CHAPTER 5

CHARACTERISATION OF ARCHAEEO MATERIALS
CHAPTER 5.1

CHARACTERISATION OF HIGH TIN BRONZE OR BELL METAL INGOT
Bell Metal or high-tin bronze alloy was popularised in Bengal before 5th century BCE. Through excavation and exploration a number of high tin bronze or Bell metal specimens were discovered. One of such earliest ingot excavated from a site Tilpi in Bengal has been characterized.

5.1.1 Details of the Excavated Specimens
The site Tilpi (22°15′N, 88°38′E) from which an ingot as sourced is located (Fig. 5.1.1 LHS) in the coastal district of South 24-Parganas, West Bengal. The excavation was conducted (Fig. 5.1.1 RHS) by the Directorate of Archaeology, Government of West Bengal in March 2006 and March 2007.

The following objects recovered: 1. Crucibles, 2. Slag, 3. Small metal ingot, (Fig. 5.1.2) and 4. - The in-situ Furnace with 8 no of hearths along with few corroded iron lumps. (Fig. 5.1.1A). All the above items at the same site, is an indicators of the presence of a guild. The guild in all probability produced Bell Metal or similar bronze articles. The hearths and crucibles confirmed the expertise of melting and castings for non-ferrous metals. Because all these arrangements replicate modern cast house known as foundry.

5.1.1.1 Antiquity
According to the excavator, the present specimen dated to c. 2nd century BCE.

5.1.1.2 Crucible
The size and shape of the crucible fragment looks different, (Figs. 5.1.2 and 3). The outside shape resembles conics with semi-circular cross section inside, unlike modern crucibles, which are flat bottomed. Considering the out side shape having a pointed end at the bottom it may be inferred that the crucible, was adequately supported by solid fuels, to keep it upright for holding liquid metal. The material of the crucible seems to be made of fired charcoal (or graphite?) and clay. The green crucible after shaping in the die was dried and then fired slowly for achieving handling strength. The traditional practice of crucible making was probably adopted. It is difficult to differentiate it from the modern crucible.
Fig. 5.1.1 Location of Tilpi, in West Bengal (in LHS). In RHS Excavation at Tilpi, showing the formation of a hearth for metal processing, probably of non-ferrous metals like copper, bronze, brass etc. The discontinuity (right hand side) at the foundation indicates the portion of the ash-pit door, for removal of cinder. The door was also used (like ‘chulas’ of sub-continental variety) for passing air blast under natural draft or forced draft, by winnowing fan, to generate heat by the combustion of fuel.

Fig. 5.1.1A Excavation at Tilpi, showing factory site. The pits presumably provide the remnants of foundation chambers for fire-place remains, or tool pockets or post-holes of working table normally operated by micro level metal workers.
5.1.1.3 Benefits of the Conical Geometry

The crucible received in the excavation has circular conics at the bottom unlike flat bottomed modern crucible. This has huge importance from technological angle.

The circular conics have more surface area than flat surface and receive more heat quickly. Whereas inside hemispherical cavity holds liquid metal in the geometry of a bun shaped ingot. The bun shaped ingot cools very slowly with respect to thin flat shaped section. The liquid metal conserves the heat due to the poor heat transfer rate during the heating period when energy was very scarce. The heat conservation principle probably helped metal casters to get a small pool of liquid metal very early during melting period. This early pool of liquid metal as always the case in any heating operation helped ancient metal workers the ease of melting Bell Metal.

The above proposition has been elucidated for two reasons:

1. Setting the crucible in the hearth using flat bottom is much easier than concave bottom. So the conical bottom is intentional and had definitely a purpose.
2. Charging the fuel or knotty wood or wood charcoal had been easier if the crucible end had a flat boot. But the conical booted crucible had to be carefully placed into the hearth. The difficulty of keeping the crucible erect had been endured by the melters. So with the associated difficulty foundry men used the geometry and this technique adopted with a purpose.

5.1.1.4 Reconstruction of the Crucible

A sketch of the crucible as-received in excavation has been indicated in Fig. 5.1.4 (LHS) and reconstructed crucible is shown in Fig. 5.1.4 (Centre). The worn out volumes of the crucible has been hatched to show the scouring volume during melting liquid metal. The excavated metal ingot has got the oval bottom which closely matches with the interior of the crucible (Fig. 5.1.5) and it indirectly points out the residual liquid metal that got solidified on cooling
Fig. 5.1.2 Analyzed objects recovered at Tilpi- (1) Slag, (2) Metal Ingot, (3) & (4) Broken crucible fragments.

Fig. 5.1.3 The external surface of the crucible

Fig. 5.1.4 (LHS) Crucible as received in excavation. (Centre): Crucible reconstructed. (All dimensions are in mm)

Fig. 5.1.5 Reconstructed crucible showing the ingot.
after close down of the furnace. The ingot took the shape of a small bun and borrowing the
term from archaeologists can be aptly called a bun shaped ingot.

5.1.1.5 Composition of Crucible Slag
The trace of attached slag taken out from the inside surface of the crucible was analyzed.
The composition in Fig. 5.1.6 and indicates major phase as silica (SiO₂) along with tin (Sn)
as the major element. The amount of Sn indicates clearly that bronze was melted in this
 crucible. From the presence of high amount of iron and sulfur the source of copper was
perhaps chalcopyrite.

5.1.2 Description of Metal Piece
The metal ingot (No. 2 in Fig. 5.1.2) discovered at Tilpi (trench ZE3, layer 1), was coated
with greenish blue hydrated copper carbonate corrosion layer, as usual like any archaeo-
copper objects. After removing the clay, the ingot was oval in appearance and irregular in
shape but flat on top with blunt edges. It was around 35 mm x 30 mm x 8 mm in dimensions
and weighed approximately 35.3242 gm. The drawing of the ingot was made and shown in
Fig. 5.1.7. From visual inspection and matching it seems that the copper object might have
been cast in the bottom hole of the given crucible which might be subjected to some kind of
cool air blast (sea breeze or rainy wind).

5.1.2.1 Bun Shape of the Metal Piece
The excavated metal object though very small in size looks like an overcoat button. The
button shape provides the geometry of a bun shaped ingot. Many of the bun shaped ingots
were used as a future forging stock.

5.1.2.2 Macroscopic Observation
Copper or Tin bronze is a good corrosion resistant material, yet under buried condition,
micro-organisms often colonize the surface, and mask outside areas, with the surrounding
moist (hydrated) environment lead to bio-corrosion of the alloy. As the microbial population
increases, ultimately those microbes gradually envelop the external surface, with the under
side metal getting corroded. The macrostructure of corroded bronze specimen has been
shown in Fig. 5.1.8 which can be divided as follows: (a) Outside Corroded layer. Mixture of Copper hydroxide and hydrated Copper carbonate, (b) Chilled Zone (finer grain structure) due to faster cooling, (c) Large volume of Columnar Grains (shown by dotted line) where coarse dendrites grow due to slow cooling inside.

So as already stated three distinct zones result:

(a) The outside corrosion layer of greenish colour.
(b) The chill zone of finer dendrites (grey) about 1.4 mm thick.
(c) The coarse grains of columnar dendrites (white) in core.

After the outside corrosion layer, the chill zone (grey areas), annular in shape is the second part, where due to faster cooling, fine grains of copper rich dendrites solidify first. The red hot crucible with liquid metal as soon as was taken out of the furnace, cooled very fast by the surrounding cool air at ambient temperature. The quenching action moves through the crucible to chill the freezing metal at the outside boundary. So, a small chill zone of around 1.4 mm developed in the solidified ingot.

With passing of time the hot crucible got colder and the temperature gradient of the crucible with outside flattened, slowing down heat transfer rate. So, the freezing rate of liquid metal also slowed down. A coarse grain structure of columnar tin rich dendrites grew inside. The slow freezing helped the nucleated crystals to grow and to get coarse.

5.1.2.3 Chemical Composition of Metal Ingot

The composition of the metal sample provides an elemental composition (in wt%) as Sn: 24.37, Ni: 0.28, Fe: 0.45, S: 1.76, Si: 0.06 and Cu: 73.09. This infers that the metal ingot comes in the group of Bell Metal, a high-tin β - bronze alloy having a composition of ~75% Cu and 22-25% Sn alloy. The ingot holds negligible amount of nickel, iron and silicon as residual, from the sulphide ore.
<table>
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<th>S</th>
<th>Fe</th>
<th>Cu</th>
<th>As</th>
<th>Pb</th>
<th>Zn</th>
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<td>0.02</td>
<td>56.09</td>
<td>62.55</td>
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</table>

Fig. 5.1.6 Constitution obtained in EPMA, showing compositions of slag inside the crucible.

Fig. 5.1.7 Ingot sample as received in excavation, 35 mm x 30 mm x 8 mm
5.1.2.4 Bulk Hardness of the metal Ingot

The bulk hardness of the bun shaped metal ingot specimen measured by Vickers machine was 231 HV 5/30 (231 Kg.mm⁻²). On an average that is close to modern Bell Metal.

5.1.3 Microstructure of Bell Metal Ingot

The SEM microstructure (Fig. 5.1.9) of the specimen shows the dendritic structure of cast material. The dark grey phase is copper rich α-phase dendrite and the light grey phase surrounding dendrites is tin rich β -phase. Some of the primary dendrites in the central region are very coarse and grew definitely from the large solidification time available in a shutdown crucible. The α-phase largely contains very fine grains also of the order of few microns. Therefore it can be concluded that the metal piece was a cast Bell metal product.

5.1.3.1 Nucleation in Core of Bell Metal Ingot

The long freezing time in core of the metal ingot allowed a convective mass transfer within the core of the freezing liquid. The convective current grows out of the buoyancy force of heavy copper (density 8940 kg/m³) and high melting point (1356K) with respect to lighter tin (density 7280 kg/m³) [Gale and Totemeier, in Smithells 2004, 14, p.19] with lower melting point (505K). Convective heat transfer further under cools the remaining last-to-freeze liquid between already solidified coarse columnar dendrites. Cluster of atoms then facilitate α – phase to nucleate between coarse dendrites lead to fine grains down to µm range. Initially low tin – high Cu percentage, copper phase (α-Cu) separates thermodynamically rejecting more solute tin inside cooling liquid. Temperature drops and the constitutional under cooling occurs. The under cooling becomes large. ∆T is designated as under cooling and defined as (T_m- T), (T_m = Freezing temperature of metal and T = Prevailing temperature of the metal during freezing).

When the large ∆T values get lowered, the critical nucleus size, \( r^* \) (as \( r^* \approx 1/\Delta T \) (Haasen 1997: 58) falls down to a very small amount. Small \( r^* \) values enhance the kinetics of nucleation. High rate of nucleation produces very fine grains because of large under cooling (∆T) below the equilibrium liquidus temperature (T_E) (Fig. 5.1.10) (Beeley 2001: 75).
<table>
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<th>Fe</th>
<th>Cu</th>
<th>As</th>
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<th>Zn</th>
<th>Sn</th>
<th>Total</th>
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<td>1 / 1</td>
<td>0.04</td>
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<td>0.12</td>
<td>0.07</td>
<td>0</td>
<td>0</td>
<td>Sn</td>
<td>57.18 63.70</td>
</tr>
<tr>
<td>2 / 1</td>
<td>0.06</td>
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<td>56.09</td>
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</table>

Fig. 5.1.6 Constitution obtained in EPMA, showing compositions of slag inside the crucible.

Fig. 5.1.7 Ingot sample as received in excavation, 35 mm x 30 mm x 8 mm
Fig. 5.1.8  The macrostructure of metal ingot: (a) the thin corrosion layer covers (black used in the picture) the surface. The chill zone and columnar zone can be clearly seen in the macrograph. (a) Outside Corroded layer. Mixture of Copper hydroxide and hydrated Copper carbonate, (b) Chilled Zone (finer grain structure) due to faster cooling, (c) Large volume of Columnar Grains (shown by dotted line) Coarse dendrites grow due to slow cooling inside.

Fig. 5.1.9 Microstructure at the central region of cast ingot. Black areas represent solid solution of tin in copper, known as $\alpha$–phase. Note some dendrites of $\alpha$–phase look blocky and some are acicular (lens shaped). Between the dendrites a large number of fine $\alpha$–grains (dendrites) are visible. The bulk phase (matrix) is held by tin-rich, solid solution of tin in copper, $\beta$–phase.
There could also be directionality of heat from freezing liquid towards the mold surface (here crucible). Due to the directional solidification a kind of columnar grains or dendrites can be located in the microstructure.

5.1.3.2 Coring in Dendrites of Metal Ingot

During solidification any grain or dendrite, at first, nucleates and then grows until restriction occurs from outside. So, the first solid composition can be obtained in the center of the grain and the last solid composition would be available at the edge of the grain. For this reason, a large grain of $\alpha$-phase (marked by arrow in Fig. 5.1.11) has been selected for analysis. EDX composition started from the center of the dendrite and ended at the boundary of the dendrite that is from point marked 1 (centre) to point marked 6 (at the edge). The center region represented by point [1] contains more solvent, Cu as expected and the skin represented by point [6] contains more solute, Sn as theoretically prescribed (Datta 1995, 207-270). Compositions within a primary dendrite taken 4 µm apart from centre to periphery, is shown in Table 5.1.1 and Fig. 5.1.12.

The first solid contains 13.66 wt.% Sn and the last solid at the frozen edge the tin percentage rises to 16.78 wt.% - a slow incremental progress of Sn% as prescribed in Cu-Sn phase diagram, showing $C_S$ (low Sn%) → $C_L$ (high Sn%). The results detailed the presence of Cu, Sn and Fe, which is shown in table cited. All these signify the phenomenon of heavy coring (Shewmon 1969, 168), (deviation from average chemical composition) of the primary dendrite, $\alpha$-phase of Cu-Sn solid solution, in the microstructure. Naturally, like all cast bronzes the bronze structure looks heavily cored.

A part of Cu-Sn phase diagram (Fig. 5.1.13) may be consulted showing the relevant portion (West 1982: 107), which indicates $C_S$- 1st solid composition that froze at the center. 1st solid (low tin copper) dendrite is at the center. The solubility of tin increase from 10 wt.% (B) to 13 wt.% (H) as shown by BH or HK line when temperature drops from 1071K (BD line) to 859K (HJ line).
Fig. 5.1.10 Thermal explanation of mixed structures in castings. (a) Chilled zone, arrow shows freezing direction (b) Columnar and equiaxed region when temperature gradient get flattened (after Beeley 2001, p. 74).

Fig. 5.1.11 A primary dendrite has been selected for micro – analysis by SEM – EDX to understand the coring characteristics. The center region represented by point [1] contains more solvent, Cu as expected and the skin represented by point [6] contains more solute, Sn as theoretically prescribed (Datta 1995, 207-270).
5.1.3.3 Non-equilibrium Freezing of Cast Bell Metal Ingot

Already stated, from the centre of the dendrite, tin percentage starts from 13.66 by wt. % and finishes at the edge by 16.78 wt. % at the surface as indicated already in Fig. 5.1.13. This coring or micro-segregation is due to the non-equilibrium freezing of the alloy during casting as expected with Cu-Sn alloy (Datta 1995). This signifies the probable knowledge of metal workers, in the long freezing range characteristics of Cu-Sn alloy family, which is unlike short freezing range (SFR) alloys of Cu-Zn family. This knowledge of long freezing range characteristics encouraged the people to have as slow as possible cooling mechanism, for achieving good feeding of freezing alloy, to avoid micro-shrinkage phenomenon at the last stage (center of the ingot). But the micro shrinkage defects associated with this bronze is surprisingly very less in this metal sample. This is not incidental but likely to be intentional. Modern physical metallurgists know that with increase in tin content in copper alloy from 10% to 24%, the solidification range shrinks from ~170K to around 20K (Table- 5.1.1) and the short freezing range, \( \beta \) – bronze casting becomes easier to feed for producing sound and strong metal (later discussed). For achieving the directional solidification, to counteract the risering problem of Cu-Sn alloy, this slow solidification was probably replaced by fast cooling of the metal \( \beta \) – bronze at the outside. This fast cooling or chilling practice was introduced by ancient metal workers so that the micro-porosity creation of bronze and the centerline shrinkage could be centralized or minimized.

5.1.3.4 The Randomness of Dendrites within Ingot

The dendrites cover the micrograph in a haphazard fashion (Fig. 5.1.11). This random orientation is an indicator of the formation of highly super cooled region within casting, where the temperature gradient of the cooling liquid lagged the equilibrium freezing temperature curve of solute rich (tin rich) freezing alloy (Datta 1995). This region is already described in the macrograph (Fig. 5.1.8). Naturally the isotropic dendritic nature rather than, preferential directionality of grains or dendrites for the casting, occurred in the last stage of freezing.
Table- 5.1.1 Compositions of a primary dendrite 4µm apart

<table>
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<th>Points</th>
<th>Cu</th>
<th>Sn</th>
<th>Fe</th>
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<td>81.96</td>
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Fig. 5.1.12 Compositions of the cross section of a primary dendrite are taken 4µm apart.

Fig. 5.1.13 A part of Cu-Sn phase diagram, showing the relevant portion (West 1982: 107).
5.1.3.5 Relationship of Dendritic Arm Spacing of Metal Ingot

A random measurement of Secondary Dendritic Arm Spacing (DAS) was undertaken to have an idea of the cooling rate expected in the casting. The relationship between the cooling rate, \( (R \text{ in } ^\circ\text{C/Sec}) \) and \((\lambda \text{ in } \mu\text{m})\) can be determined by the following (Hwang et al. 1998: 495-503),

\[
\lambda = 101 \times R^{-0.42} \quad \text{.........................................(1)}
\]

From the values of dendritic arm spacing, when (i) \( \lambda = 8 \mu\text{m} \), \( R = 380^\circ\text{C/Sec} \), (ii) \( \lambda = 14 \mu\text{m} \), \( R = 110^\circ\text{C/Sec} \), (iii) \( \lambda = 30 \mu\text{m} \), \( R = 14^\circ\text{C/Sec} \), and (iv) \( \lambda = 50 \mu\text{m} \), \( R = 5.33^\circ\text{C/Sec} \) were calculated. Against \( \lambda = 8 \mu\text{m} \), the cooling rate \( R = 380K/\text{Sec} \), indicates very fast cooling rate to be obtained for quenched metal and for \( \lambda = 50 \mu\text{m} \), the cooling rate is \( R = 5.33K/\text{Sec} \), which indicates very slow cooling rate. Both of these are extreme freezing rates of the alloy and shows a mixture of coarse and fine dendrites coexist in the central part of the casting (Fig. 5.1.10).

5.1.3.6 Short Freezing Range of Metal Ingot

The freezing range of 24Sn–76Cu alloys (analysed cast Bell Metal ingot) is short, about 20 K (Fig. 5.1.13) and can be categorized as a Short Freezing Range alloy.

5.1.3.7 Short Freezing Range Alloys – Sound Casting Easier by Risering

Solidification of short freezing range alloys (Meredith 1995:11) (Fig. 5.1.14) usually starts at the mold interface where heat extraction is greatest. The chilling action of the mould wall results in the formation of a thin skin of solid metal surrounding the liquid. With further extraction of heat through this shell of solid metal, the liquid begins to freeze onto it and the wall of solid increase in thickness overcoming mushy zone (Sylvia 1972: 135-152).

The solid and liquid portions are separated by a relatively sharp line of demarcation – the solidification front – which advances steadily towards the center of the casting. Short freezing range alloys encourage directional solidification even at relatively low thermal gradient. Schematic mode of freezing of short freezing range alloys (after Strauss 1970: 429)
Fig. 5.1.14 Schematic mode of freezing of short freezing range alloys (after Strauss 1970: 429) (1) Starting stage, Chill Zone (2) Columnar dendrites, (3) Central Equi-axed Zone, (4) End of freezing, Final grain structure.

Fig. 5.1.15 Working stress in micro pores: Bigger the crack size ‘2a’, lower the value of $\sigma$. 

\[ \sigma \]

\[ \sigma \]
identifies (1) Starting stage, Chill Zone (2) Columnar dendrites, (3) Central Equi-axed Zone, and (4) as End of freezing and final grain structure.

From metallurgical view point, Short Freezing Range Alloys produce consistent mechanical properties like Cu-Zn alloys (brass) or killed steel ingots. Short Freezing Range alloys solidify directionally close to plane front solidification that is the freezing surface starts from mold / metal interface and finishes at the center. Therefore, like killed steel, the total or final shrinkage or pipe concentrates at the center and by directional solidification, or risering, sound cast metal can be produced easily by feeding liquid metal at the last stage.

5.1.3.8. Short Freezing Range Alloys- Stronger Cast Metal

One further advantage, from technological view, accrues in case of SFR. The chance of micro-porosity formation diminishes and the micro-crack which is initiated from the porosity generally lacks momentum. Therefore, the working stress, \( \sigma \), as per modern ‘Fracture Safe’ criteria (Dieter 1988),

\[
\sigma = \frac{K_{lc}}{\{A \times \sqrt{(2\pi a)}\}}
\]

Where \( 2a \) = Inside Crack Size, \( K_{lc} \) = Fracture Toughness, \( A \) = Geometrical factor, does not deteriorate (Fig. 5.1.15). (Note, bigger the crack size ‘2a’, lower the value of \( \sigma \); when \( a \uparrow \) then \( \sigma \downarrow \)).

5.1.3.9 Freezing Range – High-tin Bronze Vs Low-tin Bronze

Compositions up to 10%Sn – 90%Cu alloys or low tin bronzes are long freezing alloys – freezing range vary as high as 180 K (Table- 5.1.3). Tin addition to pure copper increases freezing range from 0 K– 180 K, up to 13.5 wt. % Sn – Cu bronzes.

Then, further addition of Sn to bronze, reduces Freezing Range (Fig. 5.1.16). Lower freezing range improves castability as well as soundness. The reason is that all these Long Freezing Range Alloys (low tin bronzes) solidify in random dendritic solidification (Sylvia 1972, 135-152) and produce lots of micro- porosity, which are difficult to fill or feed by risering and naturally produced unsound (inside spongy) cast metals of lower, inconsistent mechanical properties. The working stress, \( \sigma \) comes down as the denominator in the equation (2) has large values. In Bell metals contra condition prevails and comparatively more sound and reliable properties are obtained than low tin bronzes.
The spongy (Sylvia 1972: 142), weak, castings of low tin bronze (10Sn90Cu alloy) were discarded in favor of short freezing, easily fed, high-tin (22 – 25%) Cu alloys. Bell Metal or β-bronze was favoured for its sound metal, generating sharp tonal quality with consistent sonic response.

**5.1.3.10 Bronze Alloys Produce Better Fluidity.**

Liquid Cu interestingly, has a viscosity (West 1982: 15) of 4.8 m Ns/ m² and Sn (liquid) has 1.15 m Ns/ m² at their respective melting points of 1356K and 485K. The gradual increase of tin to copper physically decreases the viscosity of bronzes. As viscosity is closely related as the inverse of fluidity (Geiger and Poirier 1971: 16-18) so the addition of tin to copper surely makes the foundry property of bronzes better than pure copper, so far fluidity of liquid bronze is concerned. So, being more fluid casting production by bronzes becomes easier. Simultaneously, the melting points also of Cu-Sn alloys or bronzes come down, lower than melting point of copper (Fig. 5.1.13). Bell metal has of 250⁰C lower melting point than pure copper.

Foundry alloys like bronzes melt easily because of lower melting points. Both these properties are beneficial for foundry men and high-tin bronze making became very popular. These two advantages of castability were probably noticed by Bengal metal workers and the casting technology of Bengal worker became much simpler proposition than working with liquid copper.

**5.1.3.11 Coring in Inter-Dendritic Region of Ingot**

Chemical compositions for last-to-freeze liquid (Table- 5.1.4) within the section of the Bell metal ingot were determined. The common micro-segregation phenomenon experienced elsewhere is quite apparent in the result obtained. The compositions of last-to-freeze liquid metal using EDX, outside dendrite (Fig. 5.1.17) are an interesting one. It indicates the high concentration of Sn in the last-to-freeze liquid alloy as expected (Fig. 5.1.13) by Cₜ (rich in
Table- 5.1.2 Freezing Range for Alloys due to addition of Sn to Cu

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<th>24</th>
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<td>125</td>
<td>100</td>
<td>65</td>
<td>35</td>
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Fig. 5.1.16 Freezing Range for alloys due to addition of Sn to Cu from 0 – 25.5 wt. %Sn.

Table- 5.1.3 Compositions of last-to-freeze liquid.

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<th>Cu</th>
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<td>0.501</td>
</tr>
<tr>
<td>64.54</td>
<td>34.92</td>
<td>0.13</td>
<td>0.41</td>
</tr>
<tr>
<td>73.09</td>
<td>24.37</td>
<td>0.45</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Fig. 5.1.17 Microstructure at a last-to-freeze region.

Fig. 5.1.18 The distribution of elements Cu and Sn in last-to-freeze liquid of metal ingot.

Fig. 5.1.19 Fe-Sn Phase diagram (after ASM 1992, 3: 203).
The distribution of elements Cu and Sn in last-to-freeze liquid of metal ingot is shown graphically at Fig. 5.1.18. As solidification comes to the last leg of solidification, there is an acute accumulation of low melting point solute Sn, of over 25wt% of Sn in Cu. Coring, (as discussed earlier during dendrite formation, also appears naturally. Bell metal or high-tin bronze is known to have the tin rich phase on the outside surface, called inverse segregation but could not be determined on the specimen).

5.1.3.12 Iron Content in Metal Ingot within Dendrite
Iron content within ingot metal has played a significant role is also significant, as an impurity element - starting from 1.10 wt. % at centre and it rises to 1.25 wt. %, though Fe-Sn metallic compounds can not be excluded as the reverse segregation.
The maximum solubility of tin in $\alpha$ – solid solution of copper, as per the Cu-Sn phase diagram 15.8 wt.% Sn, but the chemical composition of the center of the dendrite is 16.78 wt.% Sn. As Cu-Sn-Fe become ternary alloy system and the maximum solubility of Sn in Fe is 17.7 wt.% Sn (Fig. 5.1.19), therefore, in presence of iron the solubility of tin in the bronze system probably has increased.

5.1.3.13 Effect of Iron in Metal Ingot
Iron in small amount during solidification precipitated in the as-cast structure and refines the grain by inhibiting grain growth. The presence of free iron (West 1982; Ray 1969: 54) produces a hardening effect (later discussed) accompanied by brittleness and loss in elongation. The hardening effect and the idea of grain fineness were probably known to Bengal metal workers. The assumption is due to the fact that slag lumps contain lot of ferrous constituent in the Bell metal sample (Fig. 5.1.7).

5.1.3.14 Composition of an Interesting Dendrite
The SEM analysis of Bell Metal ingot specimen has revealed an interesting dendrite, which has heterogeneous region in the center as shown in Fig. 5.1.20. The iron- silicate compound of the core throws a new light that the addition of cassiterite (tin ore) was probably very common in Bengal / Eastern India to isolate tin from its ore. As cassiterite contains lot of
Fig. 5.1.20 The microstructure holds a special dendrite whose core or substrate looks completely different. The analysis of core revealed an iron-siliceous substrate, which acted like heterogeneous nucleants during the formation of these dendrites.

Table- 5.1.4 Vickers' Micro–Hardness
Load = 15gf, Time: 20sec.

<table>
<thead>
<tr>
<th>No.</th>
<th>Dia ($d_1, \mu m$)</th>
<th>Dia ($d_2, \mu m$)</th>
<th>Outside Dendrite (Grain) HV (Kg.mm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>7.8</td>
<td>7.8</td>
<td>454.2</td>
</tr>
<tr>
<td>2.</td>
<td>12.1</td>
<td>12.1</td>
<td>188.5</td>
</tr>
<tr>
<td>3.</td>
<td>8.7</td>
<td>8.8</td>
<td>284.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Dia ($d_1, \mu m$)</th>
<th>Dia ($d_2, \mu m$)</th>
<th>Within Dendrite (Grain) HV (Kg.mm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>8.7</td>
<td>8.8</td>
<td>362.0</td>
</tr>
<tr>
<td>2.</td>
<td>8.6</td>
<td>9.2</td>
<td>351.7</td>
</tr>
<tr>
<td>3.</td>
<td>9.3</td>
<td>9.0</td>
<td>331.0</td>
</tr>
</tbody>
</table>
silica, remnants of that silica might entrain the copper during bronze making. Note the high amount of tin, 66.68% in the analyzed core of the dendrite. The chemical composition of the center region of the dendrite in wt percentage has been Fe: 3.06, Cu: 11.90 Sn: 66.68, O: 16.10, Si: 1.94, S: 0.36 and Ni: 0.02.

Considering the very low oxygen potential of Silicon for oxide formation, the use of silica can be assumed from Si /O ratio; because the availability of oxygen in the substrate is 16.1 wt. %, which is much above the requirement, as 1.94% Si requires stoichiometrically 2.2% Oxygen to form Silica. The entrapped silica, probably as ceramic particles, helped as substrate to form the dendrites of this high-tin bronze alloy.

5.1.3.15 Source of Copper from Impurity Nickel in Metal Ingot
Ni is also a very common impurity of Singhbhum copper as identified by Sahu (et al. 2004: 949-951), contains in wt% Cu: 15.00, Ni: 10.85, Co: 0.37, Fe: 26.6 and S: 33.3. The presence of Ni in alloy gives way to an impression that metal men of South Bengal area sourced the metallic copper from the chalcopyrite belt of Singhbhum area.

5.1.4 Micro hardness of Bell Metal Ingot
Tin was added to copper to make it harder or stronger and the phenomenon goes by the name of solid solution hardening (Dieter 1988). Soft gold, in antiquity was strengthened by either silver or copper and is still the prevalent practice to make gold stronger, suitable for jewelry making. The more solute (tin) goes to the solution (of copper), stronger becomes the alloy. This hardening technique was mastered by metal workers and the workers added almost double the amount of tin (from 10% to 24%), to get a very hard bronze, almost four times harder than pure copper. VPN of pure Cu is 55 VPN and macro hardness of the Bell Metal ingot determined was 228 – 231 VPN.

The above observation is vindicated by the following results:
Both micro and macro hardness of the Bell Metal specimen were determined. Micro-hardness results are shown in Table- 5.1.4 taken on both over dendritic region and outside dendrite region.
Fig. 5.1.21 XRD Pattern of the Bell Metal ingot from Tilpi

Fig. 5.1.21A XRD Pattern of the Bell Metal ingot.
Fig. 5.1.21B  XRD Pattern of the Bell Metal ingot from Tilpi
The micro hardness results also corroborate the non-equilibrium freezing of the alloy concerned. Uniformity in the HV values has been obtained over primary dendrites. But a scatter of HV values 188.5 to 454.2 signify the presence of hard high-tin rich phase $\delta$ or $\beta''$ or micro-shrinkage within the last-to-freeze areas.

The micro hardness of dendrite is slightly more than expected in virgin Cu-Sn alloy as some impurities like Fe, Ni already inhabit the system as probably entrained the phase.

**5.1.5 X-Ray Diffraction Study**

X-Ray Diffraction pattern of the Bell Metal ingot was obtained for this specimen. Analyzing the X-ray diffraction data (Table- 5.1.5) a number of phases have been identified (JCPDS 1978, vol. 1&2). The important phases located (Fig. 5.1.21) can be summarized as: Pure tin, $\alpha$, $\beta'$ or $\beta''$ and $\delta$ solid solutions of Cu-Sn phases.

Pure tin in cast copper-tin alloys during the end of freezing squeezes out and sometimes comes outside the casting surface by means of inverse segregation (“Tin Sweat”) (Strauss 1970: 219). So, a pure tin phase appears. $\beta'$ and $\beta''$ solid solutions of copper-tin alloys are meta-stable phases, which remains untransformed during cooling. From $\beta \rightarrow \alpha + \delta$, eutectoid transformation occurs at 520 °C and the reaction product, $\alpha$ (solid solution) is copper rich and is a softer phase. $\delta$ or $\beta'$ or $\beta''$ are harder phases of copper-tin solid solution and imparts very high hardness comparable only to high-carbon steels (Smith 1993). (Note: $\beta'$ and $\delta$-phases are solid solutions of Sn in Cu ($\delta$ – phase = Cu$_{10}$Sn$_3$) and Pure Tin phase occurs from inverse segregation of tin.

**5.1.6 Differential Scanning Calorimetry (DSC) of Metal Ingot**

To understand the nature of the energy change associated with metastable phase transformations, a limited DSC study up to 600°C was conducted on the Bell Metal ingot. DSC record of the high tin cast bronze piece with endo-up has been displayed. For further detailing small endo-peak in this sample related to a kind of probable stress relieving mechanism crept into the reading. The nominal endo-peak at about 526.56 °C specifies a
Table 5.1.5 Data for XRD of Radiation: Cu/Ni 35 kV/ 30mA
Wavelength, $K_{\alpha} = 1.540598$

<table>
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<tr>
<th>No</th>
<th>Angle $\theta / \Omega$ 2.1</th>
<th>d$_{\text{Space}}$ Å</th>
<th>Rel I $I/I_0$</th>
<th>Identified Phase</th>
<th>Diffracting Plane (hkl)</th>
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<tr>
<td>1</td>
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<td>3.3733</td>
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<td>(δ phase) unidentified</td>
<td>110</td>
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<td>2</td>
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<td>3.1078</td>
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<td>(δ phase)</td>
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<td>4</td>
<td>29.6</td>
<td>3.0153</td>
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<td>5</td>
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Cu$_{81}$Sn$_{22}$
### Table 5.1.6 Data for XRD of the analysed Bell Metal Ingot

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<th>#</th>
<th>2-Theta</th>
<th>d(Å)</th>
<th>Ht</th>
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<th>I%</th>
<th>(hkl)</th>
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<th>Delta</th>
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<td>Cu₁₀Sn₃</td>
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<td>40.0</td>
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<td>48.458</td>
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</table>

Fig. 5.1.22 The DSC record of the high tin bronze ingot specimen at Tilpi with endo-up has been displayed. The phase change of eutectoid reaction starts at ~524°C and closes at ~531 °C. The area of the endo-peak is exploded in RHS.
definite phase change from metastable: phases to stabilized eutectoid phases. The phase change of eutectoid reaction starts at ~524°C and closes at ~530 °C. The area of the endo-peak is 164.004mJ, $\Delta H = 8.8651$J/g. The DSC record has been shown in Fig. 5.1.22.

5.1.7 Discussion
1. The evidence of a high tin bronze or Bell Metal guild at Tilpi was established in excavation.

2. Conical crucible- The conical crucible confirms the technological competence of metal workers in conserving the scarce energy during melting.

3. The investigation on the Bell Metal ingot confirmed the production of Bell Metal in Ancient Bengal in regular fashion. The relics of guild at the excavation site become the replica of the melting sections of a modern foundry.

4. The equilibrium Cu-Sn diagram authenticates the lowering of melting point for the Bell Metal of the order of 250 °C below that of pure Cu. The ease of melting has been manifested by the lower melting point of around 820 °C.

5. The composition of 22 to 25% Sn, balance Cu probably standardised as Bell Metal composition in Ancient Bengal with the level of Sn kept at higher end.

6. The composition of Bell Metal puts it in a single $\beta$ phase area just below the peritectic line before the peritectic reaction at (point C, 13.1 at.% Sn) liquidus solidus area during solidification produces $\alpha$-Cu-Sn phase of FCC structure of lower Sn content. At the peritectic reaction the complete phase transformation from L + $\alpha$ $\rightarrow$ $\beta$ phase remains incomplete. So last-to-freeze Sn rich $\beta$-phase remains the bulk or the matrix where $\alpha$-phase remains embedded. The super-cooling of Cu-Sn as the liquidus- solidus zone, remains very high and lowers the critical nucleus size ($r^*$) very low facilitating high rate of nucleation.
The second effect of high super-cooling introduces long solidification time and facilitates grain growth of some dendrites. Therefore, the microstructure of as cast Bell Metal consists of fine grains of $\alpha$-phase associated with large dendrites in the matrix of $\beta$-phase.

7. Though the phase diagram contains four eutectoid reactions during the cooling to room temperature but those reactions remains incomplete due to short cooling time in industrial condition.

8. The non-equilibrium cooling elaborated above gives rise to wide variation of solid (Sn) and solvent (Cu+Ni) composition, known as coring or micro segregation has been rampant throughout the section.

9. The Bell Metal ingot investigated distinctly produces three clear zones for any cast structure.

10. Bell Metal incidentally has short freezing range but due to incomplete peritectic reaction becomes a case of delayed freezing and produces some long freezing range characteristics of deep super-cooling.

11. The addition of Sn decreases the viscosity of the alloy and then slightly increases the Bell Metal range. But viscosity remains lower than pure copper and helps in easy casting.

12. The addition of Fe in ancient Bell Metal probably is un-intentional but the presence of Fe definitely improves the grain fineness of the metal ingot.

13. The presence of Ni may be the indication of sourcing primary copper in Bell Metal, as Singhbhum chalcopyrite traditionally contains Ni. So Bengal metal workers in all general assumption might have used Singhbhum chalcopyrite in copper production.

14. The addition of Sn by metal workers remains a kind of questionable mystery. Cassiterite which is chemically diagnosed as simply SnO$_2$ and be easily reduced to metallic Sn as per Ellingham diagram for oxides.
15. The addition of Sn to Cu introduces solid solution hardening of the alloy system. The lower solubility of Sn in Cu produces FCC $\alpha$-Cu phase having lattice parameters $a = 0.36146$ to 0.37046 nm (Saunders and Miodownik: 415). Higher percentage of Sn in Cu system produces $\beta$ phase of BCC crystal structure have lower lattice parameter $a = 0.29781$ to 0.29871 nm the lower size of the crystal lattice having larger solute atom produces greater hardness than $\alpha$-phase. The micro hardness result on Bell Metal ingot vindicates the theoretical observation.

16. The XRD study of cast Bell Metal becomes problematic due to the presence of equilibrium and non-equilibrium thermodynamic parameter. The limited study confirms the presence of $\alpha$- Cu-Sn phase, in the matrix of $\beta$- phase.

17. The limited DSC study does not reveal much other than the phase transformation at 524-530 °C.
CHAPTER 5.2

CHARACTERISATION OF A FORGED BELL METAL BOWL
Fig. 5.2.1 Location of Gajole (25.7° N, 89.2°E) in Maldah in West Bengal.

Fig. 5.2.2 The fragment of High-tin Bronze or Bell Metal bowl recovered from Gajole. The composition showing Sn 23.09, Fe 0.71, Zn 0.28, Pb .061, alloy has been displayed inset.
Bell Metal or high-tin bronze alloy was popular in Bengal since 5th century BCE. But many excavated specimens are cast products. Incidentally Bengal has a tradition of forged metal also and one such archaeological specimen excavated has been characterized below.

5.2.1 Description of the Specimen
A broken fragment of a Bell Metal bowl (kansar bati), about 1.1 mm thick, made of copper alloy was recovered during exploration and trial digging, in nearby village under Gajole (25.7° N, 89.2° E) Police Station in 1995 by the Directorate of Archaeology, Government of West Bengal.

The complex shape of the bowl having flat bottom with inflated curvilinear upper edge. Deep drawing with simultaneous flattening of the bottom caused heavy deformation leading to an edge crack at the corner of the ridge. The specimen is shown in (Fig. 5.2.1).

5.2.2 Antiquity
The present specimen belongs to Kushana Period, c. 2nd century CE.

5.2.3 Chemical Composition
The chemical composition was made by Gravimetric method and also by PIXE.

5.2.3.1 Chemical composition by Gravimetric method
The sample (Fig. 5.2.2) was found to contain kansha mainly of wt. % Sn 23.62, Fe 0.6, Zn 0.2, Pb 0.5 and Cu 75.04. The composition denotes the Cu-Sn alloy as Bell Metal (high tin bronze) containing Sn over 22% and belongs to (22-26%) Sn-Cu alloy, technically described as β-Sn-bronze. This analysis further identified the use of high tin (23.62%) with trace amounts of other elements.

5.2.3.2 Chemical composition by PIXE
By PIXE (Particle induced X-ray emission) analysis this specimen was further verified as of wt. % Sn 23.09, Fe 0.71, Zn 0.28, Pb 0.061, Ni 0.014, Ag 0.003 and Cu 73.80 (Fig. 5.2.3). This analysis also identified the high tin percentage (23.09) in Cu and confirmed it as
Fig. 5.2.3 The PIXE-gram for forged bowl showing Ni 0.014, Ag 0.003 and Cu 73.80.

Fig. 5.2.4 The microstructure shows the progression of the deformation along the radial contour of the bowl (marked by an arrow).
\(\beta\)-Sn bronze. The small difference of Sn percentage can be accepted as the small mass effect of the sampling during testing and so the gravimetric analysis has been taken as the yardstick of bulk material composition.

5.2.3.3 Bulk Hardness
The average bulk hardness of the bronze specimen measured by Vickers machine was 235 HV 5/10.

5.2.4 Microstructure of the Bell Metal Specimen
The microstructures of the Bell Metal specimen are being detailed below:

5.2.4.1 Microstructures
i) The microstructure (Fig. 5.2.4) of the Bell Metal sample has been developed over the transverse cross-section. The observation suggests that the metal deformation occurred in a preferred manner, as delineated from the longish second phase precipitates. The size of precipitates of the second phase varies in width from 2 \(\mu\)m to 10 \(\mu\)m while the length from 2 \(\mu\)m to 25 \(\mu\)m in the figure. The heavy metal forming (deformation) at hot working temperature, known as hot forging has been identified by the alignment of intermittent second phases (later identified as \(\beta'\)-phase) in form of lines. The longish shape of the precipitates clearly gave rise to flow lines due to forging, commonly known as fibrous structure (Dieter 1966: 460-61). The microstructures (Figs. 5.2.5 (a), (b) of a small section of this specimen put us some interesting features:

ii) At larger magnification, (Figs. 5.2.5 a, b) the surface of this specimen looks to hold the deposit of the corrosion layer of the metal surface. It is to be noted that the upper side of the figure separated from the bulk metal by a fine line. The second phase (black spots) runs along the longitudinal direction of metal deformation. The directionality of the second phase bears the signature of the metal forming action in form of conventional flow lines mentioned earlier. The precipitated phase with thin and long streaks remaining within the microstructure serves as a witness for the heavy deformation, undertaken over the initial forging stock. The intermittent nature of the phase denotes the drop forging action of
Fig. 5.2.5 (a) Lower magnification and (b) Higher magnification. In (a) the corrosion layers are shown above. The micrograph of the forged specimen shows few micro-cracks within the metal (shown by arrow). In (b) the direction of forging is shown by a large arrow. The small cracks remain witness to the heavy forging undertaken for bowl forging. The intermittent marking of second phase bears a significant signature of repetitive manual forging. Small arrows indicate micro cracks.
repetitive manual hammering. Otherwise if it were press forging almost continuous formation of second phase in a line would have formed.

**iii)** The nature of the second phase in further magnification (Fig. 5.2.5 b and 5.2.6) reveals uneven bending and lenticular edging. The spatial geometry of the bowl is the result of heavy deep drawing operation along with thinning of the metal section towards height undertaken during the cup formation of the bowl. The huge reduction ratio of the forging stock only makes the operation possible when adequate plasticity was available. During cooling the high tin bronze bowl absorbs a lot of residual stress originated during the processing. Few residual stresses produce some micro cracking within the metal section (indicated by arrows in Fig. 5.2.5 a and b). The fine cracks of irregular nature and of discontinued variety might be the result of remnants of the uncontrolled stresses in cross-section which did not progress up to the surface of the bowl.

**iv)** A large number of very small grains of micron range of sub angular nature or angular geometry Figs. 5.2.6 and 5.2.7 are totally distributed in this structure (later confirmed more distinctly in later structures).

The structure (Fig. 5.2.8) at higher magnification provides the distribution of the second phase ($\beta'$-phase) over the matrix ($\beta$-phase), by EBSD. Many second phase grains orient along a particular direction while few also set at the cross orientation of the specimen. This shows the simultaneous progression of the deformation along the height as well as the radial contour of the bowl. So, the metal deforms spatially when the height of the bowl was getting formed. A two-way deformation prevailed, marked by arrow. This becomes a case of single step forging when ‘deep drawing’ runs along with ‘stretch forming’ operation.

**vi)** The SEM structure of a similar portion (Fig. 5.2.9) depicts the matrix as $\beta$-Cu-Sn phase (light grain). The second phase of $\beta'$ Cu-Sn phase is distributed along the structure with a unusually large grain (grey grains). The $\beta'$ Cu-Sn phase keeps the preferred orientation of the forging direction. Some sub-grain formation can be visible in every large precipitate but
Fig. 5.2.6 The microstructure of bowl at surface has been revealed. The matrix is composed of $\beta$ Cu-Sn- phase with traces of deformation bands. The islands are composed of twin bands of Cu rich $\beta'$ Cu-Sn- phase.

Fig. 5.2.7 Microstructure of bowl at cross section, showing Cu rich $\beta'$ Cu-Sn islands in Sn rich $\beta$ Cu-Sn matrix.
Fig. 5.2.8 The microstructure indicates predominantly $\beta$-phase of lighter colour (green) and $\beta'$-phase of darker (red) colour as second phase. The $\beta$-phase orients itself more or less in a preferred direction of the forging operation. The metal deforms spatially when the height of the bowl was getting formed. A two-way deformation prevailed. The direction of forging are shown by arrow.

Fig. 5.2.9 The microstructure of high tin bronze shows $\beta$-Cu-Sn phase as a matrix with embedded $\beta'$-Cu-Sn phase of dark colour (martensite later shown) within the structure. Though some large grains are visible, but the number of innumerable tiny micron size grains that abound, facilities the ease of hot forging by providing super plasticity.
Fig. 5.2.10  An unusual large grain of $\beta'$-Cu-Sn phase of dark colour is being seen in the matrix of $\beta$-Cu Sn phase.

Sub-grain formation leading to recrystallization has taken place

Grains of 2 – 3 $\mu$m

Fig. 5.2.11  One large or blocky grain has developed sub-grain formation with the impression of deformation slip bands faintly visible. The sub grains have converted into new crystallized strain free grains producing dynamic recrystallization of parent $\alpha$-Cu-Sn phase of the casting ingot. This metallurgical transformation along with mechanical deformation has been called Thermo Mechanical Treatment or TMT. These recrystallized sub-grains of the order of few $\mu$m had assisted in easy super-plastic formation. The marking $\beta'$-Cu-Sn phase is intentional to indicate the subsequent transformation of martensite in form of $\beta$-Cu-Sn phase from the parent lattice of cast $\alpha$-Cu-Sn phase.
preferred directionality along the deforming operation exposed by thinning of the section and lengthening along the flow line. The simultaneous orthogonality is still kept by the large second phases.

vii) On further magnification (Fig. 5.2.10) of a particular grain $\beta'$ Cu-Sn phase the sub-grain formation talked earlier now are more clearly revealed. Though the initial grain size was quite large of the order of 300 micron by 50 micron was converted into new recrystallised grains of the size of less than 20 micron. The small size of grain is a prime condition of super plasticity (Hassen 1997, 327-9.) Most of the other grains of $\beta'$ Cu-Sn phase (grey areas bounded by white borders) comes under 4-5 micron and fine grains helped in acquiring the super- plasticity of $\alpha$-phase of cast Bell Metal. The $\alpha$-phase (later converted to $\beta'$-Cu-Sn phase) sustained the heavy deformation during bowl formation.

viii) If the grain is further magnified (Fig. 5.2.11) the deformation band of forging have been clearly revealed. Later on the deformation bands have been further magnified to identify the twins in the microstructure. The wide spread non-directionality of the bands for individual grains confirms the two-way deformation undergone by the individual grains.

5.2.5 Confirmation of Martensite by Transmission Electron Micrography

The test specimen when analysed through TEM revealed a clear structure (Fig. 5.2.17 and 5.2.18 at magnifications of 12KX, 25KX) of martensite transformed in bronze. The transformed martensite is a ‘lath’ type martensite and the ‘laths’ are clearly shown in the structure. The lath martensite is of deformable in nature and occurred with associated micro twins arranged at right angles to the lath boundaries. Micro twinning is a way for the structure to accommodate elastic stresses generated by the phase transformation during quenching.

The chemical composition investigated on the area shows Sn 24.65, Fe 0.56 and Cu 74.79. Though the percentage composition seems to be of $\beta$ Cu-Sn phase has been identified as $\beta'$ martensite phase. This transformed was originated from the earlier mentioned second phase of $\alpha$- Cu-Sn phase of the cast material. The Basket wisp structure has been revealed in Fig.5.2.17. The deformation bands have been clearly revealed at 50 KX (being signature of martensite).
Incoherent twins are visible due to the simultaneous operations of deep drawing as well as banding.

Fig. 5.2.13 SEM of forged high-tin bronze or Bell metal forged specimen shows deformation bands (marked by arrow). The $\beta'$ Cu-Sn phase a ‘lath’ type transformation of the matrix was observed. The laths might be of the martensitic $\beta$ Cu-Sn phase of the matrix. Some twin bands with micro twins can be observed but somehow the transformation did not proceed all through the structure.
The bowl fragment was further analysed through TEM microscope on a preferred location. The EDX attached to the instrument has given the composition in weight percentage as this resembles to exaggerated chemical composition of the precipitated β'-Cu-Sn phase. Graphical representation of the compositions is shown in Fig. 5.2.16. The TEM micrographs (Figs. 5.2.17 to 5.2.18) clearly indicated the formations of martensite and at 50KX basket wisp structure revealed (Fig. 5.2.19), which is a clear signature of martensitic transformation. It is also include deformation bands in matrix of β phase. In this microstructure deformation bands are visible in the matrix of β- Cu-Sn phase.

The micrograph reveals the individual martensite laths, with their associated ‘micro-twinning’ that occurs within them (seen as the fine black) lies more or less at right angles to the lath boundaries. The micro-twinning is a way for the structure to accommodate elastic stresses generated by the phase transformation.

The microstructure (Fig. 5.2.9) of the forged Bell Metal specimen clearly displays the precipitated second phase in the matrix. The common nature of orthogonal placing of the precipitated phase in form of grey areas can also be seen. The matrix is β- phase which is a solid solution of Sn over 25 weight percent in BCC copper. The dark phase has been transformed from solid solution of Sn having varying percentage from 15 to 22 percent in FCC Cu.

This has been designated as β'-Cu-Sn phase. The morphology of the long and thin section of Cu-Sn β' phase dominates the structure though the fine grains of small micron size phase (which are more abundant) are also visible in higher magnification. The transformation of Cu-Sn phase can be located in the marked portion shown by the white patches (Fig. 5.2.10).
5.2.5.1 Distribution of Tin Matrix and the Second Phase
During ingot making of the high-tin bronze or Bell Metal stock from which the bowl sample was later manufactured, the phase of lower tin content forms first (Haasen 1997). The $\beta'$-phase, which formed initially shows its chemical composition of tin as 15.77 wt. % (Table-5.2.2), lower than the $\beta$-phase, which contains 35.22 wt.% tin. The matrix $\beta$-phase should be richer in tin and the percentages of tin analyzed by EDX satisfactorily prove the general metallurgical observation.

The perpendicular orientation of the second phase in some areas implies working characteristics of the heterogeneous alloy in two directions, radial as well as transverse directions. The rounded corners and globular nature of second phase, $\beta'$-phase, in some cases are also seen in the microstructure. It is due to the repeated forging at red hot condition, when the recrystallization and annealing of the metal also occurred, and that softening process rounded the phases as well as eliminated major cracking. The contents and distribution of tin in the given microstructure obtained from SEM-EDX analyses, shows lower percentage of tin in $\beta'$-phase and higher percentage of tin in $\beta$-phase, as expected in normal heterogeneous material tabulated in Fig. 5.2.14. Distribution of Cu- Sn-Fe is shown in Fig. 5.2.15.

5.2.5.2 Dynamic Recrystallization of Primary $\alpha$-Cu-phase
The sub grain formation happened during the forging operation. Ultimately the sub grains crystallized to new smaller grains. The crystallization proceeded during mechanical deformation, so the recrystallization of the new grains has been termed as dynamic recrystallization.

The dynamic recrystallization happened due to following reasons. The preferential slide of the atoms within the parent FCC $\alpha$-Cu phase lattice. The preferential slip plains and slip directions of $\alpha$-phase facilitated easy glide during the high temperature operation. The adequate temperature helped in diffusion and overcome the general inhibitors by cross slip. The assistance from cross slip made the FCC phase more ductile over the recrystallization temperature during hot forging. The low angle grain boundaries of the giant dendrite grains
Fig. 5.2.14 TEM-EDX of composition of bowl specimen graphically representing Cu, Sn and Fe in studied area

![TEM-EDX](image)

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Sn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>74.79</td>
<td>24.65</td>
<td>0.56</td>
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</table>

Figs. 5.2.15 and 5.2.16 - The micrograph reveals the individual martensite laths, with their associated micro-twinning that occurs within them (seen as the fine black) lies more or less at right angles to the lath boundaries. The micro-twinning is a way for the structure to accommodate elastic stresses generated by the phase transformation.

![Micrograph](image)
Deformation bands are also visible in the matrix of $\beta$ phase.

Fig. 5.2.17 at 50KX Microstructure highlights the Basket-wisps structure. Deformation bands are also visible in the matrix of $\beta$-phase.
detach sub-grains from one another due to low activation energy parameter at high temperature. Both the lower inhibitions, i) due to easier cross slip, ii) due to lower activation energy made this recrystallization an easy reality. The sub grain formation has been converted into recrystallization of fine grains. Using the modern terminology the deformation of the α-phase recrystallization can be termed as dynamic recrystallization. This is the process of Thermo Mechanical Treatment or TMT which is the phenomenon of thermal excitation during mechanical deformation or minor α-Cu-Sn- phase of the initial casting converted to a forging stock.

5.2.5.3 Dynamic Recrystallization of Primary α-Cu Phase of Cast Ingot

Converted to β'-Cu-Sn-phase after heat treatment shown in the microstructure. The deformation bands look like mechanical twins and similar to the appearance of ‘lath martensite’ in quenched low carbon steel. The structure signifies the formation of martensitic phase during the quenching operation after hot forging. In some small areas the classical ‘basket wisp’ structure of martensite can be faintly located. In the mechanical twin bands due to heavy forging both uniform and non-uniform twin bands can be visible (Fig. 5.2.12).

In the SEM microstructure of the high tin bronze sample Fig. 5.2.12 investigated over the martensitic transformation of β' Cu-Sn phase so far discussed an interesting observation was felt. In the β' Cu-Sn phase a ‘lath’ type transformation of the matrix was observed. The laths might be of the martensitic β Cu-Sn phase of the matrix was observed. Some twin bands with micro twins can be observed but some how the transformation did not proceed all through the structure. Therefore, there is some sign for martensitic transformation of β Cu-Sn phase also. But the reason is not clear why transformation did not spread all through the structure and remained localized in some areas. In coherent twins are visible due to the simultaneous operations of deep drawing as well as banding.

EDX analysis in the region of the matrix β-Cu-Sn phase has composition as: 65.33 wt% Cu, 35.22 wt% Sn with few other elements. The embedded β'-Cu phase contains 82.61 wt% Cu, 15.77 wt% Sn with other minor elements. The hot forging and subsequent heating transformed the metal phases of the cast bronze stock in to more uniform composition.
Distribution of elements at points from 1 to 13

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<th>3</th>
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<td>Sn</td>
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<td>24.29</td>
<td>23.12</td>
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<td>34.00</td>
<td>34.00</td>
<td>33.59</td>
<td>32.88</td>
<td>22.54</td>
</tr>
<tr>
<td>Cu</td>
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<td>75.71</td>
<td>76.88</td>
<td>76.83</td>
<td>72.50</td>
<td>65.44</td>
<td>64.35</td>
<td>65.51</td>
<td>65.24</td>
<td>65.71</td>
<td>66.28</td>
<td>76.65</td>
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<td>0.70</td>
<td>0.84</td>
<td>0.81</td>
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</table>

Fig. 5.2.18 The contents and distribution of tin in the given microstructure obtained from SEM-EDX analyses, shows lower percentage of tin in β-Cu-Sn phase and higher percentage of tin in β-Cu-Sn phase, as expected in normal heterogeneous material.
5.2.5.4 Tin Distribution in the Forged Specimen

To identify the distribution of Sn within the precipitated and matrix $\beta$ and $\beta'$-$\text{Cu-Sn}$ phases and EDAX analyses were performed over the microstructure (Figs. 5.2.14 and 5.2.15). The analyses certified the second phases of $\beta'$ Cu-Sn phase (grey area) of lower Sn content. The matrix (white area) indicates high concentration of Sn over 33%. This comes in quite agreement with the phase analysis of Cu-Sn phase diagram at higher temperature.

This was also indicated by EBSD study shown earlier in Fig. 5.2.8. The microstructure indicates predominantly $\beta$-phase of lighter colour and $\beta'$-phase of darker colour as second phase. The $\beta'$-phase orients itself more or less in a preferred direction of the forging operation.

5.2.5.5 Micro Hardness

To estimate the micro-hardness of phases a limited data was measured. Hardness measured HK 288, 310 and 323 over matrix, $\beta$-phase and HK 206, 210 and 276 over $\beta'$-second phase at an indenting load of 10 gm wt. (Fig. 5.2.20). The matrix $\beta$-phase possessing 35.22 wt. % Sn shows higher hardness while second phase $\beta'$-phase containing 15.77 wt. % Sn measures lower hardness. The hardness measurement satisfies the common metallurgical prediction of the solid solution hardening (Haasen 1997: 347, 353) that harder phase should have higher concentration of solute tin.

5.2.6 Confirmation of Phase by the Diffraction

Diffraction pattern was obtained both by X-ray and Neutron diffraction technique.

5.2.6.1 X-Ray diffraction

X-Ray diffraction patterns were obtained using a PHILPS PW 1700 diffractometer with Cu-$K_{\alpha}$ radiation. X-Ray diffractograms (Figs. 5.2.21 to 5.2.24) of the bronze sample identifies the presence following phase: Pure tin, $\beta$-phase and $\beta'$-phase of copper-tin systems as compared by Sn (JCPDS files 5-0390, 4-0673, 18-1380), $\beta$-phase (JCPDS file 6-0621), $\beta'$-phase (JCPDS file 17-0865), respectively. The XRD data are shown in Table- 5.2.1. X-ray
Fig. 5.2.19 Distribution of Cu-Sn-Fe at selected two grains, shown at microstructure 4.2.6. Point 1 is centre of left. Point 7 is at grain boundary. Points 8-10 are at matrix, points 11-13 are at the second grain from edge. Distance between each point is 5 µm.

The transformation of Cu-Sn β-phase can be located in the marked portion shown by the white patches.

Fig. 5.2.20. The etched microstructure of the Bell Metal specimen clearly displays the precipitated second phase in the matrix. The transformation of Cu-Sn β-phase can be located in the marked portion shown by the white patches.
Fig. 5.2.21 (LHS) Banding of second phase- $\beta'$, in bronze indicates hot forged structure. The matrix is $\beta$ phase with islands of $\beta'$ phase. Microhardness readings (RHS) indicate the presence of $\delta$ - phase in $\alpha\beta$, (HK 323).

Fig. 5.2.22 X-Ray diffractogram of Bell Metal sample.

Fig. 5.2.23 X-Ray diffractogram of the bowl sample.
Fig. 5.2.24 X-Ray diffractogram of bowl sample.

Fig. 5.2.25 X-Ray diffractogram of the forged bowl sample.
diffractogram using (Table- 5.2.2) through Panalytical MRD system also confirmed the observation \( \beta \)-Cu-Sn phase having BCT structure confirmed the martensitic transformation.

5.2.6.2 Neutron diffraction

The high-tin bronze sample of forged bowl was subjected to Neutron Diffraction technique. From the Neutron Diffraction pattern, the reflections can be indexed to \( \beta \) Cu-Sn (Pmmm space group, JCPDS 06-0621) and \( \beta' \) (Cu5.6Sn, JCPDS 17-0865) (P4/n space group). From this pattern it appears that there are two phases possible in this sample. A detail of Neutron Diffractogram is shown in Fig. 5.2.25 and Fig. 5.2.26.

The cell parameters in \( \beta \) Bronze are
\[
4.578802 \quad 5.377717 \quad 5.252579 \quad 90.000000 \quad 90.000000 \quad 90.000000
\]
The cell parameters in \( \beta' \) (Cu5.6, Sn) are
\[
3.727009 \quad 3.727009 \quad 3.677952 \quad 90.000000 \quad 90.000000 \quad 90.000000
\]
The upper and lower tick marks in the above graph indicate the positions of the allowed reflections. The upper and lower ticks are for \( \beta \) Bronze and \( \beta' \) (Cu5.6, Sn), respectively.

5.2.6.3 Microstructure and Identification of Phases

Further confirmations of phases in this sample were obtained by comparing with JCPDS values. \( \beta \)-phase (Orthorhombic) JCPDs file 06-621 (>25-56.5%Sn), where \( a \neq b \neq c \) values are 4.578802 5.377717 5.252579 (all are Å units). On the other hand \( \beta' \)-phase (Tetragonal) JCPDs file 17-865 (less than 25%Sn); \( a = b \neq c \) value 3.727009 3.727009 3.677952 (all are Å units) (Thomas et al. 1963, Askeland 1990: 349).

The slip bands enclosed within 0 -grains (second phase) are also found to be oriented in different directions, confirming the movement of the grain flow in more than one direction as already suggested.

5.2.7 Texture Analysis

To further investigate the problem of the preferred orientation of the forged Bell Metal sample, X-ray pole-figures were examined by Xpert Pro PANanalytical machine. The contours (Fig. 5.2.27) of the pole-figure \{100\} do not provide much information. The contours of the pole-figure \{111\}, \{110\} and \{113\} are discontinuous and the orientations of
### Table- 5.2.1 Data for XRD through Panalytical MRD System

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### Table- 5.2.2 EDX Compositions of elements in β and β' phase

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<th>β'-phase</th>
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<td>Sn</td>
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<td>15.77</td>
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<tr>
<td>Fe</td>
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<tr>
<td>O</td>
<td>1.98</td>
<td>1.22</td>
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<tr>
<td>Zn</td>
<td>0.41</td>
<td>Nil</td>
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### Table- 5.2.3 EDX Values of Bell Metal Test piece

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<th>Ht</th>
<th>Ht%</th>
<th>Phase ID</th>
<th>d(Å)</th>
<th>I%</th>
<th>(hkl)</th>
<th>2-Theta</th>
<th>Delta</th>
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<td>78.543</td>
<td>1.216</td>
<td>11</td>
<td>21.0</td>
<td>Cu_{5.6}Sn</td>
<td>1.2180</td>
<td>20.0</td>
<td>(003)</td>
<td>78.459</td>
<td>-0.084</td>
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</tbody>
</table>
Fig. 5.2.26 The Neutron diffractogram of the specimen has been shown.

Fig. 5.2.27 The Neutron diffractogram of the same specimen has been shown. The presence of $\beta$-Cu phase as matrix with the minor phase as $\beta'$-Cu phase as XRD also is being confirmed.
the forging texture are very difficult to identify due to larger grain sizes (25 µm to 250 µm). The deformation texture due to thermo-mechanical treatment may contain the orientations of \{110\} \langle112\rangle and \{113\} \langle211\rangle. Pole-figure has been shown in Fig. 5.2.27. The stress analysis of the forged bowl specimen showing intensity and 2\theta values are shown in Fig. 5.2.28.

Forging textures are usually weak. Reasons: variable strain path. Imagine a forging with hammer blows from different directions. Also the forging texture will have deformation texture component, as well as components of annealing.

5.2.8 Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA)
The high-tin bronze sample was tested for DTA and TGA analysis up to 900°C in nitrogen atmosphere for identification of phase change characteristics. For this bronze sample two small endo peaks around (520°C) and (802°C) were observed in thermal analysis. This indicates the \gamma\text{-eutectoid} phase transformation at 520°C and then further small peritectic transformation around 800°C, after which the material fully enters the \beta\text{-region} of Cu-Sn phase diagram. This has been shown in Fig. 5.2.29.

5.2.9 Differential Scanning Calorimetry (DSC)
To understand the nature of the energy change associated with metastable phase transformations, a limited DSC study up to 600°C was conducted on Bell Metal samples. DSC record of the high tin forged bowl with endo-up has been displayed. We had obtained two small endo peaks around (520°C) and (802°C) earlier by DTA. For further detailing small endo-peak in this sample related to a kind of probable stress relieving mechanism crept into the reading. The nominal endo-peak at about 525°C specifies a definite phase change from metastable phases to stabilized eutectoid phases. The phase change of eutectoid reaction starts at ~525°C and closes at ~530°C. The area of the endo-peak is 245.844mJ, \Delta H =9.0053J/g. The DSC record has been shown in Fig. 5.2.30.
Fig. 5.2.28 Pole figure of high-tin bronze sample

Fig. 5.2.29 The stress analysis of Bell Metal specimen showing intensity and 2θ values.
Fig. 5.2.30 a) Data for DTA indicating small endo peaks at 520°C and 802°C marked by arrows, (b) Data for TGA do not provide much substantial information

Fig. 5.2.31 DSC record of the high tin or Bell Metal forged specimen with endo-up has been displayed. The phase change of eutectoid reaction starts at ~525°C and closes at ~530°C. The area of the endo-peak is exploded in RHS.
5.2.10 Other Studies

Some more studies had been conducted like the nature of non-equilibrium cooling, crystallography etc.

5.2.10.1 Non-Equilibrium Cooling of the Cast Metal

Non-equilibrium cooling in the initial cast metal before hot working also detected in the specimen. From the centre (point 1), the tin percentage by weight starts from 21.86 and finishes as 23.17 near the surface (point 6) and at grain boundary (point 7) it was 26.22%. From point 1 to 6 Fe percentage by weight was negligible, whereas at point 7 it was 1.29%. From point 7 to 12, at $\beta$ phase matrix, the weight percentage composition of Sn is increasing from 33.63% at point 7, and increasing a bit this is almost constant with around 34.00%, decreases to 33.59% at point 11, 32.88% at point 12, decreases to point 13 with a value of 22.54% by weight. Similar is the situation of the percentage composition of Fe. At point 7, it is 0.93 weight percentage, further reduced to 0.49% at point 9, at point 12 on boundary it was found to be 0.84 and at point 13 its value obtained as 0.81 weight percentage.

5.2.10.2 Crystallography

Some general comments are presented on the crystallography of the forged bowl specimen. From XRD study of forged structure (Figs. 5.2.22 and 23) confirms the presence of minor phase $\beta'$-Cu with matrix $\beta$-Cu phases. The existence of tin in the guise of Inverse segregation common to many tin-rich alloys also show their attendance. In contrast Neutron diffraction (Fig. 5.2.25) pattern indicate $\beta$-Cu phase of Orthorhombic variety having crystals of size $a=0.4578802$ nm, $b=0.5377717$ nm and $c=0.4252579$ nm in the forged, quenched and tempered structure. Whether the phase has got ordered structure cannot be confirmed but probably originated from high temperature supersaturated $\beta$-Cu phase of high Sn-concentration as the known value of BCT tin has been reported as $a=0.58194$ nm, $c=0.31753$ nm.

Alongside the bulk metastable phase, a Martensitic phase reported as $\beta'$-Cu phase (marked once as $\alpha$ -phase to indicate its parenthood from $\alpha$-Cu phase). This exhibits a lot of
Fig. 5.2.32 Rhines explanation.

Fig. 5.2.33 Portion of Cu-Sn Diagram
deformation bands and it is suggested as a very highly faulted FCC \((cF4)\) structure. The cell parameters of \(a=0.3727009\) nm, \(b=0.3727009\) nm, and \(c=0.3677952\) nm of the suggested \(\beta'\)-Cu phase had been calculated. The cell parameters are close to FCC-Cu phase of 0.3608 nm and so the metastable martensitic phase has been concluded here as \(\beta'\)-Cu phase, in absence of any suitable nomenclature.

5.2.10.3 Comparative Study for Identification of the Phase

The values shown in the Figures and Table discussed can be compared with the explanation of its various phases. The microstructure resembles similar schematic diagram proposed by Rhines 1956: 85 (shown in Fig. 5.2.31) where it departed the natural freezing of peritectic alloys. At \(\alpha\) region which was undergone peritectic reaction from liquid state, which solidified later predominantly of \(\beta\) - metastable phase confirms. The thin layer differentiates between the \(\beta\) and \(\alpha\) phase is \(\delta\) phase, though it is so thin that it is not perceptible in the microstructure.

The part (Fig. 5.2.32) shows the relevant bronze compositions as used in bronze forging. The single-phase \(\beta\) region, below the peritectic temperature of 798\(^0\) C, extends from 21.86 to 25.5\% tin. The bronze sample in interconnected \(\alpha\)- phase look more roundish in nature, indicating very close under annealing below transformation temperature like process annealing in carbon steel.

5.2.11 Conclusion

The study of high-tin bronze forged bowl proves a beautiful manufacturing process of ancient metal workers. This unique process is a unit process of utensil manufacturing by hot forging technique. Macrostructure clearly shows the fibrous structure of hot forging from the observation of second phase. Microstructure vindicates two-way plastic deformations of a cast stock (ingot) into upsetting as well as deep drawing operations simultaneously.
EDX analysis provides the compositions of individual phases of $\beta$ and $\beta'$. The softening of the hard bronze material was done by the method of diffusion at high temperature. At the high temperature during forging operation the red hot cast ingot also got homogenized. The combination of the thermal treatment as well as the hot deformation, known in modern times as thermo-mechanical treatment (TMT) was practiced by the Bengal metal workers. The knowledge of TMT is an indicator of superior knowledge of metallurgy which made possible the shaping of such hard and brittle, difficult alloy like high-tin bronze.

The selection of composition as 75Cu/25Sn is also significant and a unique achievement. Because this material at red hot condition becomes almost single phase $\beta$ or $\beta'$, fit for easy plastic deformation. This was certified by the X-Ray Diffraction, Neutron Diffraction and TEM analyses. From SEM studies (Fig. 5.2.13) partial fault revealed (similar to Kelly 1963, pp 933-39). TEM studies as revealed in Figs. 5.2.17 to 5.2.19 represents partial twinning of $\beta'$ martensite (Thomas, in Kelly 1963: 939).

The hardness of the high-tin bronze forged bowl corresponds to very high Knoop hardness values, as determined by micro hardness tester. The extreme hardness is significant as it is comparable to general cutting tip hardness. The high-tin bronze or $\beta$-bronze is a peculiar alloy which is hard and brittle material at room temperature but soft, ductile and highly deformable at red hot temperature. The ancient metal workers had this technological information without the modern knowledge of phase diagrams and this confirms the excellent development of metallurgy in ancient Bengal.

5.2.12 Discussion

1. The evidence of a high tin bronze or Bell Metal forged bowl was established in exploration.
2. The unetched micrograph of the forged specimen shows few micro-cracks within the metal. The small cracks remain witness to the heavy forging undertaken for bowl making. Directional orientation of second phase reveals in the matrix.
3. Microstructure of bowl at cross section, showing Cu rich β' islands in Sn rich β matrix. The transformation of Cu-Sn β-phase can be located in the matrix. The metal deformation occurred in a preferred manner, as delineated from the longish second phase precipitates.

4. The huge reduction ratio of the forging stock only makes the operation possible when adequate plasticity was available.

5. On the formation of martensite according to Cortie and Mavrocorodos 1991, two types of martensitic transformations occur on quenching of β phase. A martensite denoted as $\beta_1'$ or $\beta'$ can be formed by quenching β phase between 22.0 and 24.1 pct Sn to ambient temperatures. A different martensite usually denoted $\gamma_1'$ or sometimes denoted $\beta''$ when β containing from 24.1 to 25.6 percent Sn is quenched.

6. In our studies, the characterizations of $\beta$ and $\beta'$ Cu-Sn phase were established.

7. The deformation bands have been clearly revealed in SEM studies.

8. DTA indicated small endo peaks at 520 °C and 802 °C.

9. The limited DSC study does not reveal much other than the phase transformation at 525-530 °C. The nominal endo-peak at about 526.56 °C specifies a definite phase change from metastable phases to stabilized eutectoid phases.
CHAPTER 5.3

CHARACTERISATION OF COPPER HOARDS FROM WEST BENGAL AND JHARKHAND
Copper Hoards are discovered all over Eastern and Northern India. Most of the copper items explored have been named historically as copper hoard culture. From the technological point of view or historical context copper hoard items are enigma.

For the present research a number of Copper hoard samples from West Bengal and Jharkhand region has been procured from SC Ray collection, Ranchi, in ‘Man in India’ Office; from the Directorate of Archaeology, West Bengal and personal collections. Some of the copper hoard objects physical features were assessed by Yule and Thiel-Hortsmen (1985). Following are the results for characterisation of the four specimens.

5.3.1 A broken piece of Bun Shaped Ingot (Aguibani)
5.3.2 A fragment of a Bar-Celt (Khuntitoli)
5.3.3 One Double - Ended Axe (Khuntitoli)
5.3.4 A broken fragment of Copper hoard, (Bareli).

5.3.1 A Broken piece of Bun Shaped Ingot
The copper hoard sample was obtained from Aguibani (22°56'15"N, 87°22'15"E), District West Medinipur, West Bengal. The specimen is preserved in the State Archaeological Museum in Kolkata. It was discovered from surface exploration. It’s shape clearly indicate that it was a part of a bun shaped copper ingot, shown in Fig. 5.3.1.

5.3.1.1 Description of the Specimen
The upper part is flat but the lower part is oval with uneven surface indicating the impression of a sand mould. From the physical appearance of the half round section and the top flat surface it seems that the copper bun is a solidified cast object. The piece of the copper bun weighs around 200 gm. The specimen provides the geometry of a bun shaped ingot. Many of the bun shaped ingots were used as a future forging stock.

5.3.1.2 Antiquity
The present specimen belongs to c. 1000 BCE.
5.3.1.3 Chemical Composition of the Bun Shaped Specimen
The chemical composition was made by gravimetric method. The chemical analysis of the lump (Table- 5.3.1) is shown in the inset of the Fig. 5.3.1. The weight percent composition is Fe 0.08, Sn 0.05, Pb 0.02, Zn 0.05 and Cu as 99.75 and can be concluded that the sample is made of pure copper with trace amount of residual Fe, Sn, Zn and Pb which remained in metal after extraction from the ore.

5.3.1.4 Bulk Hardness
The bulk hardness of the copper bun was measured by Vickers machine and the hardness obtained was 235 HV 5/10. The hardness seems to very high with respect to pure copper (HV 50-65).

5.3.1.5 Metallurgical Structure
The optical microstructures as well Scanning Electron Microstructures are being detailed below:

5.3.1.5.1 Optical Microstructure
The optical micrograph (Fig. 5.3.2) shows a single phase structure consisting of equiaxed grains dotted with round inclusions within the grains. The equiaxed nature of grains without dendrite is metallurgically significant if the material is assumed as cast sample. The cast structure revealed no presence of dendrites and that equiaxed nature of grains signifies the application of prolonged annealing. At the grain boundary precipitates of globular phases exists at the grain boundaries. Those globules might be the residual oxide complexes. This precipitation often observed in case of ‘blister copper’. The polygonal nature of single phase signifies ‘cellular dendritic structure’. Only full annealing at high temperature can only remove dendrites and make the material grains equiaxed. These points out to high state of metallurgical knowledge of metal workers, who definitely possessed the technology of transformation of cast structure to annealed structure (around 900°C). The practice of full annealing so was a common technique already existing at that time. That ‘cellular dendritic structure’ made the copper tough.
Fig. 5.3.1 Bun Shaped Copper Ingot: Aguibani. Table 5.3.1 is the composition (Inset).

Fig. 5.3.2 (LHS) Equiaxed grain structure with random distribution of second phase is observed (Inset). Some lead (Pb) particles are shown.

Figs. 5.3.3 (LHS) (The tool bar indicates 20µm) and 5.3.4 (RHS) (The tool bar indicates 100µm) – showing different types of inclusions in (unetched state).

Fig. 5.3.5 (L) SEM microstructure at 75X showing shrinkage cavity. Fig. 5.3.6 (R) at 200X.
5.3.1.5.2 Scanning Electron Microstructures
The microstructure obtained through SEM is shown in Figs. 5.3.3 and 5.3.4 on an unetched sample shows the irregular shrinkage cavities. The etched structures further reveal the shrinkage cavity at the grain boundary at Figs. 5.3.5, 5.3.6 and 5.3.7. The inclusion seen in Fig. 5.3.3 is enlarged further as Fig. 5.3.8. SEM micrograph showing Se-Cu Sulphide inclusion (Type II, after Flinn 1963: 234) and irregular shrinkage cavity.

SEM analysis further reveals the second phase as revealed in the microstructure. SEM EDX composition for the analysed specimen is graphically shown in Fig. 5.3.9. The wide presence of arsenic confirms the intentional addition of arsenic to refine and deoxidize the metal at the ingot stage. The presence of arsenide in copper sulphide is a distinguished feature in Singhbhum copper ores. EDX at the centre (Table- 5.3.3 A) also proves the presence of lead arsenide and copper sulphides, which are generally present in Singhbhum ores (Mitra, 1984). The wide presence of arsenic in noted through Table- 5.3.3 B confirms the intentional addition of arsenic to refine and deoxidize the metal at the ingot stage. The EDX at matrix at other two selected points are shown in Tables 5.3.3 C and 5.3.3 D.

5.3.1.6 Micro Hardness
The micro hardness measured in all cases over 180 HK in Knoops’ scale. Pure copper in annealed condition only possess around HV 60-65. That high hardness value is an indication of solid solution hardening due to the presence of impurities like Fe, Sn and Zn. According to Rollason (1973:303), soft temper refers to annealed material HV 60, ‘half hard’ is slightly cold worked HV 70-80, and ‘hard temper’ is more heavily cold worked to yield a hardness of 100 or more. In this case, the hardness is above all these varieties, signifying the probable solid- solution type of hardening referred above. Fig. 5.3.10 indicates the micro hardness readings ~ HK 184 show harder material (Load 50 gm), confirming the presence of arsenic bearing second phase.

5.3.1.7 Relationship of Dendritic Arm Spacing of Bun Shaped Ingot
A random measurement of Secondary Dendritic Arm Spacing (DAS) was undertaken to have an idea of the cooling rate expected in the casting. The relationship between the cooling rate, \( R \) in \( ^\circ \text{C}/\text{Sec} \) and \( \lambda \) in \( \mu \text{m} \) can be determined by the following (Hwang et al. 1998: 495-503),

\[
\lambda = 101 \times R^{-0.42} \quad \text{.........................................(1)}
\]
Fig. 5.3.7 SEM microstructure at 200X showing shrinkage cavity at other location

Table- 5.3.2

SEM-EDX in Atomic percentage at centre.

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Fig. 5.3.8 SEM micrograph showing irregular grey Cu-Se Sulphide inclusion (Type II) and shrinkage cavity.

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Table- 5.3.3

EDX of Bun Shaped Copper Ingot from Aguibani. A and B is at inclusions, C and D at matrix, showing the EDX values at different points A, B, C and D.
This was calculated on basis of the etched micro structure. The dendritic arm spacing was calculated as ~100 µm, which indicates slow cooling (~1 K/Sec) as expected in a shut-down crucible or within an open sand mould.

5.3.2 A Fragment of a Bar-Celt
The bar-celt is a type of copper hoard, used as a cutting end for scooping the earth of agricultural field, locally known as “khurpi”. The present specimen, (Fig. 5.3.11) was discovered (Brown, 1916) at Khuntitoli, District Ranchi.

5.3.2.1 Description of the specimen
This is a pure copper casting (99%) but full of gas holes and seems to be made in open molds with poor gating. The melting and casting techniques deserves more improvement for good casting production. The specimen is about 30 mm square and 120 mm in length with sharp edge at one end.

5.3.2.2 Antiquity
The present specimen belongs to c. 1000 BCE.

5.3.2.3 Chemical Composition
The chemical analysis (Table- 5.3.2) of the bar-celt is shown in the inset of the Fig. 5.3.11. The weight percent composition is Fe 0.08, Sn 0.40, Pb trace, Zn 0.05 and Cu is 99.50. The purity (over 99%) is an excellent example of pure copper production in this region.

5.3.2.4 Un-etched Macrostructure
Un-etched close macrostructure indicating pits and blow holes of regular and irregular shape is shown in Fig. 5.3.12.

5.3.2.5 Un-etched Microstructure
Un-etched microstructure of bar-celt revealed basically three types of inclusions. The microstructure shown in Fig. 5.3.13 indicates those inclusions. In this figure, round half tone inclusions indicate oxide, irregular black spots indicate sulphide and inclusions of white spots are arsenide. The tool bar indicates 100µm. At another location, similar inclusions are also revealed in Fig. 5.3.14.
Fig. 5.3.9 (LHS) Total composition as revealed in SEM-EDX. Fig. 5.3.10 (RHS) indicates the micro hardness readings show harder material (Load 50 gm), confirming the presence of arsenic bearing second phase.

A Fragment of a Bar-Celt

Fig. 5.3.11 Bar-Celt, Khuntitoli. Table- 5.3.4 The chemical composition is showing in inset.

Fig. 5.3.12 Unetched macrostructure of Bar-celt indicating pits and blowholes of regular and irregular shape (scale bar indicates 1 mm).
5.3.2.5.1 Optical Microstructure
Annealed microstructure revealed partially annealed dendritic pattern revealed dendritic cast structure at (125 X), (Fig. 5.3.15).

5.3.2.5.2 Metallurgical Structure
The optical microstructures as well Scanning Electron Microstructures are being detailed in Fig. 5.3.15. That shows the remnants of dendrites, visible with wide distribution of microvoids and inclusions as well as diffusive layers of dendrite arms. All these reveal unsound metallurgical knowledge either in foundry or in heat treatment.

5.3.2.5.3 Scanning Electron Microstructure
The SEM was conducted on polished but unetched sample to identify the nature and distribution of inclusions. The grain boundary has revealed preferential segregation of the second phase particles. This is well revealed in Fig. 5.3.16. SEM-EDX was conducted at the microstructure to further identify the nature of the inclusions. Table 5.3.4 indicates the EDX values at different regions A, B, C and D. It is interesting to be seen with the microstructure. The Fig. 5.3.17 is the enlarged view of Fig. 5.3.13, shown earlier. Un-etched microstructure is full of different inclusions as indicated above. Bulk phase is copper, along with different metals in trace amounts even Pb, Bi, Co, Se and arsenide are rare. SEM EDX values are different at different inclusions at points C, B and A. Where A is the matrix consists of pure copper. The different values of the components are farther scanned. Those are shown in Fig. 5.3.18. It is interesting to obtain the SEM microstructure where EDX study revealed 15.02 Bi, As 1.78 with 15.02 Bi, As 1.78 with high O and S concentration shown at Fig. 5.3.19. Presence of white arsenide inclusions are well revealed at Fig. 5.3.20. Whereas, cast dendritic structures with arsenides along with usual oxides were revealed at Fig. 5.3.21. Fig. 5.3.22 is a region where the segregation of inclusions is more. In RHS of that figure revealed Pb 17, As 14, O 53, S 3, Fe 0.2 in Cu 14%, in the enlarged area with oxide (in atomic %). The graphical representation of the EDX value at matrix is shown at Fig. 5.3.23, and at other region is shown at Fig. 5.3.24.

5.3.2.6 Micro hardness
The micro hardness measured in all cases over 60-61 HK in Knoop’s scale (165 BHN) (565 N/mm²) indicates in area with similar to Cu (Fig. 5.3.25). Whereas, in other region (Fig. 5.3.26), the value is 65 to 71 HK. This indicates at higher hardness than the hardness of the blister copper (HV 60-65). Perhaps this is due to working at the edges.
Fig. 5.3.13 Unetched microstructure of bar-celt revealed basically three types of inclusions. Round half tone inclusions indicate oxides, irregular black spots are sulphides and white spots are arsenides. The tool bar indicates 100µm.

Fig. 5.3.14 Unetched microstructure of bar-celt in other location showing similar inclusions. The tool bar indicates 100µm.

Fig. 5.3.15 Partially annealed dendritic pattern resembling cast structure (125 X).
Fig. 5.3.16 (L) Preferential segregation of the second phase particles at the grain boundaries are seen. Fig. 5.3.17 (R) Rare presence of Bi in white round phase corresponds to Table 5.3.4 D.

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<td>Bi</td>
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Table-5.3.4 EDX of Bar celt showing at different points A, B, C and D respectively.

C          B          A

Co - 0.33  Cu - 69.89  Cu -100
Ni - 0.36  S  - 30.11  Base Metal
Cu -48.12  Sulphide inclusion
Sn - 0.79  (Irregular, black)
O - 50.40  Oxide inclusion
(Round, gray)

Fig. 5.3.18 This is enlarged view of Fig. 5.3.13 Unetched microstructure is full of different inclusions as indicated above. Bulk phase is copper, along with different metals in trace amounts even Pb, Bi, Co, Se and arsenides are rare. SEM EDX values are different at different inclusions at points C, B and A. Where A is the matrix consists of pure copper. The tool bar indicates 100µm.
Fig. 5.3.19 SEM Microstructure  
Fig. 5.3.20 Presence of arsenides.  
Fig. 5.3.21 Cast dendritic structure with arsenide along with usual oxides.  

Fig. 5.3.22 This is a region where the segregation of inclusions is more. In RHS the enlarged area with oxide (in atomic %) is shown. The tool bar indicates 2µm.

SEM-EDX in Atomic percentage at centre

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>S</th>
<th>Co</th>
<th>As</th>
<th>Cu</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>46.18</td>
<td>10.71</td>
<td>0.42</td>
<td>1.78</td>
<td>24.30</td>
<td>15.02</td>
</tr>
</tbody>
</table>
Fig. 5.3.23 The EDX value at matrix showing pure copper.

Fig. 5.3.24 The EDX value at another region showing presence of Sn, Co and Ni.

Fig. 5.3.25 (LHS) with usual micro - hardness readings on the structure (Load 10 gm) which are similar to copper. Fig. 5.3.26 (RHS) Micro hardness (Load 10 gm) markings are on the structures which indicate higher hardness than the hardness of the blister copper.

Table - 5.3.3 XRD Results
Sample: Bar-Celt. Radiation: CO / FE  35 kV / 30 mA
Wavelength, \(\lambda_a = 1.791\) Å

<table>
<thead>
<tr>
<th>No</th>
<th>Angle(2θ)</th>
<th>d, Å</th>
<th>I / I₀</th>
<th>Identified Phase</th>
<th>Diffracting Plane (hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50.8°</td>
<td>2.088</td>
<td>100</td>
<td>(α)-Cu</td>
<td>111</td>
</tr>
<tr>
<td>2</td>
<td>59.2°</td>
<td>1.813</td>
<td>41</td>
<td>(α)-Cu</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>88.6°</td>
<td>1.282</td>
<td>30</td>
<td>(α)-Cu</td>
<td>220</td>
</tr>
</tbody>
</table>
5.3.26), the value is 65 to 71 HK. This indicates at higher hardness than the hardness of the blister copper (HV 60-65). Perhaps this is due to working at the edges.

5.3.2.7 X Ray Diffraction
The XRD of the bar celt produced major peaks has been made. Three major peaks have been shown in Table- 5.3.3) predominant of alloy $\alpha$ - Cu phase present in the sample with a few minor Cu – phases  (Ref: JCPDS, 1978).

5.3.2.8 Discussions
The sample of bar-celt found to be a forged form of blister copper – a copper with enough dissolved, residual oxygen which expose itself in from of ‘blister’s over the copper surface. Later on this type of copper was deoxidized with arsenic-bearing ore, lÖlingite/ orpiment, so that the material of axe is less gassy. After the intentional degassing by small amount of arsenic which volatilizes during deoxidizing, a little amount remains within as residual arsenide. The arsenic could be found in the structure of the copper bar celt from Khuntitoly. As also produces solid- solution hardening - raising the hardness, useful for a tool material.

5.3.3 Double Ended Axe
The axe (Fig. 5.3.27) has in plane, convex lead edges; slightly concave side edges which converge towards the rounded butt (Yule and Thiel-Horstmann 1985). It weighs around 600 gms and has length around 160 mm and thickness 5 mm at the midriff. Made of pure copper (over 99%) the metal was probably deoxidized with arsenic before pouring in a closed mold. The beautifully cast piece was then probably hot-forged in super plastic temperature (~800 °C) to develop sharp edges, while residual cast structure were allowed to remain in central section.

5.3.3.1 Chemical Composition
Chemical analysis of the double ended axe shows at Table- 5.3.4. A composition in wt.%  Fe 0.03, Sn 0.30, Zn 0.20, with trace amount of Pb and balance Cu 99.36. Similar to other copper hoard items it was also a piece of pure copper.
Double Ended Axe

Fig. 5.3.27 Double-ended Axe

Table- 5.3.4
Chemical Composition of Double ended axe

<table>
<thead>
<tr>
<th>Cu</th>
<th>Fe</th>
<th>Sn</th>
<th>Zn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.36</td>
<td>0.03</td>
<td>0.30</td>
<td>0.20</td>
<td>Trace</td>
</tr>
</tbody>
</table>

Table- 5.3.5 SEM EDX Composition at four different points of the Double ended axe.

Figs. 5.3.28 (LHS) and 5.3.29 (RHS) Microstructure reveals the basic cast nature of the axe. Dendritic pattern is revealed. Secondary Arm Spacing has been estimated to be of the order of 30 to 40 microns.
5.3.3.2 Microstructure of the Specimen

The microstructure of the specimen was revealed by optical microscope in as polished as well as in etched condition.

5.3.3.3 Optical Microscopy

For the double ended axe specimen (Fig. 5.3.27), microstructures (Figs. 5.3.28 and 5.3.29) revealed the remnants of dendrites confirming as cast items. Both the figures mentioned last were revealed with wide distribution of micro-voids and inclusions. The diffusive layers of dendrite arms might reveal a kind of confusing knowledge of metal workers in heat treatment (?). A presumption has been postulated that metal workers did not take liberty in full annealing the cast item. Annealing could so. So metal workers often use this technique and jeopardize the effectiveness of the edge of the axe. Again without annealing brittleness of the cast structure could not be recovered and there remained the chance of failure during use. So, metal workers probably selected a middle option of low tempering.

The microstructure of axe also shows the breakdown of coarse dendritic structure in form of equiaxed grains, free from gas holes with segregation of inclusions and second phase particles of oxides mostly in grain boundaries. This indicates not only superior techniques of foundry like degassing, closed molds, gating etc. but also the development of good working and heat treatment practice using recrystallization-recovery-grain growth mechanism for producing sound metals.

5.3.3.4 Micro Hardness

The micro-hardness (HK 70-71) indicates that the sound material of axe has become softer (HK 60-61) than that of bar-celt on annealing (Figs. 5.3.25 and 5.3.26).

5.3.3.5 Scanning Electron Microscopy

Under scanning electron microscope, the double ended axe confirms the wide presence of inclusions of oxides and arsenide. The SEM-EDX value obtained has been tabulated in Table- 5.3.5 at four points. The EDX value over the white arsenide spots proves the presence of Fe-Cu-Pb – oxide- sulphide-arsenide aggregate. On the other hand black precipitates identified as complex oxides-arsenide or sulphide. The blackish grain boundaries consist of Cu2O-O precipitates. That precipitates proved that originally it was cast later the edges were finished with forging.
Fig. 5.3.30 Different types of inclusions in SEM EDX Table- 5.3.5 C

Fig. 5.3.31 SEM EDX values of Axe

Fig. 5.3.32 X-Ray diffractogram of Axe

Table-5.3.6.
Data for XRD of Double Ended Axe,
Radiation: Cu/Ni 35 kV/ 30mA Wavelength, $\lambda_\alpha = 1.540598$

<table>
<thead>
<tr>
<th>No.</th>
<th>Angle (2θ)</th>
<th>$I_{\text{max}}$</th>
<th>$d_{\text{space}}$</th>
<th>Rel I</th>
<th>Identified Phase</th>
<th>Diffracting Plane (hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>31.325</td>
<td>90.6</td>
<td>2.8532</td>
<td>26</td>
<td>Undefined</td>
<td>Undefined</td>
</tr>
<tr>
<td>2.</td>
<td>36.324</td>
<td>91.1</td>
<td>2.4712</td>
<td>26</td>
<td>$\delta$ -phase (Cu-Sn)</td>
<td>022</td>
</tr>
<tr>
<td>3.</td>
<td>42.444</td>
<td>85.9</td>
<td>1.8454</td>
<td>243</td>
<td>$\beta$ -phase (Cu-Sn)</td>
<td>111</td>
</tr>
<tr>
<td>4.</td>
<td>49.344</td>
<td>85.9</td>
<td>1.8454</td>
<td>243</td>
<td>$\alpha$-Cu, $\beta$ -phase (Cu-Sn)</td>
<td>200, 200</td>
</tr>
<tr>
<td>5.</td>
<td>62.218</td>
<td>67.6</td>
<td>1.4909</td>
<td>19</td>
<td>$\beta$ -phase (Cu-Sn)</td>
<td>112</td>
</tr>
<tr>
<td>6.</td>
<td>72.433</td>
<td>1002.9</td>
<td>1.3037</td>
<td>284</td>
<td>$\beta$ -phase (Cu-Sn)</td>
<td>202</td>
</tr>
<tr>
<td>7.</td>
<td>87.739</td>
<td>628.5</td>
<td>1.1115</td>
<td>178</td>
<td>$\beta$ -phase (Cu-Sn), $\alpha$-Cu</td>
<td>401, 311</td>
</tr>
<tr>
<td>8.</td>
<td>92.717</td>
<td>304.4</td>
<td>1.0644</td>
<td>86</td>
<td>$\beta$ -phase (Cu-Sn), $\alpha$-Cu</td>
<td>004,222</td>
</tr>
</tbody>
</table>
The structure of the axe is the proof of sound metal, as most of the expected pores look welded during annealing and forging, which contains inclusions of arsenides (Fig. 5.3.31) along with usual oxides and sulphide, as residual deoxidation products. The presence of arsenides is shown in Fig. 5.3.32. The central portion, after etching, reveals cast structures, which still retains the dendrites of pure copper undisturbed. SEM EDX Composition obtained at four different points of the Double ended axe is shown (Table- 5.3.4).

Microstructure reveals the basic cast nature of the axe. Dendritic pattern is clearly revealed. Secondary Arm Spacing has been estimated to be of the order of 30 to 40 microns Figs 5.3.28 (LHS) and 5.3.29 (RHS).

5.3.3.6 X Ray Diffraction
The X-Ray diffractograms produced by the double ended axe (Table- 5.3.6) identified pure $\alpha$-Cu phase in the specimen, shown in Fig. 5.3.32. The characteristics of As in Cu may be explained by As-Cu diagram in Fig. 5.3.33.

5.3.3.7 Relationship of Dendritic Arm Spacing of Double Ended Axe
Random measurement of Secondary Dendritic Arm Spacing (DAS) was undertaken to have an idea of the cooling rate expected in the casting. The relationship between the cooling rate, (R in $^\circ$C/Sec) and ($\lambda$ in $\mu$m) can be determined by the following (Hwang et al. 1998: 495-503),

$$\lambda = 101 \times R^{-0.42} \quad \text{……………………………….}(1)$$

Microstructure reveals the basic cast nature of the item. The secondary arm spacing has been calculated as 30 - 40 $\mu$m, indicating slightly faster rate of cooling.

5.3.3.8 Discussions
The double ended axe from Khuntitoli is a very well shaped material for tooling purpose. Though it contains predominantly $\alpha$-Cu phase, the casting as well as the shaping of the tool, looks very nice. Even the softness of the tool is comparable to modern pure Cu objects. But the materials within seems to be of very sound character helpful for any impact load during cutting or shaping operation. This manifest indicates the ingenuity of metal workers, in forming useful socially relevant objects.
Figs. 5.3.34, 5.3.35 and 5.3.36 are the optical microstructures of the specimen at magnification of 50X, 100X and 200X respectively.

Fig. 5.3.37 SEM microstructure at 100X  
Fig. 5.3.38 SEM microstructure at 200X
The impurity and trace element pattern of the copper hoard objects indicate that there is no presence of tin alloying amongst the analysed artifacts. We have the evidence of copper arsenic alloy in some of those. However, no deliberate evidence of alloying of copper with lead detected. Only in few cases the use of malachite ore was detected, but mostly chalcopyrite ore was used for manufacturing those objects. The application of crucible shaped furnace with slag notch at the bottom while air-blast at the top, fluxing with silica, deoxidation with first arsenic or tin and later on zinc in historical period are quite unique and characteristically different from medieval copper technologies available in other parts of the world. Each of these establishes the notion about the indigenous origin of copper technology in East India although some assimilation of outside knowledge cannot be discounted. Tin in the form of cassiterite was also available in this part of country.

5.3.4 Copper Hoard from Bareli
A fragment of from a copper hoard specimen was provided to the present researcher for characterization, by an archaeologist of Bareli. The specimen was collected from an axe which has a plane convex lead edge; slightly concave side edges which converge.

5.3.4.1 Chemical Composition
The chemical composition in wt. % composition is Ni 0.27, Co 0.08 and Cu is 99.50. (Table-5.3.8).

5.3.4.2 Microstructure of the Specimen
Both optical and scanning electron microscopy was made for this specimen.

5.3.4.2.1 Optical Microscopy
The microstructures are shown in Figs. 5.3.32 to 34 represent the optical microscopy of the specimen. The remnants consist of dendrites, of α-copper, with wide distribution of micro-voids and inclusions as well as diffusive layers of dendrite arms.

5.3.4.2.2 Scanning Electron Microscopy
The precipitation of Cu-Cu₂O eutectics, are present within the grains. The micro pits of entrapped oxygen or oxides are revealed along the grain boundaries. Fig. 5.3.35 represents the SEM microstructure at 100X. Fig. 5.3.36 the microstructure at 200X. Cu-Cu₂O
Fig. 5.3.39 SEM microstructure at 500X  Fig. 5.3.40 SEM microstructure at 1000X

Fig. 5.3.41 Diffractogram of the copper hoard specimen indicating primary $\alpha$-Cu phase.

Table- 5.3.7 Vickers' Micro – Hardness MODEL: LEICA VMHT

<table>
<thead>
<tr>
<th>No.</th>
<th>Dia. (d1, $\mu$m)</th>
<th>Dia. (d2, $\mu$m)</th>
<th>1st Phase (Hv, Kg. mm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.1</td>
<td>18.5</td>
<td>138.7</td>
</tr>
<tr>
<td>2</td>
<td>17.9</td>
<td>17.5</td>
<td>138.7</td>
</tr>
<tr>
<td>3</td>
<td>17.4</td>
<td>17.7</td>
<td>151.2</td>
</tr>
<tr>
<td>4</td>
<td>17.3</td>
<td>17.6</td>
<td>152.3</td>
</tr>
<tr>
<td>5</td>
<td>17.1</td>
<td>17.6</td>
<td>154.4</td>
</tr>
</tbody>
</table>

Table- 5.3.8

Average composition of copper, SEM EDX

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>89.53</td>
<td>69.33</td>
</tr>
<tr>
<td>O</td>
<td>7.42</td>
<td>22.83</td>
</tr>
<tr>
<td>C</td>
<td>1.37</td>
<td>5.61</td>
</tr>
<tr>
<td>Cl</td>
<td>1.06</td>
<td>1.47</td>
</tr>
<tr>
<td>Co</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>Ni</td>
<td>0.27</td>
<td>0.23</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
eutectics are resolved. A number of recrystallised grains are detected at Fig. 5.3.39 at 500X. Fig. 5.3.40 is obtained at 1000X. A number of small annealing twins and coalescence of dendrites marked in the microstructures might be the witness of the metal forming operation. Probably the hot forging on cast structure caused breakdown of dendrites along with some recrystallisation.

The SEM-EDX indicates the presence of minor elements like Ni, Co and Al. The presence of Ni and Co probably indicates the source of copper ore, originated from Singhbhum copper belt. Huge amount of oxygen confirms the lack of poling – the poor deoxidation practice.

5.3.4.3 Measurement of Secondary Dendritic Arm Spacing

A random measurement of Secondary Dendritic Arm Spacing (DAS) was undertaken for that specimen was determined by the following (Hwang et al. 1998: 495-503), $\lambda = 101 \times R^{-0.42}$. The dendritic arm spacing was measured as ~50 µm, which is moderate and indicates slightly faster rate of solidification.

5.3.4.4 Micro Hardness

Micro hardness was obtained for the axe to get an idea of the copper material. The values indicated unusual hardness either due to micro alloying elements or. The micro-hardness were obtained. Vickers’ Micro Hardness Machine of (Leica VMHT model no HPO-250. The values obtained are tabulated in Table- 5.3.6.

5.3.4.5 X Ray Diffraction

The XRD of the hoard specimen has been made. Three major peaks have been shown in Table 4.1.6. The diffractogram obtained is shown in Fig. 5.3.41. That indicates primary $\alpha$-copper phase. The consecutive phase clearly FCC $\alpha$- Cu phase. Table- 5.3.8 indicates the XRD results obtained through the XRD machine PW-1710 and comparing with JCPDS files. The result show predominant $\alpha$ - Cu phase on the basic of main peaks, with some minor Cu – phases (Ref: JCPDS, 1978).
5.3. Discussions

1. The copper hoard from Bareli is a very well shaped material for tooling purpose. The shape was also nice plane convex lead edge; slightly concave side edges which converge.

2. The chemical analysis indicated the presence of Ni and Co which indicated the probable source from Singhbhum mines.