Forging Technology of High-Tin Bronzes in Ancient Bengal

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Abstracts
High-tin bronze or β-bronze, commonly known as Kansa in Bengal and Bell Metal to the outside world came into existence as cast metal since late second millennium B.C. The general composition of 23Sn-Cu holds a very good reputation as a castable alloy. But it offers enormous difficulty in forging due to its narrow forging range as well as its metastable thermodynamics of incomplete phases prevalent in Cu-Sn system. Though widely used in castings for manufacturing gongs and bells throughout the world only few people of ancient world could achieve the mastery of forging the alloy into thin sheet. Ancient Bengal had been one of those few fortunate centers where circular bowls or glass or plates of very thin sections were manufactured. Close on the heels, some ethno-archaeological study were also conducted on Bengal.

Keywords
High-tin bronze forging super-plasticity DSC TEM Neutron XRD

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Introduction
Tin bronze or commonly simple Bronze found its applications in castings throughout the ancient world from the East to the West in Asia, Africa and Europe. Increasing the addition of tin to copper system lowers the melting points of alloys (Figure 1). The addition of 20% tin to copper takes the melting point down to ~800°C and thus helped ancient artisans to easily produce molten high tin bronze. Bronze, known for lower viscosity (~1.5 mPa.s from Cu’s ~4 mPa.s), assisted in higher fluidity of liquid metal for quick filling of mould cavity by streamline flow in manufacturing thin domestic articles or sculptures. Surface tension of tin bronze also sharply drops (~700 mN/m) in comparison to copper (~1200 mN/m) producing easy wetting of the mold surface for sharp reproduction of intricate designs of fine details. All of these properties aided
bronze to be a favorable casting material for foundry men. Over and above these, acoustics quality of Cu-23Sn alloy, the normal bell metal or high-tin bronze for archaeologists, nominated further this alloy to a hot choice for the manufacture of percussion instruments or gongs or bells.

In spite of all the finer points so far attributed, for the production of sound cast metal by plane front solidification, the thermo-chemistry of Cu-Sn system betrays the common solidification thermodynamics. As categorized by ASM\textsuperscript{5} foundry men designate tin bronzes as a Castable alloy of Group III in Cu-Sn system. The long freezing range of the alloys with wide liquidus – solidus gap recommends the alloy as very difficult for the production of sound metal. Castings produced from the alloy suffer from the inherent feeding problem leading to incipient micro-porosity between dendrites throughout the sections. The problem further accumulates by the pick-up of hydrogen porosity\textsuperscript{6} at the closing stage of solidification. To eliminate the sponginess of the alloy for improving the mechanical property hot working or forging remained a probable option in the ancient world.

Thermodynamics of Cu-Sn system remains disloyal to metal men at this end also. Sn-atom (0.158 nm) contrasts widely in size from Cu-atom (0.128 nm) though both form Hume-Rothery phases. The crystal structure of Sn (BCT) also differs from that of Cu (FCC). The solid solubility of Sn in \( \alpha \)-phase (FCC) rises from \( \sim 13.5 \) wt\% at 798 \( ^{\circ} \)C to \( \sim 16 \) wt\% at 520\( ^{\circ} \)C before abruptly falling to \( \sim 1 \) wt\% at room temperature initiating cracking trouble during phase transformations (Figure 1). The plasticity of Cu-Sn \( \alpha \)-phase (FCC) at hot working zone requires prolonged preheating for its exhibited coring and then could be hot worked within a narrow temperature range with difficulty\textsuperscript{7}. The 3-4 wt\% Sn-Cu can be hot worked and for 8 wt\% Sn-Cu hot working needs care in a limited temperature range.

Bell metal having Peritectics composition (22 wt\% Sn) complicates the system as Peritectic reactions never comes to end. Normally containing predominantly \( \beta \)-phase (metastable BCT) 23Sn-Cu alloy can be termed \( \beta \)-Bronze at 700\( ^{\circ} \)C. The solid solubility of Sn increases to 24.6 wt\% with lowering of temperature up to 586\( ^{\circ} \)C before eutectoid transformation to (\( \alpha + \gamma \)) phases. Hot working naturally favors a narrow temperature range starting down from \( \sim 650^{\circ} \)C or 700\( ^{\circ} \)C and only could be continued \( \sim 50^{\circ} \)C below the eutectoid line (586\( ^{\circ} \)) not to precipitate any damage due to phase transformation. With lowering of temperature thermodynamically the solubility of Sn increases in the \( \alpha \)-phase and encroaches into the zone of earlier \( \beta \)-phase compositions of metastable nature. Sub-grain formations have also been observed in Pala-Sena period\textsuperscript{8} or earlier.

Sub-grain formations occur usually in any hot deformation of FCC crystals, known as Dynamic Recrystallization which makes Cu-FCC phase docile for GBS.\textsuperscript{9} So, whether ancient or modern metal forming physics does not change and this easy technique was known even at that time though cause became clear recently in last forty years. In any hot deformation of High Tin Bronzes or High Zinc brasses – because both are subjected to unusual Peritectic alloying – part of \( \beta \) disordered phases in Hume-Rothery phases in Cu-alloys.\textsuperscript{9b}
Super plasticity is a phenomenon where metal deformed in an extremely slow strain rate and only grain boundaries are participated in plastic deformation. However, in the present case authors described the forming process with very high strain rate (using hammering) and formation of strain induced martensite during forming.

In case of hot deformation, unlike cold working, in presence of BCC $\beta$-Cu phase (actually Sn-rich solid solution of Cu-Sn crystal) round FCC Cu-phase the whole scenario changes, which occurs in case of peritectic alloying of High Tin Bronzes – diffusion and vacancy increases abnormally high, cross slip becomes as easy as turn-of-neck by the partials (Note most dislocations are screw being of lower free energy) in alloy system due to high SFE and high chemical potential at grain boundaries due to vibrational entropy $^{9c}$. The hot deformation rate for high SFE, Al or 60/40 Brass becomes fantastically high. Note high extrusion rate of Al [10-80 m/min.] Or Muntz metal [used in ordnance shell making by any military India included]. The unbelievable high plasticity of FCC metals with inherent BCC phase within [theoretically can be called $\alpha$-\$\beta$ alloy] may be very modern technology [Note hot plasticity of Semi-austenitic SS (Mo-base) (Low Ni-SS) presently being made by SAIL, ASP] but this was noted by past East Indian metal makers. High Tin Roman razors imported from Bengal still bear testimony to this. China and far eastern people also mastered the technology and author tried to impress the technology which can be seen in ethno-archaeological reports of present Bengal practised by Bronze metal workers in Khagra, Murshidabad, W.B, where in-situ hot forging was done for comparison.

**Experimentation at Khagra:**

To understand the technology of ancient bowl forming or bronze forging of Eastern India and Bangladesh, ethno-archeological studies were conducted at Khagra and Kenjakura. Further to the studies, a reconstruction of the perceived forging process by the traditional bronze casters were experimented at a site of Khagra, in the suburb of Behrampur (24°06'N, 88°19'E) the district headquarter of Murshidabad, Bengal (Figure 2). 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.

(a) Casting of forging stock of Chunky sections:

For the spoon production a rough blank of semi-elliptical design was made in an open fine sand mold, using floor molding. A high tin bronze alloy was melted within a graphite crucible over a coal fire, at Khagra as per the conceived replication of the probable archeological environment. The one end of the casting conforms (Figure 3) 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.

(b) 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.
(c) Thermo-mechanical treatment (TMT) or thermo-mechanical controlled processing (TMCP) of the stock:
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. The forging stock of the appendage was drawn to a rectangular section. The forging continued until dull red heat to complete the desired shape of the spoon. Both thermal treatment as well as mechanical forming continued simultaneously. 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 (Figure 4).

(d) Heat treatment of Forged article: Quenching and Tempering:
The hot forged article was quenched in water as soon as the forging operation stopped to suppress any kind of possible phase transformation. 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.

(e) 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.

Analyses of High –Tin Bronze Article Produced at Khagra
The cast and forged samples produced at Khagra was analyzed in the laboratory and then compared with the analysis of the ancient bowl recovered at Gajole (25°7’N, 89°2’E) dated to Pala-Sena period (Figure 5).

(a) Chemical composition of the Samples: The chemical analysis of the reconstructed bronze as cast observes Cu: 77.96 wt%, Sn: 21.27 wt% and Pb: 0.007 wt%; and as forged is Cu: 77.76 wt%, Sn 22.02 wt% and Pb: 0.05 wt% respectively. The analysis shows a little deviation in copper tin percentages between the two forms due to the segregation of the alloy. Both show close to Peritectics of 22 wt% Sn (L+ α →β) and also very closely embrace pro-eutectoid β-range composition. The non-equilibrium nature of industrial alloy must have shifted the curve towards left and made the alloy a complete β-Bronze.

(b) Microstructures of Samples: The microstructure of the cast spoon (before forging) reveals α-Cu phase dendrites (black) embedded within matrix β-phase. Dendrites of the α-phase are blocky in nature within the core of the metal section, showing slow cooling rate of the sand casting. 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 due to the chilling of the surface and β-phase remains in form of the thin white layers surrounding α dendrites (Figure 6). The microstructure of the forged bronze spoon under SEM (Figure 7), at 2000X 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 can be 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 $\beta'$-Cu phase as revealed by X-ray diffraction analysis later. The simultaneous mechanical deformation, as well as, phase transformation from $\alpha$-Cu to $\beta'$-Cu phase, occurred in tandem.

Forging operation became easy due to lower flow stress of $\beta$-Cu phase, a super plastic material. The phase transformation during heating (thermal treatment) and mechanical shaping during forging (mechanical treatment) at modern time, called Thermo-Mechanical Treatment (TMT) happened simultaneously (like modern steel). TMT gifted high tin bronze forging possibility to ancient Bronze makers.

**Comparison with High-tin bronze specimen Found at Gajole**
The microstructure of the archaeo-metal (Cu: 75.09 wt.%, Sn: 23.62 wt.%, Fe: 0.6 wt.%, Zn: 0.2 wt.%, Pb: 0.5 wt.%) of forged high-tin bronze bowl, found at Gajole in Figure 8 shows $\beta$-Cu phase as a matrix with embedded $\beta'$-Cu phase within the structure. EDX analysis show the matrix $\beta$-Cu has composition 65.33 wt% Cu, 34.22 wt% Sn with few other elements. The embedded $\beta'$-Cu phase contains 82.61 wt% Cu, 15.77 wt% Sn with other minor elements. The hot forging and subsequent heating transformed the metal structure of the cast bronze stock to different phases. The confirmation about the phases was already detailed in the publication⁸.

**TEM Study on Past and Present High-Tin Bronze Samples**
The TEM samples for the forged bronzes were prepared through a series of process: first through diamond saw (Isomate 1000), polishing with Struers Rotopol 15, disc punch, Dimpler, ion miller and jet polisher. For examination, electrolyte solutions were used as 30% HNO₃ and 70 % methanol. The specimen was then observed through JEOL TEM, model JEM-2100.
The specimens were analysed with kind support of IIT-Kharagpur. The TEM result was obtained from IIT,Kharagpur. The routine data with voltage and other criterions can be made available from them only.

The TEM micrograph of Khagra specimen (Figure 9) at 50000X 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 transformation¹¹.

The TEM micrographs (Figure10) of the archaeo bronze at Gajole clearly testify the formation of martensite at magnifications of 12KX and 50KX respectively. Basket wisp structure¹² has been revealed inside.

The micrograph further confirms the individual martensitic laths, with their associated micro twinning¹³ observed in Khagra bronze. 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-shape¹⁴ ingots. A simplified heat transfer for the cooling time can be deduced. The choice of metal workers in Chunky⁰¹ hemispherical shapes or similar sections.
The selection of lump geometry 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 Eastern India till today\textsuperscript{16}.

The large or blocky grains also get further divided into sub-grains (Figure 11) and assist the development of fine grain formation of few μm ranges. The SEM image in this figure mentioned was further enlarged when the known sub-grain formation was revealed, and modern SEM resolution may be a matter of envy, one must appreciate.

Generally by grain boundary sliding, without work hardening, Cu or its alloys of very fine grains or two-phase structure (note α-β brass) exhibit super plasticity. Corresponding to Ashby model\textsuperscript{17}, a mutual displacement of the grains, which acquire new neighbors – 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\textsuperscript{18}. BCC crystal structure is not densely packed, having more atomic voids (Atomic packing factor = 67% & 8- nearest neighbors 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\textsuperscript{18}. These precise mutual atomic displacements of grains which acquire new neighbors produce favorable state for super plasticity. At the tin concentration of 22-25 wt% Sn, at 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, the artisans at Khagra replicate that knowledge to manufacture deep drawn bowls or plates at ease.

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 than 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 $\beta$-phase variant at lower temperature. Ultimately the V-form of the $\beta$ field varying from $(e/a) < 1.4$ to $>1.4$ converges to 1.446 in Cu-Sn system. The $\beta$-phase also shows a wide field of disordered Cu-solid solution. The structure of foundry bell metal (Figure 6) becomes a two-phase aggregate having unstable FCC $\alpha$-Cu phase with BCC $\beta$-Cu phase.

On quenching after severe plastic deformation the $\beta$-Cu phase collapses into close packed martensitic structures\textsuperscript{19} 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\textsuperscript{20}.

**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\textsuperscript{21}. 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 $\beta$-bronze during hot forging has been marked by deformation slip bands (Figure 12).

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 J/m\textsuperscript{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 $\sim 0.01$ J/m\textsuperscript{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\textsuperscript{22}. 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 favorable situation for Cu-Sn FCC $\alpha$-Cu phase lattice. A similar twinning mechanism has been proposed for BCC lattice\textsuperscript{23}, 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:

- **FCC**  \{111\} Plane, $<$112$>$ Direction, $1/\sqrt{2}$ Twinning shear,
- **BCC** \{112\} Plane, $<$111$>$ Direction, $1/\sqrt{2}$ Twinning shear

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 cooperative 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 (Figure 9, 10). 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 the brittle vulnerable phase kept few micro-cracks unattended as can be noticed in the optical metallograph (Figure13).

**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 (Figure 14, 15). An initial 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 525°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 (∆H) over less worked Khagra bronze can be justified by 3-D cupping operation organized for bowl making.

**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 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 (Figure 16) 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 (Figure 17) 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 $\beta'$-Cu phase (marked once as $\alpha'$-phase to indicate its parenthood from $\alpha$-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 $\beta'$-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.

Some research workers in the recent past like Srinivasan or Nagae 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.

**Conclusions**

The special geometry of Chunky shape or lump shape provided the thermal help to keep enough time for mechanical deformation of forging. The available time was the cause of concern for metal smiths. So, East Indian artisans, particularly in Bengal highly appreciated the working geometry of Chunky shape.

The unique super plasticity of $\beta$-Cu phase at high temperature is the key to the success of hot forging of high-tin bronze with respect to poor plasticity shown by low tin bronze (having primarily $\alpha$-Cu phase). This unique phenomenon of super plasticity @ Cu-23Sn composition having sole $\beta$-Cu phase above $\beta$- eutectoid reaction temperature, 586°C had been utilized to the hilt. A master stroke of those metal-smiths was seven-part Cu and two-part Sn ratio for developing the alloy composition known as Kansha in Bengal.
The narrow forging zone from red hot, 700/650°C to 550°C for high –tin bronze having the wide β-Cu phase area must be the second inhibiting factor for ancient metal workers. Bengal metal workers any way could have built a notion about the narrowness and solved the problem by fast kinetics of hammering on red metal only.

Those metal workers not only developed thermo mechanical controlled processing (TMCP) for hot forging of high-tin bronze but also used accelerated cooling or quenching the metal in water. Thus they could successfully manufacture deep drawn bowls or glasses in ancient Bengal.

The freeze of β-Cu phase by quenching in water, were notionally identified by some bronze casters in ancient Bengal. Otherwise, slow cooling of Bronze thermodynamically would render them in finished brittle material. Large number of incomplete transformations associated with Cu-Sn system and little solubility of Sn in α-Cu (~1 wt %) at room temperature could have produced unusable products.

The remarkable adaptation of cyclic quenching and tempering (Q & T) techniques like steels enabled the metal workers to heat treat high-tin bronzes for the case and the core of the material. Thus ancient Bengal accomplished strong and tough forgings of Cu-23Sn alloy free from brittleness.

An in-depth reconstruction of forging technology of High-Tin bronzes were made in Jadavpur University to visualize the alloying problems faced by early Bengal metal workers in attaining this peritectic alloy, β-bronze composition. That was the technological solution by Ancient Bengal workers in hot forging of cast bronze stock.

Recent researches on high tin bronze artifacts revealed the spread of high tin bronze technology across the subcontinent. Bronze objects from five megalithic sites of Vidarva region were studied in-depth with composition and the presence of β-martensite indicates that the specimen was quenched at or above 600 °C while the retained γ phase suggests that quenching was performed at a temperature between 520 °C and 586 °C. The average tin level was 17% and 18% as contributed by Park and Shinde.

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Figures

![Cu-Sn system diagram showing forgeability range and different phases in transition.](image)

Figure 1. A section of Cu-Sn system showing the forgeability range and different phases in transition.
Figure 2. Experimentation at Khagra, Murshidabad (Measuring temperature of the hot blank) at site of the forging shed.
Figure 3. Cast ingot of High-tin Bronze having Chunky sections of elliptical disc and triangular shaped handle.
Figure 4. The kitchen spoon reconstructed at Khagra: after final finishing became the drawn cup of 80 mm long, 50 mm wide and 16 mm deep with an average thickness of ~1.0 mm.
Figure 5. The fragment of High-tin Bronze Bowl recovered from Gajole. The composition of the alloy has been mentioned at the center.
Figure 6. The microstructure of cast high tin bronze ingot at Khagra. 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.
Figure 7. The microstructure of bronze after forged and heat treated at Khagra. 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.
Figure 8. The microstructure of high tin bronze found at Gajole shows $\beta$-Cu phase as a matrix with embedded $\beta'$-Cu phase (martensite later shown) within the structure.
Figures 9. TEM photographs of forged Khagra specimen clearly confirm the presence of the individual martensite laths, with their associated micro twinning at right angles to the lath boundaries. The micro-twinning is a usual way for the structure to accommodate elastic stresses generated during martensitic phase transformation.
Figure 10. The TEM of the archaeo bronze at Gajole (LHS) clearly testifies the formation of martensite at magnifications of 12KX with associated micro-twinning inside the laths. At 50KX (RHS) the signature of martensitic transformation in form of Basket wisp structure has been revealed.
Figure 11. In case of Gajole archaeo bronze, one large or blocky grain has developed sub-grain formation with the impression of deformation slip bands faintly visible. These sub-grains of the order of few μm had assisted in easy super-plastic formation. The SEM image in this figure was further enlarged when the known sub-grain formation was revealed.
Figure 12. SEM of Gajole high-tin forged specimen shows deformation bands in martensite β'-Cu-phase, which has already been marked in Figure 11 as α' phase.
Figure 13. The unetched micrograph of the forged archaeo-specimen of Gajole keeps few micro-cracks within the metal. The small cracks remain witness to the heavy forging undertaken for bowl making.
Figure 14: DSC record of the archaeo-high tin forged specimen at Gajole 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.
Figure 15: DSC curve of reconstructed high tin forged specimen of Khagra specimen up to 540°. The phase change of eutectoid reaction starts at ~523°C and closes at ~531 °C, with detailing at RHS.
Figure 16: XRD diffractogram of High tin bronze specimen at Gajole. Note the presence of $\beta$-Cu phase as matrix with the minor phase as $\beta'$-Cu phase.
Figure 17. Neutron diffractogram of the same Gajole 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.