	Viscosity of Bronze	(mPa.s)
ρ	Density of Bronze	(kg/m^3)
v_s	Sprue Velocity	(m/sec)
t_f	Time of filling	(sec)
R	Reynolds's No.	(-)
A_{cu}	Cup Area	(m^2)
d_{cu}	Cup Diameter	(m)
M_c	Modulus of the Casting	(m)
M_r	Modulus of the Riser	(m)
d_r	Riser Diameter	(m)
h_r	Height of the Riser	(m)
T	Thickness of the Casting	(m)
T_c	Thickness, Actual Casting	(m)
f_d	Feeding Distance	(m)

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