CHAPTER-6

RECONSTRUCTION OF TECHNOLOGY OF HIGH TIN BRONZE OR BELL METAL
6.0 Introduction
A limited Ethno archaeological survey of some surviving metal artisans was conducted close on the heels, on Bengal Kansharies at present sites of Khagra in Murshidabad district, Muragachha in Nadiya District, Bishnupur and Kenjakura in Bankura District and Kalyanpur, Egra in Purba Medinipur District. These are mainly to fine tune the present practice. Understanding the nuances of forging limitations and technological innovations, repeated experimentations at Khagra were performed to reconstruct the ancient bowl making process.

Hot forging starts with the forging stock which is generally cast material or ingot. In case of high tin bronze or Bell Metal copper–tin system the metallurgical structure consists of $\alpha$-Cu islands in the matrix of $\beta$-Cu-Sn phase with lot of segregation. The reconstruction of high tin bronze or Bell Metal is classified into four parts:

I Planning
II Experimentation
III Characterisation
IV Establishment of TMT and related metallurgy in High Tin Bronze, or Bell Metal Technology.

PART I
6.1 Planning for the Reconstruction of Technology.
The wonder of the forming techniques of the bronze artisans of the Ancient Bengal has been revealed by studying the material characterization or archaeo metal vis-a-vis the present ethno archaeological field work. The present research identifies the following stages in forging Bell Metal or high tin bronze referred here as $\beta$-bronze.

1. Selection of $\beta$-bronze composition
2. Casting of Forging Stock of Chunky Sections
3. Soaking of the Forging stock at the $\beta$ range temperature
4. Thermo-Mechanical Treatment (TMT) or Thermo-Mechanical Controlled Processing (TMCP) of the stock
5. Quenching in water after completion of forging
6. Multiple tempering for stabilization of martensite
7. Finishing including Grinding and polishing of the hot forged article.
PART II

6.2 Experimentation of Manufacturing Technique of Bell Metal or High Tin Bronze

To understand the technology of ancient bowl forming or high tin bronze or Bell Metal forging ethno-archaeological studies were conducted at Khagra. Further to the studies, a reconstruction of the perceived forging process by the traditional bronze casters were experimented by the present researcher at a site of Khagra, in the suburb of Baharampur (24°06'N, 88°19'E) - the district headquarter of Murshidabad, West Bengal. The reconstructed high tin bronze product was then compared with archaeo high tin bronze to arrive at the practice of ancient forming technology. A long kitchen spoon (hata) of high tin bronze was designed and as such the reconstructed plan was formulated. The experimentation is shown in Fig. 6.1. The details of processing - casting, forging and thermomechanical treatment of kitchen spoon at Khagra are shown in a series of steps in Fig. 6.2.

6.2.1 Selection of \( \beta \)-bronze Composition

At Khagra, traditional practice is the preparation of alloy at the initial state, where copper and tin at proportion of 75/25 is made with virgin copper and tin alloy, under a slightly oxidizing atmosphere of charcoal. The best quality of Bell Metal or kansha is manufactured at this traditional site is 77% Cu and 23% Sn. The traditional practice is to get 7 kg of copper and 2 kg of tin and get 9 kg of Bell Metal. Pure Cu wire, Sn lump metal and Scrap Bell Metal in the form of turnings and old utensils were used to make the Bell Metal.

6.2.2 Preparation of Kitchen Spoon

During experimentation, present researcher took 3.5 kg pure copper in the form of wire and 1 kg Sn lump and 3.5 kg scrap in the crucible. Old utensils were heated to red hot temperature then after hammering those broke easily like glass. Total charges were weighed before putting it in the crucible. Turnings and scrapings are charged first then other pieces. The scrap and copper wire were first filled in the crucible put on the furnace. After prolonged heating when the first part was melted totally then the other part of the charge was put in the crucible. Tin lumps were charged at last. The furnace with crucible inside was then closed with an iron cover. After opening the cover greenish and yellow flame noticed. Note that no flux was added during melting of Bell Metal.
Fig. 6.1 Experimentation at Khagra, showing measuring of temperature during forging of kitchen spoon.
<table>
<thead>
<tr>
<th>Process</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The furnace is ignited. Coal and wood are the basic fuel.</td>
<td><img src="image1.jpg" alt="Image" /></td>
</tr>
<tr>
<td>2. Large Scraps are placed on the crucible. Small scraps are placed first. Then pure copper wire, and copper scraps are charged. Tin lumps are also added after total melting.</td>
<td><img src="image2.jpg" alt="Image" /></td>
</tr>
<tr>
<td>3. Crucible is being preheated. After melting the first part the second part of the scraps are placed in the crucible.</td>
<td><img src="image3.jpg" alt="Image" /></td>
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<tr>
<td>4. The mould for spoon. The cavities of the mould are then filled with burnt mobile.</td>
<td><img src="image4.jpg" alt="Image" /></td>
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Fig. 6.2 Processing of casting, forging and thermomechanical treatment of kitchen spoon at Khagra
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<tr>
<td><strong>5</strong></td>
<td>Casting of Pro-Eutectoid (α + β) bronze (Sn % &gt; 20%). Liquid alloy has been taken in an iron ladle.</td>
<td><img src="image1" alt="Image" /></td>
</tr>
<tr>
<td><strong>6</strong></td>
<td>Heating: Soaking over eutectoid temperature (586 °C) at single-phase β region around 650°C. (Full cherry red-700 °C). Chunky ingots are being heated for forging.</td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td><strong>7</strong></td>
<td>Soaking at the top range of forgeability temperature. The casting used as forging stock was heated to a temperature of ~ 700°C to a deep cherry red temperature, and was soaked with adequate caution avoiding any kind of nominal fusion.</td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td><strong>8</strong></td>
<td>Thermo-mechanical treatment (TMT) of the stock was experimented. At first the head of heated bloom was subjected to repeated drop forging over an open blocking die by means of a 2 kg-point hammer within seconds for the deep drawing operation necessary to develop the cup.</td>
<td><img src="image4" alt="Image" /></td>
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<tr>
<td><strong>9</strong></td>
<td>Forging: i) Primary Drop Forging, starting at 650 °C with Heavy Reduction of cast ingots into a rough contour of the object by means of an open blocking die. The forging continued until dull red heat of around 500°C.</td>
<td><img src="image5" alt="Image" /></td>
</tr>
<tr>
<td><strong>10</strong></td>
<td>ii) Finishing of Drop Forging around 500 °C with lower reduction ratio to the nearest shape.</td>
<td></td>
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</tbody>
</table>
11. Fig. 6.2 Processing of casting, forging and thermomechanical treatment of kitchen spoon at Khagra

12. Repetition of stages (i) and (ii) until further development of web and rib sections and/or drawing of bar or handle portions, using open dies. Forging twice or thrice heating at around 650 °C after cold finishing blunting flash and rims.

13. Heat treatment: Heating again to 650 °C with salt and clay coating and quenching in water again - 2nd quenching for the core and relieving of internal strains. Quenching into water after raising at β region keeping β-phase untransformed - 1st quenching for the case. (Recovery).


15. Heating again to 650 °C with salt and clay coating and quenching in water again - 2nd quenching for the core and relieving of internal strains (Recovery).

16. Scraping of cold forging to get shiny surface.

17. Buffing and polishing.

18. Finished product ready for market.

Fig. 6.2 Processing of casting, forging and thermomechanical treatment of kitchen spoon at Khagra
Close to the shape of the desired article an open mould was made at clay sand aggregate using a suitable pattern. The mould was fully dried before any casting production. The liquid alloy in a superheated condition was poured into the mould without any interruption in a streamline fashion to produce the casting.

Our experimentation was concerned with two types of kitchen spoon making, for that two types of ingot/ cast blank were made. The kitchen spoon blanks were of two types. (a) The Elliptical disc has got 42.5 mm by 36.4 mm axial lengths with 12.5 mm thick semi-spherical section with handle 9.1 mm side triangular thickness having a length of about 175 mm (Fig. 6.3). (b) The Elliptical disc has got 24 mm by 12 mm axial lengths with 8 mm thick semi-spherical section with handle 13 mm side triangular thickness having a length of about 74 mm (Fig. 6.4).

Metallurgical Characterisation was made exclusively with a type (a) spoon blank. The spoon blank of type (b), was used for experimentation on thermo mechanical treatment (TMT).

6.2.3 Casting of Forging Stock of Chunky Sections
We have performed experimentation the manufacturing process of spoon making here. The chunky section of elliptical disc shaped cast spoon blank bottom surface of the mould is shown in Figs. 6.2 and 6.3. Surfaces are shown, which is flat in shape. The spherical portion is forged to a circular disc; the other part is forged into long handle.

The mould is made of clay is actually a brick piece. The mould shown in (Fig. 6.2.4) is about 15x12 cm. Four numbers of grooves with the shape of spoon are made on it. For making other objects the shape of the mould is different. For example for making bun shaped ingot for making That is used number of times. Before pouring the alloy artisans repair the mould with clay. The repaired mould is subsequently preheated by placing it by the side of fire on the furnace. The hot mould is then wrapped with burnt mobil, before tapping of the liquid alloy.

6.2.4 Soaking at the Top Range of Forgeability Temperature
The casting used as forging stock was heated to a temperature of ~ 700°C to a deep cherry red temperature, and was soaked with adequate caution avoiding any kind of nominal fusion.
Fig. 6.3a Cast forging stock for kitchen spoon a. This face is flat, reverse side is hemispherical.

Fig. 6.3b Cast forging stock for kitchen spoon b. This face is hemispherical in shape.
6.2.5 Thermo-Mechanical Treatment (TMT) or Thermo Mechanical Treatment with Controlled Processing

Thermo-mechanical treatment (TMT) of the stock was experimented. At first the head of heated bloom was subjected to repeated drop forging over an open blocking die by means of a 2 kg-point hammer within seconds for the deep drawing operation necessary to develop the cup. The forging stock of the appendage was drawn to a rectangular section of the handle later. The forging continued until dull red heat of around 500°C and the cycle of heating-and-forging recurred number of times to complete the desired shape of the spoon. Both thermal treatment as well as mechanical forming continued simultaneously.

6.2.5.1 First Forging

The forging temperature is around 750-550 °C. That is forging is carried at the cherry red stock. The artisans stop forging below that region. The stock is reheated to maintain the forgeability range. This cycle of soaking and hot forging has been repeated long enough so as to make the article fully complete. We may divide it first part as only forging till its take the shape of the product. In second step, after reheating the stock, that is quenched in mud water. We had measured the temperatures and other details at each step. The initiation of this experimentation is already shown with measuring temperature of the hot blank, at site of the forging shed at Fig. 6.1.

The completion of first stage of forging is shown in Fig. 6.2.9. The bun shaped portion is forged to an oval disc. The specimen is again put in the reheating furnace. Fig. 6.2.17 indicates the forging of flat into cup shaped spoon and that further shaped into final forged shape of spoon (Fig. 6.2.17). The forging further indicate the forging on open blocking die, where spherical portion of the blank forged into a circular disc shape. Handle portion is totally elongated. Till now no quenching has been made. The Fig. 6.2.19 is the shape after completion of the first stage of forging. The total length of the spoon blank in that figure is 200 mm in length. The oval shape of the forged chunky portion became 49x44 mm and elongated handle is 150 mm.

The disc portion of the ingot became the drawn cup of 80 mm long, 50 mm wide and 16 mm deep with an average thickness of ~1.0 mm. The triangular blank was simultaneously forged by drawing operation to become the handle of the spoon of 190 mm length and a maximum rectangular cross-section of 15.0 mm by 2.5 mm at the middle.
6.2.5.2 Second Forging with Repeated Quenching

The first forging of the blank is checked if excess of material is left, if it is then chiselled out. In second step, after reheating the stock, the flat portion of the blank is forged with the help of a die block. To maintain the $\beta$-phase in the material, the hot forging was directly quenched in mud water from above the eutectoid temperature, twice, to avoid any discrepancy between the case and the core.

Soaking furnace and quenching tank is shown very close (Fig. 6.2.14). After complete shaping of the spoon the hot forged article was quenched in water as soon as the forging operation stopped to suppress any kind of possible phase transformation that can occur. After quenching the article spoon was again heated to $\sim 650$ °C with adequate soaking for tempering operation (as iron makers normally do) and quenched in water to eliminate any kind of brittleness associated with high-tin bronze.

Quenching and tempering operations continued for the forged piece twice (last time with a coat of Na-salt layer) to transform the phases of the case and the core respectively. In the bath of about 2 liters of water, 200 gms of table salt is added to 500 gms of clayey soil ($etel mati$). This muddy salted solution bath is shown at right side and at left side of the figure lays the soaking furnace. **Multiple tempering** is practiced by the artisans for stabilization of martensite. Finished product the spoon after scraping is shown in Fig. 6.2.17. Thus TMCP of high tin bronze spoon was finished.

6.2.5.3 Finishing of Forged Article

The black skin of the forging layer for the finished spoon was burnished out by a metal scrubbing tool, properly ground and polished for shipment.
PART III

6.3 Characterisation of the Materials Produced by Experimentation
The characterisation of casting (the forging stock) and the finished spoon - hot forged product has been placed as follows:

6.3.1 Description of the Cast Forging Stock of Chunky Sections
The cast or forging stock for kitchen spoon made of Bell Metal (high tin bronze) is shown in Fig. 6.3.1. The one end of the casting conforms to the elliptical disc shape of around 42.5 mm by 36.4 mm axial lengths with 12.5 mm thick semi-spherical section connected to a triangular section of 9.1 mm side-thick of a length of about 175 mm.

6.3.1 Chemical Composition
The chemical composition of the cast spoon blank as analysed was wt. % Sn 21.27, Pb 0.007 and Cu 77.96.

6.3.2 Bulk Hardness
The average bulk hardness of the cast Bell Metal blank was 235 HV 5/10.

6.3.3 Metallurgical Structure of the Cast Bell Metal Stock
The optical microstructures as well Scanning Electron microstructures are being detailed below:

6.3.3.1 Optical Microstructure of Cast Bell Metal Stock
Samples were taken from the initial cast spoon stock. The optical microstructure of the stock (Fig. 6.3.2) of the cast bronze product, obtained at a magnification of 600 X 0.9. The microstructure consists of two phases. One is dendrites of α-Cu phase (black) embedded within matrix β-phase. Dendrites of the α-phase are blocky in nature and the other matrix of β-Cu phase. As usual with copper-tin system, Peritectic β-transformation has been suppressed due to the starting solid β-phase surrounding α-phase. Further to this β-phase, all the reaction products remain untransformed (ASM Metals Handbook, 1992, 15, 126) due to the chilling of the surface and β-phase remains in form of the thin white layers surrounding α dendrites. That indicates slow cooling rate of the sand casting.
Fig. 6.3.1. Cast forging stock for kitchen spoon.

Fig. 6.3.2 The optical microstructure of cast forging stock at 600X. The microstructure of the cast spoon blank (before forging) reveals $\alpha$-Cu phase dendrites (black) embedded within matrix $\beta$-phase. Dendrites of the $\alpha$-phase are blocky in nature within the core of the metal section, showing slow cooling rate. The fringe of the primary $\alpha$-Cu phases show fine residual eutectoid product of ultimate $\delta$-phase transformed from incomplete peritectic reactions of $\beta$-phase from high-tin bronze.

Fig. 6.3.3 SEM microstructure of cast forging stock at 400X, reveals $\alpha$-Cu phase dendrites (black) embedded within matrix $\beta$-phase.
Table 6.3.1 EDX Analysis of Khagra cast sample

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition, Wt %</th>
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<td>β - phase</td>
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<td>Cu</td>
<td>75.78</td>
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<tr>
<td>Sn</td>
<td>24.22</td>
</tr>
</tbody>
</table>

Table 6.3.2 XRD values of cast sample

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<td>0.96313</td>
<td>1.64</td>
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</table>

2Theta

Fig. 6.3.4 X-Ray Diffractogram of Cast Bell Metal Sample

Fig. 6.3.5 X-Ray Diffractogram of Cast Bell Metal Sample with some modification.
6.3.3.2 SEM Microstructure of Cast Bell Metal Stock
The SEM structure of β-Sn phase (Fig. 6.3.3) depicts the matrix as β Cu-Sn phase (light grain). The microstructure obtained at 400X. The second phase of β Cu-Sn phase is distributed along the structure with some unusually larger grains (grey grains). The β Cu-Sn phase keeps the preferred orientation of the forging direction. Some sub-grain formation can be visible in every large precipitate but preferred directionality along the deforming operation exposed by thinning of the section and lengthening along the flow line.

6.3.4 SEM -EDX of Cast Bell Metal Stock
The casting of the high-tin bronze shows the usual dendritic structure of any cast material (Fig. 6.3.3). The α-dendrites are copper-rich and the surrounding inter-dendritic regions are tin-rich, as indicated by EDX results (Table 6.3.1). That also indicates natural heavy coring, characteristics of tin bronzes. Wt% of Sn obtained are 14.90 in α phase and 24.22 in β phase; wt% of Cu are in α phase 85.10 and 75.78 in β phase.

6.3.5 X-Ray Diffraction of Cast Bell Metal Blank
X-Ray diffraction of the cast specimen is shown at Fig. 6.3.4. For cross checking, the X-Ray diffraction pattern of the cast specimen taken is shown at Fig. 6.3.5 is also the X-Ray diffractogram with some modification. The obtained XRD value of the specimen is shown in Table 6.3.2.

6.3.6 Secondary Dendritic Arm Spacing (DAS)
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 °C/Sec) and (λ in µm) can be determined by the following (Hwang et al. 1998: 495-503),

\[ \lambda = 101 \times R^{-0.42} \]

From the values of dendritic arm spacing, when (i) \( \lambda = 16 \) µm, \( R = 73^\circ C/Sec \), (ii) \( \lambda = 28 \) µm, \( R = 20^\circ C/Sec \), (iii) \( \lambda = 10 \) µm, \( R = 208^\circ C/Sec \), and (iv) \( \lambda = 7 \) µm, \( R = 548^\circ C/Sec \) were calculated.
Fig. 6.3.6 Pole Figures in cast Bell Metal Sample.

Fig. 6.3.7 EBSD studies on analysed cast specimen. The left Image is Inverse pole figure map. The right image is phase map. The analysis revealed some big grains and fine grains of Cu rich Cu-Sn phase and small grains of Sn rich Cu-Sn phase. The colour code map indicates the orientations of grains.
6.3.7 Texture Analysis of Cast Bell Metal
Pole figures have been obtained for the cast sample. The pole figures (Fig. 6.3.6) bears the signature of the past treatment. Here we find the absence of any preferred orientation sample clearly represent that it was cast structure (Kockelmann et al 2006).

6.3.8 EBSD Studies of Cast Specimen
The Fig. 6.3.7 indicates some big grains of Cu and small grains of tin rich phase. The colour code map indicates the orientations of grains.

6.3.9 TEM of Cast Bell Metal Blank
TEM-EDX studies have been made for the cast blank. Following figures are obtained for the specimen Fig. 6.3.8 (at 12KX), Fig. 6.3.9 (at 12KX) and Fig. 6.3.10 (at 40KX). TEM has identified dendritic structure with partial dislocation and stacking fault in a region shown in (Fig. 6.3.11). TEM has identified an interesting combination at Fig. 6.3.12 at 12KX.

6.3.10 TEM-EDX of Cast Bell Metal Blank
The EDX at a particular location (Fig. 6.3.13) indicates a composition in wt.%, obtained as Sn 13.81, Zn 0.53, Pb 0.27 and Cu 85.57.

6.4 Characterisation of Forged Bell Metal spoon
The finished spoon is shown at (Fig. 6.3.14). The object is finished with scraping and polishing. Different series of metallographic analyses have been carried out with the samples obtained at different stages of production of finished forged spoon. That include chemical analyses, metallography, XRD, DSC, SEM and TEM.

6.4.1 Chemical Composition of Forged Bell Metal Spoon
Both Gravimetric and PIXE analyses were conducted for this specimen. The chemical composition was made by Gravimetric method and checked by PIXE. The sample was found to contain wt. % Sn 22.02, Pb 0.005 and Cu 77.76. PIXE result indicates wt.% as Sn 20.19, Ni 0.023, Zn 0.004, Ag 0.002, Pb 0.009, Fe 0.001 and Cu 78.46. The PIXE-gram is shown in Fig. 6.3.15.
Fig. 6.3.8 TEM at 12KX Fig. 6.3.9 TEM at another location at 12KX

Fig. 6.3.10 TEM at 40KX

Fig. 6.3.11 TEM at 40KX Fig. 6.3.12 TEM at 12KX

Fig. 6.3.13 TEM EDX of the cast specimen. Composition at analysed area has a composition of 13.81 Sn, 0.53 Zn, 0.27 Pb and 85.57 Cu wt%.
Fig. 6.3.14 Finished Spoon after forging, quenching and scraping.

<table>
<thead>
<tr>
<th>LabNo</th>
<th>Cu</th>
<th>Fe</th>
<th>Sn</th>
<th>Ni</th>
<th>Zn</th>
<th>Ag</th>
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<td>K1</td>
<td>78.46</td>
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<td>20.19</td>
<td>0.023</td>
<td>0.004</td>
<td>0.002</td>
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Fig. 6.3.15 PIXE-gram of Finished Spoon

Fig. 6.3.16 The microstructure of bronze after forged and heat treated. During hot forging, with the knock-down of primary $\alpha$-Cu phase dendrites within metal, its transformation to $\beta$-Cu phase also proceeds. The duplex cast structure of $\alpha$-Cu phase and $\beta$-Cu phase, transforms to metastable diverse $\beta$-Cu phases of two different compositions. On quenching, primary $\alpha$-Cu phase converts itself into martensite $\beta$ -Cu phase (later revealed). Both phases co-exist showing the directionality of forging along the direction of the arrow.
Figs. 6.3.17-19 TEM-EDX of Khagra forged specimen, reveal 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.

Fig. 6.3.20 TEM-EDX of forged specimen indicating %-age composition as Sn 13.81, Zn 0.53, Pb 0.27 and Cu 85.57 in the analysed area.
6.4.2 Bulk Hardness
The average bulk hardness of the bronze specimen measured by Vickers machine was 236 HV 5/10.

6.4.3 SEM Microstructure of Forged Bell Metal Specimen
Scanning Electron Microstructures are being detailed below:
During hot forging, α dendrites are found to completely break down before getting oriented along the forging direction. And in the process, coarse individual dendrites become squeezed due to the heavy forging impact obtained longitudinally in the section making the common forging texture.

During the repeated forging operations, the general homogenization proceeds within the matrix as well as in the second phase, though the eutectoid transformation of β- phase is adequately suppressed by quenching in water to keep the β'-phase intact in the microstructure. However, some transformation into face centered cubic solid solution holding upto 12% Sn in α- phase cannot be ruled out, even by steep temperature gradient obtained during water-cooling.

The microstructure of the forged Bell Metal spoon under SEM (Fig. 6.3.16), at 400X illustrates tin-rich β-Cu as the major phase, having β'-Cu phase as the second phase, in a discontinuous or divorced entity along the flow lines, showing the forging direction (shown by arrow). Intermittent manual forging are visualized by the lenticular morphology of the second β'-Cu phase. The α-Cu phase of the cast structure, during hot forging and heating, have been transformed to β'-Cu phase as revealed by X-ray diffraction analysis. The simultaneous mechanical deformation, as well as, phase transformation from α-Cu to β'-Cu phase, occurred in tandem.

6.4.4 Micro Hardness
The microstructure obtained earlier was found in dual phases. As an average value of five points Micro hardness in VPN for α-Cu phase was found to be of 254.3 and that of β -Cu phase was determined as 311.2.
Fig. 6.3.21  EBSD Observation of Forged Bell Metal Specimen. The left image is Inverse pole figure map. The right image is phase map. The analysis revealed some big grains and fine grains of Cu rich Cu-Sn phase and small grains of Sn rich Cu-Sn phase. The colour code map indicates the orientations of grains.

Fig. 6.3.22  Pole figure of the forged specimen
6.4.5 Confirmation of Martensite by Transmission Electron Micrography
The test specimen when analysed through TEM revealed a clear structure (Figs. 6.3.17, 18 and 19 at magnifications respectively of 12KX, 25KX and 50KX) of martensite transformed in Bell Metal. 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 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 β phase has been identified as β martensite phase. Transformed from second phase mentioned earlier, originated from α-Cu-Sn phase of the cast material.

The TEM micrograph of Khagra specimen (Fig. 6.3.19) at 50KX reveals the individual martensite laths, with their associated micro twinning that occur within them (seen as the fine black) and lie more or less at right angles to the lath boundaries. The micro-twinning is a way for the structure to accommodate elastic stresses generated during martensitic phase transformation (Cortie and Mavrocordatos 1991).

6.4.6 TEM EDX
TEM EDX results (Fig. 6.3.20) provide the compositional characteristics of phases involved in the microstructure. In the analysed area composition detected 13.81 Sn, 0.53 Zn, 0.27 Pb and 85.57 Cu in Wt%.

6.4.7 EBSD Observation of Forged Spoon
EBSD Observation of Forged Bell Metal specimen is shown in Fig. 6.3.21. The left Image is Inverse pole figure map. The right image is phase map. The analysis revealed some big grains and fine grains of Cu rich Cu-Sn phase and small grains of Sn rich Cu-Sn phase. The colour code map indicates the orientations of grains.

6.4.8 Texture Analysis
To further investigate the problem of the preferred orientation of the forged Bell Metal sample, X-ray pole-figures were examined. The contours of the pole-figure {100} do not provide much information. The pole figure is shown in Fig. 6.3.22. The contours of the pole-
6.3.23 Residual Stress in forged Bell Metal Specimen that indicates compressive stress.

Fig. 6.3.24 Stress measurement in forged spoon showing intensity with 20 values.

Fig. 6.3.25 Stress measurement: only sigma phi value i.e, -89.0 MPa. It is compressive residual stresses that are acting at phi = 0°.

Fig. 6.3.26 XRD of the forged Bell Metal piece.
Fig. 6.3.17 X-Ray Diffractogram of the forged spoon

Table 6.3.4 XRD values of Forged Bell Metal Spoon

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Enlarged portion of the XRD of the forged Bell Metal piece as shown in Fig. 6.3.26.

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figure \{111\}, \{110\} and \{113\} are discontinuous and the orientations of deformation texture due to thermo-mechanical treatment may contain the orientations of \{110\} \{111\} and \{113\}.

The stress analysis of the forged bowl specimen showing intensity and 20 values are shown in Fig. 6.3.23. Fig. 6.3.24 indicates Stress measurement in forged spoon showing intensity with 20 values. Fig. 6.3.25 Stress measurement: only sigma phi value i.e., -89.0 MPa. It is compressive residual stresses that are acting at phi = 0°.

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.

6.4.9 Confirmation of Phase by the Diffraction

X-Ray diffractogram of the forge specimen is shown at Fig. 6.3.26. The portion of this diagram is enlarged. The obtained XRD value of the specimen is shown in Table 6.3.3. The specimen is also taken second time as shown in Fig. 6.3.27. The corresponding value of that is shown in Table 6.3.4. XRD study of forged structure confirms the presence of minor phase \(\beta^\prime\)-Cu-Sn with matrix \(\beta\)-Cu-Sn phases.

6.4.10 Differential Scanning Calorimetry (DSC)

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. 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. 6.3.28.

6.4.11 Discussions

1. The micrograph obtained for the forged Bell Metal spoon confirms the individual martensitic laths, with their associated micro twinning (Wayman 1964:331).

2. During hot forging of chunky ingot, the initial \(\alpha\) dendrites of cast ingot are found to completely break down before getting oriented along the forging direction. And in the process, coarse individual dendrites become squeezed due to the heavy forging impact obtained longitudinally in the section making the common forging texture (Fig. 6.3.25).
Fig. 6.3.27 DSC record of the experimental high tin or Bell Metal forged specimen with endo-up has been displayed. The phase change of eutectoid reaction starts at \(\sim 528^\circ C\) and closes at \(\sim 531^\circ C\). The area of the endo-peak is exploded in RHS.
3. During the repeated forging operations, the general homogenization proceeds within the matrix as well as in the second phase, though the eutectoid transformation of β-phase is adequately suppressed by quenching in water to keep the β'-phase intact in the microstructure. However, some transformation into face centered cubic (FCC) solid solution holding up to 12% Sn in α-phase cannot be ruled out, even by steep temperature gradient obtained during water-cooling.

4. For a crystal, instead of deforming inhomogeneously by slip, sometime it is easier to deform homogeneously in shear by formation of twinning. Twinning stress $\tau_t$ has been reported to be much lower than the passing stress of the order of G/20 for Cu. The characteristic mirror symmetry can be possible for both coherent and incoherent twin boundary. Twinning reproduces the initial structure but changes its orientation.

5. The formation of martensite according to Cortie and Mavrocordatos 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.

6. The TEM micrograph of Bell Metal spoon specimen (Fig. 6.3.19) at 50KX reveals the individual martensite laths, with their associated micro twinning that occur within them (seen as the fine black) and lie more or less at right angles to the lath boundaries.

7. The bell metal ingot is more texture than the forged spoon specimen and also Bulk texture: The cast Bell Metal ingot specimen as seen in pole figures (111) and pole (113) is more texture than the than the fragment of High-tin Bronze or Bell Metal recovered from Gajole Fig. 5.2.2 and the forged spoon specimen.

8. XRD study of forged structure confirms the presence of minor phase $\beta'$-Cu with matrix β-Cu phases.

9. The evidence of Bell Metal guild at Tilpi and presence of Bell Metal Specimens at Chandraketugarh, Bahiri, Mangalkote, Mahasthan and other sites of Bengal indicate that c. 5th century onwards the artisans of Bengal were capable of producing of Bell Metal or high tin bronze. That tradition is still continuing at present sites of Khagra in Murshidabad.
District; Muragachha and Nabawip in Nadiya District, Bishnupur and Kenjakura in Bankura District and Kalyanpur, Egra in Purba Medinipur District. In case of Bangladesh, tradition is well established at Dhamrai of Dhaka District.

10. In excavated sites wide presence of conical crucibles confirms the technological competence of metal workers in conserving the scarce energy during melting.

11. 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.

12. The investigation on the Bell Metal ingot confirmed the production of Bell Metal in Ancient Bengal in regular fashion. 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.

13. 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.

14. The limited DSC study does not reveal much other than the phase transformation at 524-530 °C.
PART IV

6.5 Establishment of TMT and Related Metallurgy in Bell Metal Technology

We shall discuss now the technology and related metallurgical parameters pertaining to the forging of Bell Metal utensils.

6.5.1 Facilitation of Hot Forging by Unique Geometry of Forging Stock

Mechanical deformation of cast blank for forging was the crucial necessity for ancient bronze makers. The inhibiting factor was the short forging range of temperatures, where the available forging time was quite insufficient for deep drawing or any long drawing operation. The possibility of holding or preserving heat within the forging block was solved by the Chunky shaped cast sections or commonly described by archaeologists as Bun-shaped ingots (Tylecote 1976:12). Our observation has been confirmed with the traditional practice at Khagra, Muragachha and other sites.

Assume only Newtonian convective Heat Transfer (Q, J) of cooling of the heated cast blank (T_m, K), from its heat dissipating Surface Area (A, m^2). Neglect conduction and radiation, for a fixed mass of bronze to the ambient (T_a, K). Consider Lump method for cooling time ‘t’ sec, Then,

\[ \left| \frac{dQ}{dt} \right| = h \cdot A \cdot (T_m - T_a), \]

where ‘h’ is the average convective heat transfer co-efficient, W/m^2-K.

For a fixed temperature drop (from T_m to say T_m1) it can be written approximately as,

\[ dt \approx \frac{dQ}{h \cdot A \cdot \Delta T}. \]

Where, \( t_c \) is the cooling time for the fixed temperature drop. Then,

The time of cooling, \( t_c \propto \frac{1}{f(\varphi)} \)

If f (\( \varphi \)) can be designated as a function of Forging Stock Fineness Number, then FSFN, \( \varphi \) then ‘\( \varphi \)’ can be defined as,

\[ \varphi = \frac{\text{Length} + \text{Width}}{\text{Thickness}} \text{ or, } \frac{(L + W)}{T} \]

(i) For a Cube of side ‘a’, \( \varphi = (a + a)/a = 2 \),

Half – cube, \( \varphi = 2a / (1/2) a = 4 \),

Quarter-cube, \( \varphi = 2a/ (1/4) a = 8 \),

One tenth- cube, \( \varphi =2a/ (1/10) a =20 \), so on and so forth.
The cooling times become \( t_1: t_2; t_3: t_4: \ldots = \frac{1}{2} : \frac{1}{4} : \frac{1}{8} : \frac{1}{20} \ldots \)
\[= 20 : 10 : 5 : 2 : \ldots \]

Therefore, Chunky shapes conserve heat for longer time and are best fit geometry for forging to be undertaken.

Finer or thinner thickness will lead to lower time of \( t_c \), or heat preservation and would pose more difficulty in forging.

(ii) For a hemi-spherical stock of ‘\( r \)’, \( \phi \approx \frac{2\pi r}{r} = 2\pi \approx 6.28 \), where volume is \((\frac{2}{3})\pi r^3\)

If that lump is flattened to a circular blank of half-thickness to \( r/2 \),
\[ \phi \approx 2[(2/\sqrt{3})r + (2/\sqrt{3})r]/(r/2) \approx 16/\sqrt{3} \approx 2 \times 4.6 = 9.24, \]

To quarter thickness \( r/4 \) of a circular section, \( \phi \approx 2 \left[ (2\sqrt{2}/\sqrt{3})r + (2\sqrt{2}/\sqrt{3})r \right] / (r/4) \approx 32\sqrt{2}/\sqrt{3} \approx 26.12 \)

To one tenth thickness \( r/10 \) of a circular section, \( \phi \approx 2 \left[ 2\sqrt{(20/3)}r + 2\sqrt{(20/3)}r \right] / (r/10) \approx 80\sqrt{(20/3)} \approx 206.56 \)

\[ \rightarrow \text{The cooling times become } t_1: t_2; t_3: t_4: \ldots = 1/2\pi : 1/9 : 1/26 : 1/206 \ldots \]
\[\approx 312: 208: 72: 9: \ldots \]

Higher values of \( (\phi) \) produces lower available time of forging.

Larger surface area with thinner section will increase heat dissipation rate and lead to shorter time available. The same rationality follows for semi-spherical sections also and ethno-archaeological reports of experimental work confirmed the choice of metal workers in Chunky (Chattopadhyay et al. 2006: 347-57) hemispherical shapes or similar sections.

6.5.2 The Selection of Lump Geometry

The selection facilitated easy forging of high-tin bronze ingot. Probably ancient hammers completed the forgings within very short time, by engaging a number of hammerers to strike blows on the red-hot stocks in quick succession till the metal blacken. The blackened stock
was put into fire again to achieve cherry red condition for forging. The tradition continues in some corners of Eastern India till today (Mukherjee 1978).

6.5.3 Super Plasticity of High-Tin Bronze

Super plasticity has been defined as unusually large homogeneous strains of the order of 100 to 1000% at elevated temperature. The characteristic stable deformation without work hardening (n) in a tensile stress is given by strain rate sensitivity (m’) factor,

\[ m' = \left( \frac{\partial \ln \sigma}{\partial \ln \dot{\varepsilon}} \right) \]

\[ n = \left( \frac{\partial \ln \sigma}{\partial \ln \varepsilon} \right) \bigg|_{\dot{\varepsilon} \approx 0}, \sigma = \text{Stress}, \varepsilon = \text{Strain rate} \]

This leads to super plastic behavior of metals at high temperature, \( \sigma \propto \dot{\varepsilon} \), a viscous flow.

The mechanical deformation can occur but no strain hardening is taking place.

For \( \beta \)-bronzes, the situation arises at a temperature, \( T > \frac{2}{3} T_m \) or \( \sim 2/3 \times (798+273) \)

or,

\[ > 714 \text{ K or } 541^\circ \text{C}, \text{ where aided by} \]

two phase peritectic mixtures of highly diversified small grains of \( \mu m \) range \( \beta \)-Cu phases.

[Note the cast \( \alpha \)-Cu phase is already super saturated with \( \sim 15 \text{ wt}\% \) Sn and behaves like \( \beta \)-Cu phase]. The large or blocky grains also get further divided into sub-grains (That was shown earlier in Fig. 5.2.11) and assist the development of fine grain formation of few \( \mu m \) ranges.

The reason is Sn-bronzes have very wide S-L gap, and gets constitutionally under-cooled heavily. In that case nucleation rate, \( \dot{n} \) increases with more undercooling, \( \Delta T \) (\( \dot{n} \propto \Delta T \)) but Growth rate, \( \dot{G} \) decreases (\( \dot{G} \propto 1/\Delta T \)). The resultant microstructure becomes - high nucleation of fine grains, of the order of \( \mu m \), conducive for superplastic behaviour.

Generally by grain boundary sliding, without work hardening, Cu or its alloys of very fine grains or two-phase structure (note \( \alpha \)-\( \beta \) brass) exhibit super plasticity. Corresponding to Ashby model (Ashby 1972, 20. 882, 887-897) a mutual displacement of the grains, which acquire new neighbours – facilitates the deformation in place of elongation of grains that occur at low temperature Tension test. With higher temperatures dislocation glide or dislocation climb or grain boundary sliding by grain boundary diffusion or bulk diffusion
dominate the deformation process as mentioned by ‘deformation mechanism map’ of the particular metals.

In case of Bell metal or β bronzes (>22 wt% Sn) the rapid solidification produces FCC α-Cu phase with BCC β-Cu phase of Cu-Sn system. At high temperatures of red heat the cast structure of Bell metal transforms to almost complete β-Cu phase and the BCC structure gets stabilized (Haasen 1997, 120-25). BCC crystal structure is not densely packed, having more atomic voids (Atomic packing factor = 67% & 8- nearest neighbours at 0.866a) produce easy atomic diffusion for work softening. At high temperature, further lattice vibrations enhance the ‘uncertainty of position’ leading to easy gliding associated with high vibrational entropy (Haasen 1997, 120-25).

These precise mutual atomic displacements of grains which acquire new neighbours produce favourable state for super plasticity. At the tin concentration of 22-25 wt% Sn, @ red heat, Bell metal acquires the stabilized β-Cu phase that encourages the super plastic ability. The Ancient Bengal workers either with lots of experimentation or with imports of technology reached that conclusion empirically. The bronze at Gajole articulates the observation. The physical metallurgical knowledge of ‘Super plasticity’ of Bell metal propagated through generations. Even at this age, without the help of any metallurgist the artisans at Khagra replicate that knowledge to manufacture deep drawn bowls or plates at ease.

6.5.4 Characteristics Solid Solutions of Electron Phases for Bell Metal

Copper-tin system undergoes a number of solid solutions starting with α-Cu phase, a close packed cubic or FCC like Cu. The next phase with higher concentration of 13.5 wt% Sn forms β-Cu phase, a loose packed structure of BCC. The interesting thing is the widening of β-field with rise in temperature - in other words, the decrease in solid solubility of Sn with increase in temperature. Other then this conventional Hume-Rothery α-Cu phase guided by +15% atomic radii variation, the addition of tin, like the addition of Zn forms a number of Electron phases. The ‘magic’ valance electron concentration (e/a) ratio of the order of around 1.4 causes the spatial distribution of electrons in β-phase. With higher concentrations there is a possibility of an ordered β-phase variant at lower temperature. Ultimately the V-form of the β field varying from (e/a) <1.4 to >1.4 converges to 1.446 in Cu-Sn system. The β-phase also shows a wide field of disordered Cu-solid solution. The structure of foundry bell metal (Fig. 6.3.2) becomes a two-phase aggregate having unstable FCC α-Cu phase (metastable due to
untransformed peritectic and super-saturated nature of Sn in crystal structure) with BCC $\beta$-Cu phase.

On quenching after severe plastic deformation the $\beta$-Cu phase collapses into close packed martensitic structures (Sleeswyk 1962:705) due to generated shear stress within the grains. The large deformation of super plastic nature transfigures itself to microscopic deformation within grains in form of twinning. Even repeated heating and quenching could not restore the equilibrium structures and only metastable phases result in industrial alloys being discussed. There is a lot of misperception about phases and few agreements among researchers on confirmation of residual functioning phases either stable or metastable or ordered exist (Saunders and Miodownik 1989: 412-17).

6.5.5 Twinning and Resultant Martensite Transformation in High Tin Bronze

For a crystal, instead of deforming inhomogeneously by slip, sometime it is easier to deform homogeneously in shear by formation of twinning. Twinning stress $\tau_t$ has been reported to be much lower than the passing stress of the order of $G/20$ for Cu. The characteristic mirror symmetry can be possible for both coherent and incoherent twin boundary (Mahajan and Williams 1973: 43). Twinning reproduces the initial structure but changes its orientation.

The twinning result originates from their interactions with the forest of dislocations, which are also widely dissociated. Twins appear to form only in metals that have suffered previous deformation by slip. The heavy deformation of $\beta$-brass during hot forging has been marked by deformation slip bands (Fig. 5.2.11), shown earlier in a broken fragment of a Bell Metal bowl recovered from Gajole as shown in Fig. 5.2.2.

When partial dislocations are too much separated, incidentally in the case of low stacking fault energy metals (e.g. Pure-Cu of the order of $0.06\text{ J/m}^2$ at 300K), it leads to the high plastic deformation. The smaller stacking fault energy in case of $\beta$-Cu phase [due to greater $(e/a)$ ratio with higher Sn content, this further decreases, probably of the order of $\sim0.01\text{ J/m}^2$] facilitates the easier nucleation of FCC twins by dissociations of perfect dislocations. After nucleation the twins propagate across macroscopic distances under decreasing load at almost with the speed of sound (Hassen 1997, 327-9). In the FCC lattice, like zinc-rich $\alpha$-brass, in bell metal twin lamellae form easily on account of the wide dislocation splitting but they can
hardly grow. Due to dissimilarity of atomic sizes between Cu (0.128 nm) and Sn (0.141 nm) the phenomenon attains more favourable situation for Cu-Sn FCC α-Cu phase lattice. A similar twinning mechanism has been proposed for BCC lattice (Lagerlof 1994, 601), where the twin grows in thickness by double cross slip onto next parallel {112} plane. The usual twinning elements shown below could not been confirmed:

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Plane</th>
<th>Direction</th>
<th>Twinning shear</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
<td>{111}</td>
<td>&lt;112&gt;</td>
<td>1/√2 Twinning shear</td>
</tr>
<tr>
<td>BCC</td>
<td>{112}</td>
<td>&lt;111&gt;</td>
<td>1/√2 Twinning shear</td>
</tr>
</tbody>
</table>

The shear associated with twinning becomes of the order of unity. Therefore, twinning plays a very important role after plastic deformation of high-tin bronzes for its metastable FCC and BCC phase constituents.

The shear controlled mechanism provides us the basis of transformations, where in addition to the volume change the lattice deformations also take place. Thus a co-operative atomic movement produces a ‘military nature’ transformation in form of martensite transformation in contrast to ‘civilian nature’ of diffusion controlled transformation (individual atomic movement). The kinetics has been instantaneous, where a change in temperature causes the requisite driving force.

In high-tin β-bronze, during quenching in water from high temperature provided the necessary impulse. The twinning helped in phase transformations from α-Cu and β-Cu phases to their twinned martensite phases. Similar to hardening of steels (Maraging steels), the martensitic transformation took place as shown in TEM photographs, though this martensite was of deformable nature like Fe-Ni martensite. Deformation bands testify the proposition (Fig. 5.2.12). So, the material attained both the strength and toughness of lath martensite. Forged high-tin bronze became very strong and tough. To stabilize the structure of the core and the case, repeated quenching and tempering accelerated the necessary requirement, while the thermodynamic inhibition (poor solubility of Sn in α-Cu at room temperature) could be surmounted. But, the brittle vulnerable phase kept few micro-cracks unattended as can be noticed in the optical metallograph (Fig. 5.2.5).
6.6. Thermodynamics

To understand the nature of the energy change associated with metastable phase transformations, a limited DSC study up to 600°C was conducted on β-bronze samples (Fig. 6.3.27). A small endo-peak in all two samples related to a kind of probable stress relieving mechanism crept into the reading. The nominal endo-peak at about 528°C and closes at ~531 °C specifies a definite phase change from metastable phases to stabilized eutectoid phases. The similarity of curves for the two bronzes testifies almost identical condition of operation. The increase in enthalpy value in case of Gajole bronze (ΔH) over either less worked Khagra bronze can be justified by 3-D cupping operation organized for bowl making.

6.6.1 Crystallography

The crystallographic study of forged and quenched structure is quite complex due to the mixed nature of phases and the presence of stable and metastable phases. A lot of ambiguity (Saunders and Miodownik 1989: 412-17) regarding the crystallographic data as well as the actual crystals as often quoted by researchers prevented us from making some rigid conclusions. Only some general comments are presented.

XRD study of forged structure (Fig. 6.3.26) confirms the presence of minor phase β'-Cu with matrix β-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 obtained for Gajole (Fig. 5.2.27) pattern indicate β-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 β-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 β'-Cu phase (marked once as α'-phase to indicate its parenthood from α-Cu phase). This exhibits a lot of 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 β'-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 β'-Cu phase, in absence of any suitable nomenclature.
As some research workers in the recent past like Srinivasan or Nagae (Ranganathan et al. 2010; Nagae 2010) had got distinctive marked twins in few forged and quenched high-tin bronze samples in distorted $\alpha'$-Cu phase. Some had been reported as reminiscent of annealing twins of FCC Cu-phase. But the postulation about twins seems highly debatable. Excessive soaking at high temperature prior to forging in ease of metal working sometime can lead to this kind of twin formation in few spots. But those twins as a consequence of heavy forging would be destroyed or distorted. After severe quenching operation mechanical twinning should proceed, transforming $\alpha$-Cu into martensite or similar metastable phase. Although there might be post heat treatment operation after metal working when during solutionizing anneal of tempering (prior water quenching) there might be growth of few annealing twins that remain unaffected. Therefore, the report on the microstructure should very specifically mention the condition of the high-tin bronze sample, whether post heat treatment or prior heat treatment after forging, mentioning twin typology. Otherwise some confusion quite likely will impede the observations.

The unambiguous crystallographic identification is not always straightforward due to the vulnerable size and distribution of the various phases present in industrial high-tin bronzes. The above crystallographic conclusions are open to question. But hardly any confusion exists in the presence of metastable Martensite mentioned here as $\beta'$-Cu phase alongside a deformed supersaturated $\beta$-Cu-phase. Both are strong at room temperature and deformable at high temperature. This martensite holds a lot of similarity with Fe-Ni Martensite in Maraging steels at modern time. At historic period the type of $\beta'$-Martensite operated as lath Martensite and served very much industrially as an effective hard and tough material for mankind.

**6.7 Thermo-Mechanical Treatment (TMT) of Bell Metal**

Thermo-mechanical treatment (TMT) of the stock was experimented, and that had been discussed earlier part of this chapter in 6.2.5.

The experimentation was a two step process. First one is thermo mechanical treatment (controlled forging) and the second part is controlled cooling. The chunky shaped ingot is heated from room temperature to above 650 °C ~ 700 °C and kept for some time. Forging starts from 650 °C and continued upto 550 °C. Then again the stock is reheated to 650 °C. Forging is very quick and controlled. Therefore during mechanical deformation achievement
of shape as well as metallurgical transformation is achieved. The experimental TMT and TMCP processing at Khagra have been shown in Fig. 6.7.1.

In the next step was controlled cooling. The specimen is reheated again to 650 °C and quenched in water. The heat treatment process practiced two times one for core and the other for the case; both quenching and tempering is practiced. During hot forging large grains are broken into multiple grains known as dynamic recrystallisation. As recrystallisation occurs due to high strain rate, \( \dot{\varepsilon} = \frac{d\varepsilon}{dt} \). The recrystallisation occurs to (FCC) \( \alpha \)-phase. \( \beta \)-phase softening occurs known as recovery. High strain rate is achieved = Change in shape per unit time.

Here \( \beta \)-Cu-Sn phase is put under dynamic recovery and \( \alpha \)-Cu-Sn phase is under dynamic recrystallisation. During quenching martensitic transformation occurs, where \( \alpha \)-Cu-Sn phase is transformed to \( \beta' \) Cu-Sn phase.

When copper is deformed to high plastic strain (\( y \approx 34 \)) at high strain rates (\( \approx 10^4 \) s \(^{-1} \)) a microstructure with grain sizes of \( \approx 0.1 \) micron can be produced. It is proposed that this microstructure develops by dynamic recrystallization, which is enabled by the adiabatic temperature rise. By shock-loading ethe material, and thereby increasing its flow stress, the propensity for dynamic recrystallization can be enhanced. The grain size-flow stress relationship observed after cessation of plastic deformation is consistent with the general formulation proposed by Derby (1991), Andrade et al. 1994.

### 6.7.1 Heat Transfer of Ingots as Experimented at Khagra

#### The Physical Problem

Our observation on forging of table spoon at Khagra clearly identified that the chunky ingots used by the artisans for manufacturing their products are of the shape of hemisphere or a sector of sphere. During the hot working process, forging starts at 700 °C the ingot cools due to convective and radiation cooling and the hot working process are not continued below a temperature of 500 °C. The partly finished job is again heated to make it fit for further working. The problem is, therefore, to find the cooling behaviour of ingots for the present process the Elliptical disc has got 24 mm by 12 mm axial lengths with 8 mm thick semi-
Second 22 strokes in 19 sec  First 5 strokes  Last 44 strokes in 19 sec.

Fig. 6.7.2 Cast forging stock for kitchen spoon b.
This face is hemispherical in shape.

Fig. 6.7.3 Geometry of chunky shape ingot

Fig. 6.7.4 After first forging change of shape.
spherical section with handle 13 mm side triangular thickness having a length of about 74 mm (24 + 50 mm) (Fig. 6.7.2). The dimension is shown in sketch Fig. 6.7.3.

The forging started at the joint and 5 strokes of hammering was done within a time span of 5 sec. Then, the forging was done on the hemispherical portion to convert it into a disc, with 22 strokes within a time span of 19 sec. Then the handle portion was made with 44 strokes in 34 sec, converted it into 140 mm long and 10 x 2.8 mm in cross section.

Volume of hemispherical portion, \( V = \frac{1}{2} \times \frac{4}{3} \pi x .012^3 = 3.619 \times 10^{-6} \text{ m}^3 \)

Initial area, \( A = 4 \pi x \frac{1}{2} x .012^2 = 0.000905 \text{ m}^2 \)

Final area = 0.006362 \text{ m}^2 with radius of 45 mm.

### 6.7.2 Mathematical Formulation on Heat Transfer

Though we have manufactured a spoon from chunky shaped ingot but for mathematical formulation we shall consider only a hemisphere of 24 mm diameter and 12 mm height as shown in Fig. 6.7.3 which forged to a 45 mm diameter disc of 2 mm thickness.

The ingot temperature, during cooling while hot working, was considered to remain uniform over the bulk of the ingot. A lumped parameter analysis was made by taking the temperature of the ingot a function of time only, while remaining spatially constant in the ingot. A balance of energy yields the following equation. Furthermore, the surface area \( A_s \) is also taken as varying with time, as is the case in the actual processing.

\[
\frac{dT}{dt} = \frac{h A_s (T_\infty - T) + \varepsilon A_s \sigma (I_\infty^4 - T^4)}{mc_p} \quad \ldots (1)
\]

Where,

- \( m = \) mass of the ingot, 0.03 kg
- \( c_p = \) specific heat capacity of the Bell Metal = 3430 J/kg-K
- \( T = \) temperature of the ingot, K
- \( T_\infty = \) Ambient temperature, K
- \( h = \) convective heat transfer coefficient= 0.04957 W/m²-K
- \( A_s = \) top surface area of the ingot= 0.000905 m²
- \( \varepsilon = \) emissivity of the surface of the ingot = 0.8
- \( \sigma = \) Stefan-Boltzman constant, W/ m²-K⁴
- \( \rho = \) ( of Bell Metal) = 8660 kg/m³

The top curved surface of the ingot is taken as the surface of heat transfer as the bottom surface would be in contact with the anvil and hence assumed to be insulating in nature. The
heat transfer coefficient (h) for the ingot is taken to be that for natural convection for a sphere and is calculated using the following correlation.

\[
\frac{hD}{K} = 2 + \frac{0.598 \text{Ra}^{1/4}}{1 + (0.469/\text{Pr})^{9/16}}^{4/9} \quad (2)
\]

Where, Nu = Nusselt number

\[ D = \text{Characteristic length, taken as, V/A_s, m} \]

\[ V = \text{Volume of the head of the spoon (m}^3) \]

\[ \text{Ra} = \text{Rayleigh number} = \frac{g\beta(T_\infty - T) D^3}{\alpha v} \]

\[ \text{Pr} = \text{Prandtl number} = \frac{\alpha}{v} \]

\[ \beta = \text{coefficient of isobaric expansion} = 1/T, \text{K}^{-1} \]

\[ \alpha = \text{thermal diffusivity of air, m}^2/\text{s} = 85.78 \times 10^{-6} \text{ m}^2/\text{s} \]

\[ v = \text{kinematic viscosity of air, m}^2/\text{s} = 58.51 \times 10^{-6} \text{ m}^2/\text{s} \]

Equation (1) is a non-linear ordinary differential equation. This is solved numerically as an initial value problem using Euler’s explicit scheme. At each time level, the heat transfer coefficient (h) is updated according to equation (2), as well as the surface area of the head of the spoon is updated emulating the area in the actual processing (See Fig. 6.7.5). The mass of the ingot is taken as 0.03 kg. The diameter of the dish-like flat part is taken as 0.024 m and the initial temperature of the ingot is taken as 700 °C. Fig. 6.7.6 shows the time for cooling in dependence of the diameter of the ingot. These figures depict the cooling history and time for cooling down to around 500 °C.

In Fig. 6.7.5, for the first 5 sec there was no change of area for the hemispherical region. During forging increase of area in m² is shown in Y-axis with respect to time in seconds shown in X-axis. After first forging, the area is fixed after 25 sec. Similarly in Fig. 6.7.6 indicates that forging continued up to 500 °C. After that it was allowed to cool for some time until reheating for heating and quenching.
Fig. 6.7.5 During forging increasing of area in m² is shown in Y-axis with respect to time in seconds shown in X-axis.

Fig. 6.7.6 The heat transfer in ingot is shown through Y-axis as temperature in °C. X-axis indicates the time in seconds.
Fig. 6.7.1 Experimented TMT - DQ&T procedures at Khagra as obtained for forging Bell Metal Spoon. Upper portion of the left shows controlled forging- comprises of heating and soaking, then forging. The range of forging is restricted from 700 - 550°C. This is then undergone with controlled cooling where the forged stock is quenched in water two or three times.
6.8 Comparison with the Microstructure Refinement of Austenite During Hot Deformation

The refinement of austenite microstructure by making use of dynamic recrystallisation (DRX) has been proved to be effective by the studies of Maki 1980 and Nagai 2002. Similarly in case of copper during deformation to high plastic strain (\(\gamma \sim 34\)) at high strain rates (~104 s\(^{-1}\)) a microstructure with grain sizes of ~0.1 \(\mu\)m can be produced. It is proposed that this microstructure develops by dynamic recrystallization, which is enabled by the adiabatic temperature rise. The grain size-flow stress relationship observed after cessation of plastic deformation is consistent with the general formulation (Derby 1991: 39, 955). In case of austenite grain refinement is depending on a parameter of strain rate compensated with temperature \(Z\) (Zenner Holomon parameter).

\[
Z = \dot{\varepsilon} \exp \left( \frac{Q}{RT} \right) = A \sigma_p^n
\]

where, \(\dot{\varepsilon}\) is strain rate; \(Q\) is deformation activation energy; \(R\) is gas constant; \(T\) is absolute temperature; \(A, n\) are constants; \(\sigma_p\) is first flow stress peak value. This may be concluded that for obtaining refinement of austenite grain size to several microns, the strain rate should be fairly high and deformation temperature fairly low.

Similarly in case of bell metal forging this is conducted at high strain rate, the initial \(\beta\) grain sizes are of a few microns (as confirmed by metallography) and \(\beta\)-phase is under dynamic recrystallisation state. As to whether austenite grain refinement is taking place or not depends on dynamic recrystallisation.
