# Forging technology of high-tin bronzes in ancient Bengal

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**High-tin bronze or *β*-bronze, commonly known as bell metal came into existence as a cast metal since late second millennium BC. The general composition of 23 Sn–Cu holds 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 the Cu–Sn system. Though widely used in castings for manufacturing gongs and bells throughout the world, only few people of the ancient world could achieve the mastery of forging this alloy into thin sheets. Ancient Bengal had been one of those few centres where circular bowls or tumblers or pots of very thin sections were manufactured. Some ethno-archaeological studies were also conducted on Bengal artisans presently engaged in this forging trade.**

**Keywords:** Forging technology, high-tin bronze, super-plasticity.

TIN bronze or commonly simple bronze found application in castings throughout the ancient world from the East[1] to the West in Asia, Africa and Europe[2]. Addition of tin to copper lowers the melting point of the alloys (Figure 1). The addition of 20% tin to copper lowers the melting point to ~800°C. This helped ancient artisans to easily produce molten high-tin bronze. Since bronze, has low viscosity (~1.5 mPa s is ~4 mPa s for Cu), this assisted in higher fluidity of liquid metal for quick filling of mould cavity by streamline flow in manufacturing thin domestic articles or sculptures[3]. Surface tension of tin bronze also sharply drops (~700 mN/m) in comparison to copper (~1200 mN/m), producing easy wetting of the mould surface for sharp reproduction of intricate designs of fine details[4]. All these properties favoured bronze as the casting material in the foundry. Also, the acoustic quality of 23 Sn–Cu alloy, the normal bell metal is excellently good and that elevated this metal further as a hot choice for the manufacture of precussion instruments or gongs or bells.

In spite of the above-mentioned attributes, for the production of sound cast metal by plane front solidification, the thermo-chemistry of Cu–Sn system complicates the usual solidification phenomenon. As categorized by

ASM[5], tin bronzes are castable alloys of Group III in the Cu–Sn system. The long freezing range of the alloys with wide liquidus–solidus gap makes it 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 gets aggravated with the appearance of porosity in castings due to hydrogen pick-up[6]. To eliminate the sponginess of the alloy for improving its mechanical properties, hot working or forging was a suitable option in ancient times.

Thermodynamics of the Cu–Sn system remained a mystery to metal men from solubility angle 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 Cu in the $\alpha$-phase (FCC) increases from ~13.5 wt% at 798°C to ~16 wt% at 520°C before abruptly falling to ~1 wt% at room temperature, initiating cracking during phase transformation (Figure 1). The plasticity of Cu–Sn $\alpha$-phase (FCC) at the
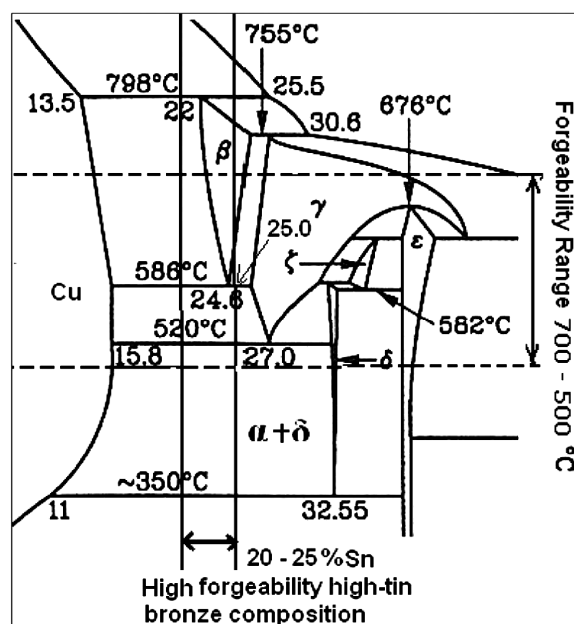


**Figure 1.** A section of Cu–Sn system showing forgeability range and different phases in transition.

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hot working zone requires prolonged preheating for its exhibited coring and then it could be hot-worked within a narrow temperature range with difficulty[7]. The 3–4 wt% Sn–Cu can be hot-worked, while for 8 wt% Sn–Cu hot-working, a careful approach is needed in a limited temperature range.

Bell metal has in general peritectic composition (23% Sn–Cu) and this further complicates the total solidification characteristics as thermodynamically we know that peritectic transformations never come to completion in reality. Normally containing predominantly $\beta$-phase (metastable BCT), 23Sn–Cu alloy can be termed $\beta$-bronze at 700°C. The solid solubility of Sn increases to 24.6 wt% with decrease in temperature up to 586°C, before eutectoid transformation to ($\alpha + \gamma$) phases. Hot-working naturally favours a narrow temperature range starting from ~650°C or 700°C and could be continued only ~50°C below the eutectoid line (586°C) 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 the Pala-Sena period[8] or earlier.

Sub-grain formations occur usually in any hot deformation of FCC structure, known as dynamic recrystallization, which makes Cu-FCC phase docile for Grain Boundary Sliding (GBS)[9]. This phenomenon has been recently established in last forty years but physics of the process (like wheel or fire) whether ancient or recent has no respect of times and does not change. So, the easy metal forming technique was practised without knowing the actual inside phenomenon. Both high-tin bronze and high-zinc brass have peritectic alloy compositions and behave similarly during hot deformations, as Hume-Rothery phases of disordered BCC-structure appear. The BCC phase is well known for easy flowing characteristics during hot working of any Cu-alloy.

Super-plasticity is a phenomenon by which a metal deforms through an extremely slow strain rate and only grain boundaries participate in plastic deformation. However, in the present study, we describe the forming process with very high strain rate (using hammering) and formation of strain-induced martensite during the process.

Unlike cold-working, in case of hot deformation, the presence of BCC Cu-$\beta$-phase (Sn-rich solid solution of Cu) round the matrix FCC Cu-$\alpha$-phase changes the whole scenario. At high temperature, in BCC Cu-$\beta$-phase, diffusion increases very rapidly and vacancy shoots up, so cross slip becomes easy. Note most partial dislocations are screw and those move by cross slip easily in the alloy system making deformation fast and effortless. Also simultaneous assistance from high SFE and high chemical potential at grain boundaries come handy due to vibrational entropy[9]. The hot-deformation rate for high

SFE Al or 60/40 brass becomes very extraordinary. Note the 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 round its boundary (theoretically can be called $\alpha$–$\beta$ alloy) may be a modern technology (note hot plasticity of semi-austenitic SS (Mo-base) (low Ni–SS) presently being made by SAIL-Alloy Steels Plant), but this was noted by past East Indian metal-makers. High-tin Roman razors imported from Bengal still bear testimony to this. China and the Far East also mastered the technology and authors tried to impress the technology which can be seen in ethno-archaeological reports of present-day West Bengal (WB). The hot forging is still practised by Bronze metal workers in Khagra, Murshidabad, WB, where *in situ* hot forging experimentation was conducted during the project work.

## Experimentation at Khagra

The reconstructed plan was executed to understand the technology of ancient bowl-forming or bronze forging of eastern India and Bangladesh, ethno-archaeological studies were conducted at Khagra and Kenjakura, WB. A reconstruction of the perceived forging process by traditional bronze-casters was done at Khagra, in the suburb of Behrampur (24°06′N, 88°19′E) Murshidabad district (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.

### 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 mould, using floor



**Figure 2.** Experimentation at Khagra, Murshidabad district, West Bengal (WB) (measuring temperature of the hot blank) at the site of the forging shed.

moulding. A high-tin bronze alloy was melted within a graphite crucible over a coal fire, according to the conceived replication of the probable archaeological environment. The spoon casting (Figure 3) had its cup resembling an elliptical disc of 42.5 mm-major axis by 36.4 mm minor axis having a height of 12.5 mm in the middle of the oval section and the handle was 175 mm long with a triangular cross-section of 9.1 mm side each.

### 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.

### Thermo-mechanical treatment or thermo-mechanical controlled processing of the stock

At first, the head of the 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 was 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 which was 80 mm long, 50 mm wide and 16 mm deep



**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 80 mm long, 50 mm wide and 16 mm deep with an average thickness of ~1.0 mm.

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).

### Heat treatment of the 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 (the last time with a coat of Na-salt layer) to transform the phases of the case and the core respectively.

### 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 articles produced at Khagra

The cast and forged samples produced at Khagra was analysed in the laboratory and then compared with an ancient bowl recovered at Gazole (25°7′N, 89°2′E), WB, dated to Pala-Sena period (Figure 5).

### Chemical composition of the samples

Chemical analyses of the reconstructed bronzes in (i) as cast and (ii) as forged condition were, Cu: 77.96 wt%, Sn: 21.27 wt% and Pb: 0.007 wt%, and Cu: 77.76 wt%, Sn 22.02 wt% and Pb: 0.05 wt% simultaneously. The analyses show a little deviation in copper and tin percentages between the two forms due to segregation defect of the bronzes. But, both results come close to peritectic
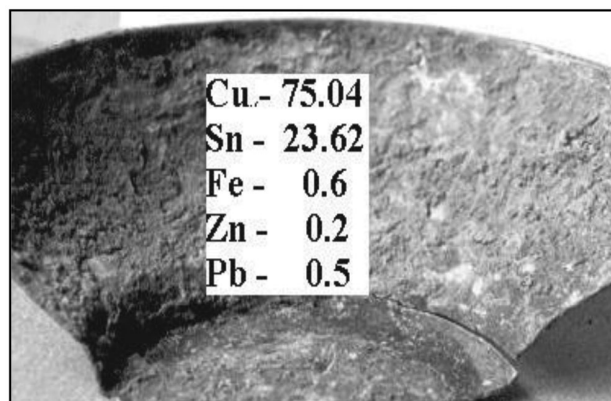


**Figure 5.** A fragment of high-tin bronze bowl recovered from Gajole, WB. The composition of the alloy has also been mentioned.

composition of 22 wt% Sn $(L + \alpha - \beta)$. The non-equilibrium cooling of the industrial alloy shifted the lines of the phases towards left and made the alloy come into a full $\beta$-bronze structure.

*Microstructures of samples*

The microstructure of the cast spoon (before forging) reveals Cu $\alpha$-phase dendrites (black) embedded within the matrix $\beta$-phase. Dendrites of the $\alpha$-phase are blocky in nature within the core of the metal section[9], showing slow cooling rate of the sand casting. As is the case with copper–tin system, peritectic $\beta$-transformation was suppressed due to the starting solid $\beta$-phase surrounding the $\alpha$-phase. Further to this $\beta$-phase, all the reaction products remained untransformed due to chilling of the surface[10] and the $\beta$-phase remained in the form of thin white layers surrounding $\alpha$-dendrites (Figure 6). The microstructure of the forged bronze spoon under SEM at 400× illustrates tin-rich Cu $\beta$-phase as the major phase, having Cu $\beta'$-phase entity as the second phase, in a discontinuous or along the flow lines, showing the forging direction (arrow Figure 7). Intermittent manual forging can be visualized by the lenticular morphology of the second Cu $\beta'$-phase. The Cu $\alpha$-phase of the cast structure, during hot forging and heating, have been transformed to Cu $\beta'$-phase as revealed by X-ray diffraction (XRD) analysis. The simultaneous mechanical deformation as well as phase transformation from Cu $\alpha$ to Cu $\beta'$-phase occurred in tandem.

Forging operation became easy due to lower flow stress of Cu $\beta$-phase, a super-plastic material. The phase transformation during heating (thermal treatment) and mechanical shapin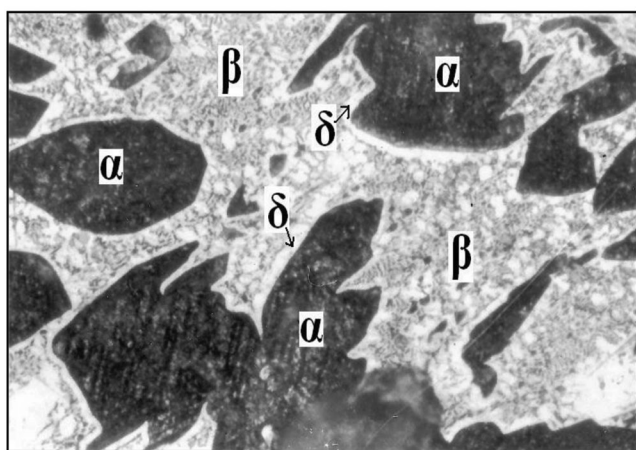g during forging (mechanical treatment), called thermo-mechanical treatment (TMT) occurred simultaneously (like modern steel). TMT made high-tin bronze forging a possibility to ancient bronze-makers.

## 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 (Figure 8) shows Cu $\beta$-phase as a matrix with embedded Cu $\beta'$-phase within the structure. EDX analysis shows that the matrix Cu-$\beta$ has 65.33 wt% Cu and 34.22 wt% Sn with few other elements. The embedded Cu $\beta'$-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 has been already detailed in the literature[8].

## TEM study on past and present high-tin bronze samples

TEM samples of the forged bronzes were prepared through a series of processes: first through diamond saw (Isomate 1000), polishing with (Struers Rotopol 15), disc punch, Dimplier, ion miller and jet polisher. For examination, electrolyte solutions were used, viz. 30% $HNO_3$ and 70% methanol. The specimens were then studied using a TEM observed through (JEOL TEM, model JEM-2100).
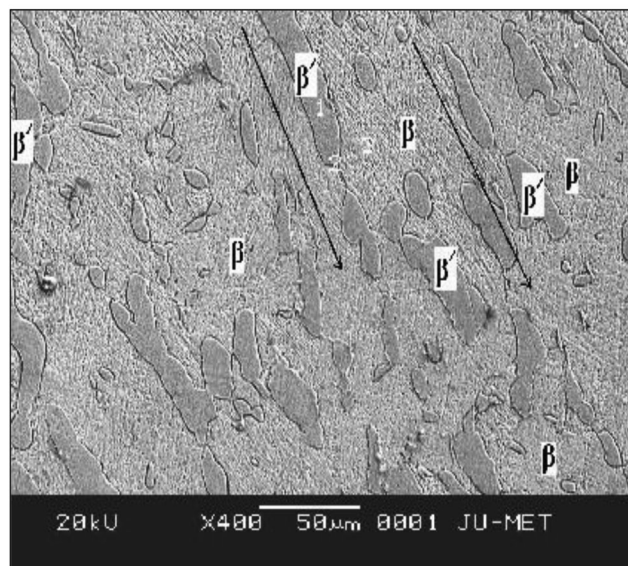


**Figure 6.** The microstructure of cast high-tin bronze ingot at Khagra. The microstructure of the cast spoon blank (before forging) reveals dendrites (black) embedded within a matrix $\beta$-phase. Dendrites of the $\alpha$-phase are blocky in nature within the core of the metal section showing slow cooling rate. The fringe of the primary Cu $\alpha$-phases shows 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 being forged and heat-treated at Khagra. During hot-forging, with the knockdown of primary Cu $\alpha$-phase dendrites within metal, its transformation to Cu $\beta$ and $\beta'$ phase also proceeds. The duplex cast structure of the Cu $\alpha$-phase and Cu $\beta$-phase transforms to metastable diverse Cu $\beta$-phases of two different compositions. On quenching, primary Cu $\alpha$-phase converts itself into martensite.

The specimens were analysed with kind support of IIT-Kharagpur and the results have been presented here only.

The TEM images of the Khagra specimen at 50,000× reveals the individual martensite laths, with their associated micro twinning that occurs within (seen as the fine black), and which lies more or less at right angles to the lath boundaries (Figure 9). Microtwinning is a way for the structure to accommodate elastic stresses generated during martensitic phase transformation[11].

The TEM images of the archaeo bronze at Gajole clearly testify the formation of martensite at magnification 12 and 50 kX (Figure 10). Basket wisp structure is also revealed inside[12].

The photomicrographs further confirm the individual martensitic laths, with their associated micro twinning observed in Khagra bronze[13].

The possibility of preserving heat within the forging block was solved by the chunky-shaped cast sections or commonly described by archaeologists as bun-shaped ingots[14]. A simplified heat transfer for the cooling time can be deduced. The choice of metal workers in chunky or hemispherical shapes or similar sections[15] had been a clever ploy to achieve their objective.

The selection of lump geometry facilitated easy forging of high-tin bronze ingot. Probably ancient forgers completed the hammerings within a short time, by engaging a number of forgers to strike blows on the red-hot stocks in quick succession till the metal blackened. The blackened stock was put into the fire again to achieve cherry-red condition for forging. The tradition continues in eastern India till today[16].

The large or blocky grains also get further divided into sub-grains (Figure 11) and assist in the development of fine-grain formation of a few microns range. The SEM image (Figure 11) mentioned was further enlarged when
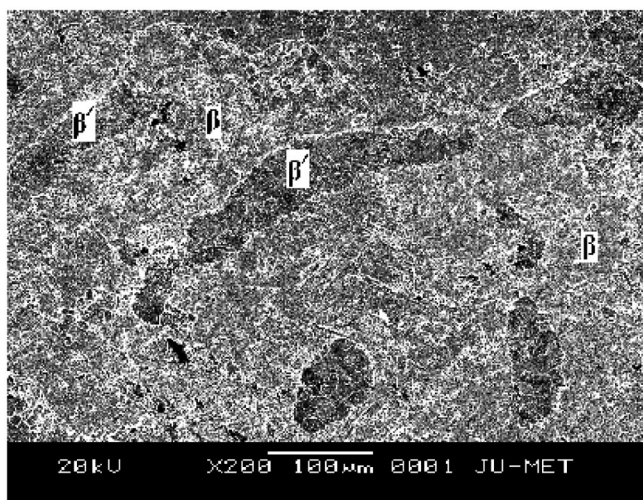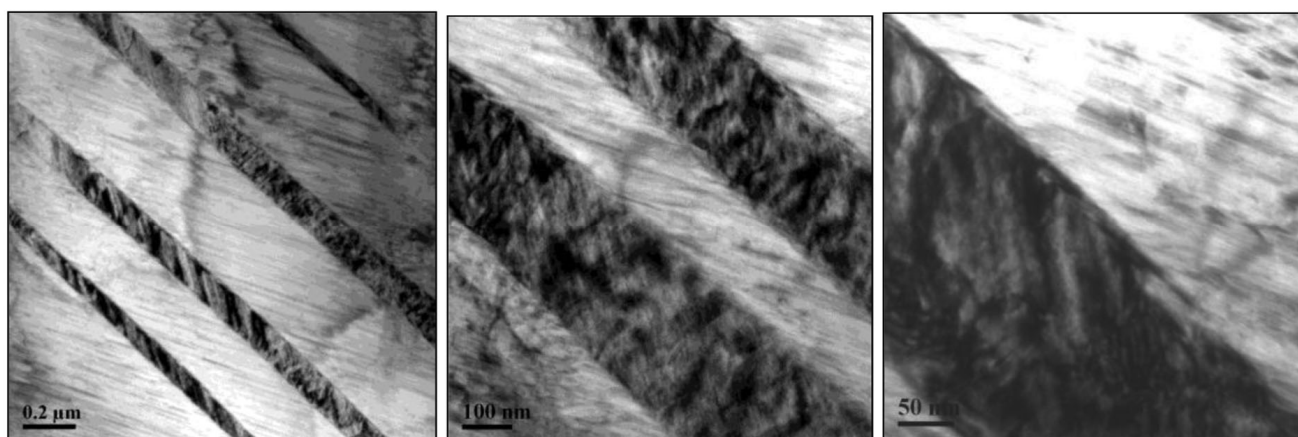
the known sub-grain formation was revealed, and one must appreciate that such a fine work would have been a matter of envy even to a modern man.

Generally by grain boundary sliding, without work hardening, Cu or its alloys of very fine grains or two-phase structure ($\alpha$–$\beta$ brass) exhibit super-plasticity. Corresponding to the Ashby model[17], a mutual displacement of the grains which acquire new neighbours – facilitates deformation instead 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 dominates the deformation process as revealed by 'deformation mechanism map' of the particular metal.

In case of bell metal or $\beta$-bronzes (>22 wt% Sn), the rapid solidification produces FCC Cu-$\alpha$ phase with BCC Cu $\beta$-phase of the Cu–Sn system. At high temperatures of red heat, the cast structure of bell metal transforms to almost complete Cu $\beta$-phase and the BCC structure gets stabilized[18]. The BCC crystal structure is not densely packed, having more atomic voids (atomic packing factor = 67% and eight nearest neighbours at 0.866a) that 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[18]. These precise mutual atomic displacements of grains which acquire new neighbours produced favourable state for super-plasticity. At 22–25 wt% Sn, at red heat, the bell metal acquires the stabilized Cu $\beta$-phase that encourages super-plastic. The ancient Bengal workers reached this conclusion empirically either through experimentation or import of technology. The investigation of bronze from Gajole confirms the above observation. The physical metallurgical knowledge of 'super-plasticity' of bell metal has been propagated through generations. Even now, artisans at Khagra replicate that knowledge to manufacture deep-drawn bowls or plates at ease.

## Characteristics of solid solutions of electron phases for bell metal

The copper–tin system undergoes a number of solid solutions starting with Cu-$\alpha$ phase, a close packed cubic or FCC like Cu. The next phase with higher concentration of 13.5 wt% Sn is the Cu $\beta$-phase, a loose packed structure of BCC. The interesting aspect is the widening of the $\beta$-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 Cu $\alpha$-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 the $\beta$-phase.



**Figure 8.** The microstructure of high-tin bronze found at Gajole showing Cu $\beta$-phase as a matrix with embedded Cu $\beta'$-phase within the structure.

**Figures 9.** TEM images of forged Khagra specimen clearly confirms the presence of individual martensite laths, with their associated micro twinning at right angles to the lath boundaries. Micro-twinning is the usual way for the structure to accommodate elastic stresses generated during martensitic phase transformation.

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 the Cu–Sn system. The $\beta$-phase also shows a wide field of disordered Cu-solid solution. The structure of foundry bell metal becomes a two-phase aggregate having unstable FCC Cu $\alpha$-phase with BCC Cu $\beta$-phase (Figure 6).

On quenching after severe plastic deformation, the Cu $\beta$-phase collapses into close packed martensitic structures due to generated shear stress within the grains[19]. The large deformation of super-plastic nature transfigures itself to microscopic deformation within grains in the form of twinning. Even repeated heating and quenching could not restore the equilibrium structures and only metastable phases result in the industrial alloys being discussed. There is a lot of misperception about phases and few agreements among researchers on the confirmation of residual functioning phases, either stable or metastable or ordered[20].

## Twinning and resultant martensite transformation in high-tin bronze

For a crystal, instead of deforming inhomogeneously by slip, sometimes it is easier to deform homogeneously by shear by the formation of twinning. The 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 is possible for both coherent and incoherent twin boundaries[21]. Twinning reproduces the initial structure, but changes its orientation.

The twinning originates from the result of 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. In Figure 12,

the heavy deformation of $\beta$-bronze during hot forging is marked by deformation slip bands.

When partial dislocations are well separated, in the case of low-stacking fault energy metals (e.g. pure Cu of the order of 0.06 J/m$^2$ at 300 K), it leads to high plastic deformation. The smaller stacking fault energy in case of Cu $\beta$-phase (due to greater ($e/a$) ratio with higher Sn content; this further decreases, probably of the order of ~0.01 J/m$^2$) facilitates easier nucleation of FCC twins by dissociation of perfect dislocations. After nucleation the twins propagate across macroscopic distances under decreasing load at almost the speed of sound[22]. In the FCC lattice, like zinc-rich $\alpha$-brass and 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 condition is more favourable for Cu–Sn FCC Cu $\alpha$-phase lattice. A similar twinning mechanism has been proposed for BCC lattice[23], where the twin grows in thickness by double cross slip onto the next parallel {112} plane. The usual twinning elements shown below could not been confirmed:

FCC {111} plane, ⟨112⟩ direction, 1/√2 Twinning shear.

BCC {112} plane, ⟨111⟩ direction, 1/√2 twinning shear.

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

The shear-controlled mechanism provides us the basis of transformations, where in addition to volume change, lattice deformations also take place. Thus, a co-operative atomic movement produces a 'militaristic transformation' in form of martensite formation in contrast to ordinary 'civilian transformation' in form of diffusion controlled

process (of individual atomic movements). The kinetics is instantaneous, where a change in temperature causes the requisite driving force. In high-tin $\beta$-bronze, during quenching in water at high temperature provided the necessary impulse. The twinning helped in phase transformations from Cu $\alpha$- and Cu $\beta$-phases to their twinned martensite phases. Similar to hardening of steels (maraging steels), the martensitic transformation took place, though this martensite was of deformable nature like Fe–Ni martensite. Deformation bands testify the proposition (Figures 9 and 10). So the material attains both the strength and toughness of lath martensite. Forged high-tin bronze is strong and tough. To stabilize the structure, repeated quenching and tempering were conducted to

remove the brittleness. Though the tempering process could keep the vulnerable brittle phase within control, few micro-cracks due to heavy forging done to develop the contour, remained unattended as can be noticed in the optical metallograph (Figure 13).

## Thermodynamics

To understand the nature of the energy change associated with metastable phase transformations, a limited Differential Scanning Calorimeter study up to 600°C was conducted on $\beta$-bronze samples (Figures 14 and 15). An initial small endo-peak in the two samples related to a 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
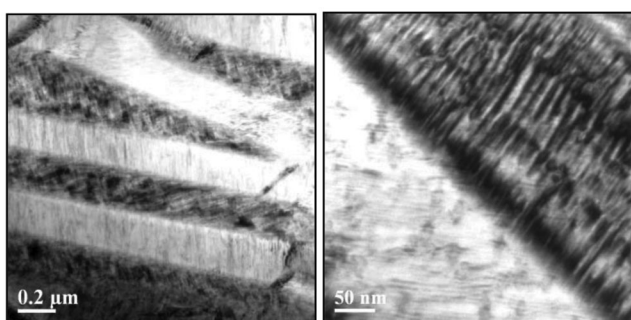


**Figure 10.** (Left) TEM image of the archaeo bronze at Gajole clearly testifying the formation of martensite at magnification of 12 kX with associated micro-twinning inside the laths. (Right) At 50 kX the signature of martensitic transformation in the form of basket wisp structure is revealed.
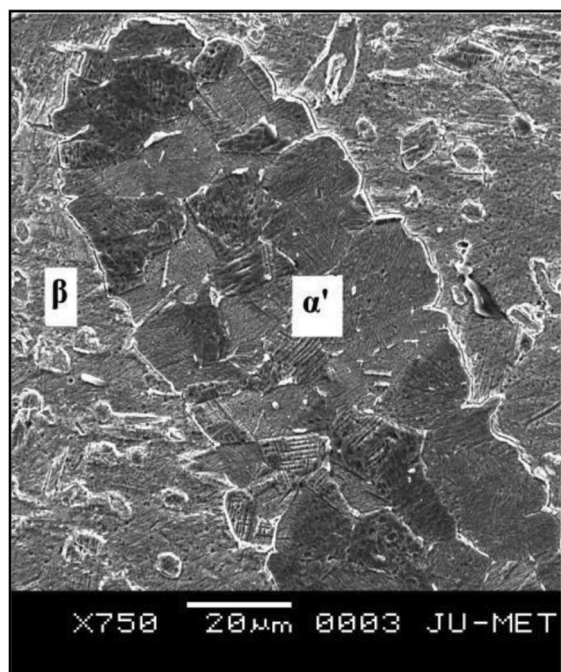


**Figure 12.** SEM image of Gajole high-tin forged specimen showing deformation bands in martensite Cu $\beta'$-phase, which has already been marked in Figure 11 as $\alpha'$ phase.



**Figure 11.** SEM image of the Gajole archaeo bronze showing that 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 a few microns had assisted in easy super-plastic formation. The SEM image was further enlarged, when the known sub-grain formation was revealed.
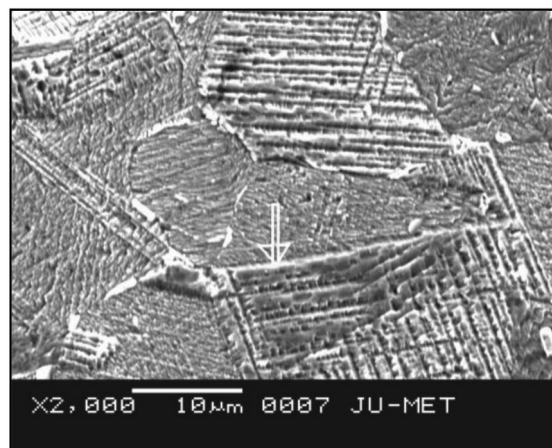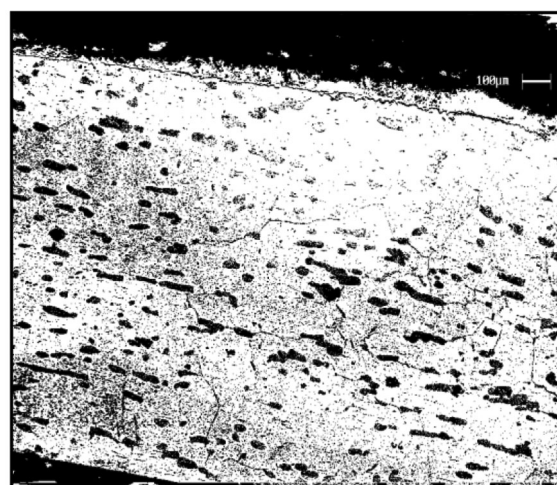


**Figure 13.** The unetched photomicrograph of the forged archaeo-specimen of Gajole retaining few micro-cracks within the metal. The small cracks are witness to the heavy forging undertaken for bowl-making.
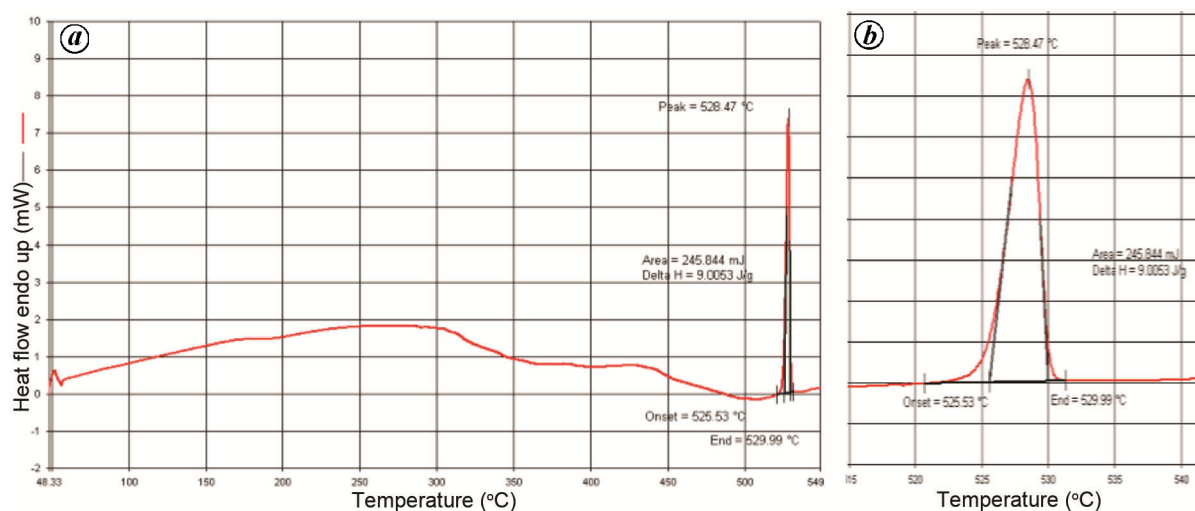
**Figure 14.** *a*, DSC record of the archaeo high-tin forged specimen at Gajole with endo-up. The phase change of eutectoid reaction starts at ~525°C and ends at ~530°C. *b*, The area of the endo-peak is enlarged.
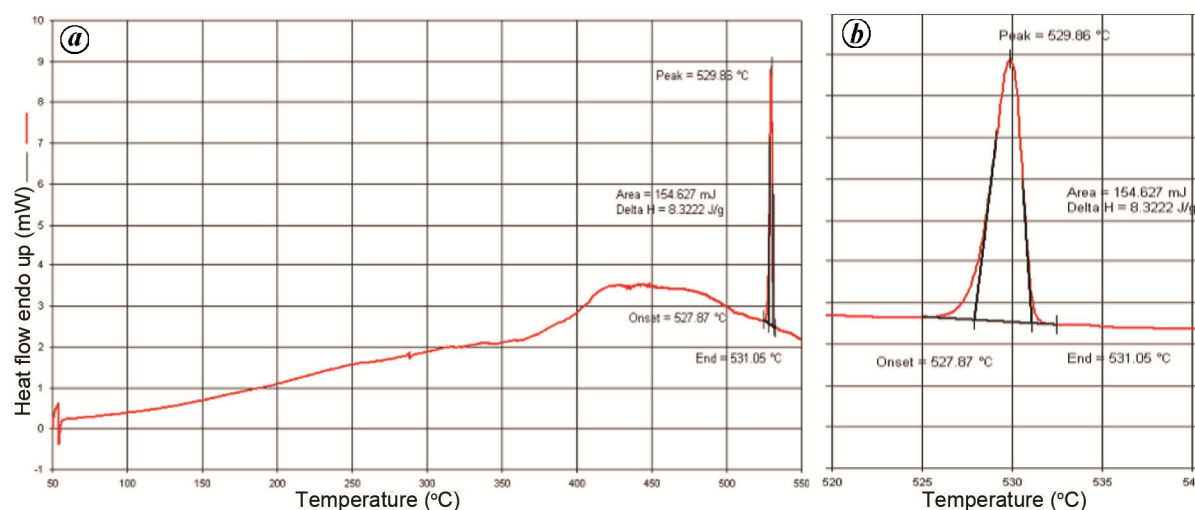


**Figure 15.** *a*, DSC curve of reconstructed high-tin forged specimen at Khagra up to 540°. The phase change of eutectoid reaction starts at ~523°C and ends at ~531°C. *b*, Enlarged.

two bronzes testifies almost identical condition of operation. The increase in enthalpy value in case of Gajole bronze ($\Delta H$) over the less-worked Khagra bronze can be justified by 3D 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. The ambiguity regarding crystallographic data as well as the actual crystals prevented us from making any rigid conclusions[24]. Only some general comments are presented here.

X-ray diffraction analysis of forged structure confirms the presence of minor phase $\beta'$-Cu with matrix Cu-$\beta$-phase (Figure 16). The existence of excess tin in the guise of 'inverse segregation' common to many tin-rich Cu-alloys also express their appearance. In contrast, neutron diffraction pattern indicates Cu $\beta$-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 (Figure 17). Whether the phase has an ordered structure cannot be confirmed, but probably originated from high-temperature supersaturated Cu $\beta$-phase of high Sn-concentration as the known value of BCT tin has been reported as $a = 0.58194$ nm and $c = 0.31753$ nm.

Alongside the bulk metastable phase, a martensitic phase has been reported as Cu $\beta'$-phase (also marked as

$\alpha'$-phase to indicate its origin from Cu $\alpha$-phase). This exhibits several deformation bands and it is suggested as a highly faulted FCC ($cF4$) structure. The cell parameters of the suggested Cu $\beta'$-phase are $a = 0.3727009$ nm, $b = 0.3727009$ nm and $c = 0.3677952$ nm. The cell parameters are close to FCC-Cu phase of 0.3608 nm, and so the metastable martensitic phase has been identified here as Cu $\beta'$-phase, in absence of any suitable nomenclature.

Some researches in the recent past[25] had obtained distinctive marked twins in few forged and quenched high-tin bronze samples in distorted Cu $\alpha'$-phase. Some have 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



**Figure 16.** X-ray diffraction (XRD) of high-tin bonze specimen at Gajole. Note the presence of Cu $\beta$-phase as the matrix with Cu $\beta'$-as the minor phase.



**Figure 17.** Neutron diffractogram of the same Gajole specimen as in Figure 16. The presence of Cu $\beta$-phase as matrix with Cu $\beta'$-phase as the minor phase as in XRD is also confirmed.

forging in ease of metal working sometimes can lead to this kind of twin formation in a 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, any report on the microstructure should specifically mention the condition of the high-tin bronze sample, whether post-heat treatment or pre-heat treatment after forging, mentioning twin typology.

The unambiguous crystallographic identification is not always straightforward due to the vulnerable size and distribution of various phases present in industrial high-tin bronzes. The above crystallographic identifications are open to debate. But hardly any confusion exists regarding the presence of metastable martensite mentioned here as Cu $\beta'$-phase alongside a deformed supersaturated Cu $\beta$-phase. Both are strong at room temperature and deformable at high temperature. This martensite is similar to Fe–Ni martensite in maraging steels in modern times. At different historical periods the type of $\beta'$-martensite in high-tin bronze operated as a deformable martensite but, as hard as a tool material and served mankind effectively in many cutting applications.

## Conclusion

The chunky shape in red hot condition for the starting forging stock of high-tin bronze did not allow temperature to drop quickly and thus the stock was kept soft for shaping for longer time. This simple technique provided enough time to East Indian metal smiths to forge the metal as per their choice during drawing operation. So, from technological perspective, the gravity of the chunky shape was very much respected by metal smiths even at that time. Compared to (copper age) ancient artisans of other parts of the world, this was a great achievement of East Indian artisans in Bengal.

The unique super-plasticity of Cu $\beta$-phase at high temperature is key to the success of hot forging of high-tin bronze with respect to poor plasticity shown by low-tin bronze (having primarily Cu $\alpha$-phase). This unique phenomenon of super plasticity @ Cu–23Sn composition having sole Cu $\beta$-phase above $\beta$-eutectoid reaction temperature, 586°C has been utilized in ancient times. The metalsmiths used a seven-part Cu and two-part Sn ratio for developing the alloy, also known as kansha in Bengal.

High-tin bronze has a very narrow hot forging temperature from red hot 700°CC/650°C to 550°C where the easily deformable (BCC) Cu $\beta$-phase is available. This must be the second most stumbling block for ancient
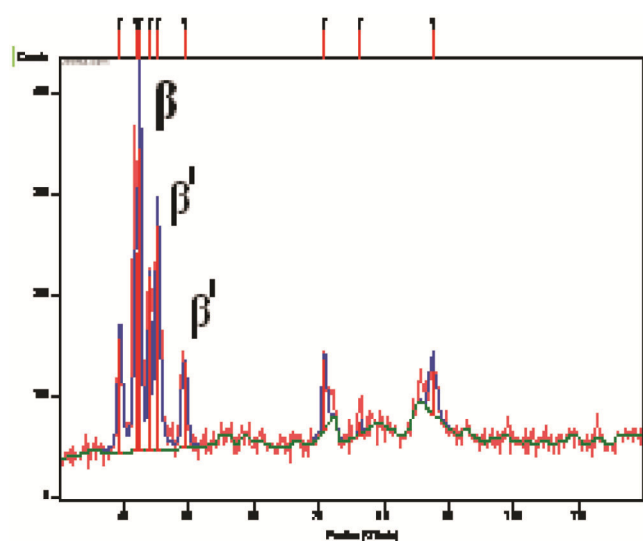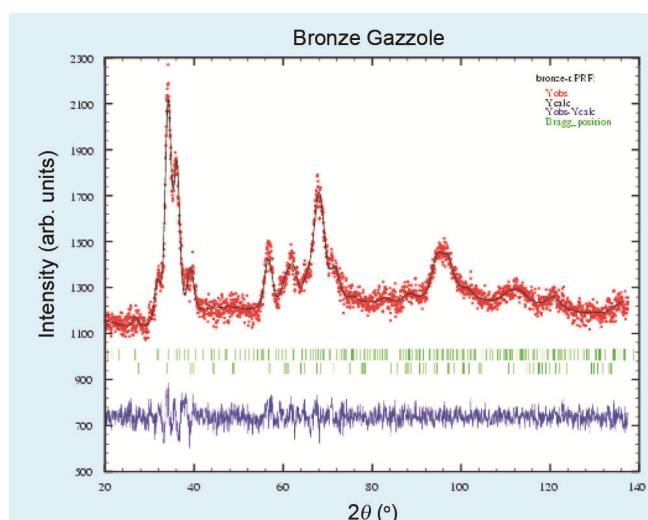
metal workers during hot forging. But, Bengal metal workers could identify the narrowness of forging temperature and solved the problem by fast kinetics of hammering on red hot metal only.

After forging the drop in temperature also transforms the phases in High-tin bronze and this must be arrested to avoid brittleness. So, simultaneous thermal treatments as well as hot (mechanical) deformation are conducted in modern industries and this is known as thermomechanical controlled processing. Incidentally at that early age, these metal smiths developed such a thermo mechanical controlled processing technique for High-tin bronze. They hot forged the metal and then used accelerated cooling (or quenching of the metal) in water to keep plasticity intact. Thus East Indian artisans could successfully manufacture deep-drawn bowls or pots in ancient Bengal.

The freezing of Cu $\beta$-phase by quenching in water was notionally identified by some bronze-casters in ancient Bengal. Otherwise, slow cooling of bronze thermodynamically would render a finished brittle material. A large number of incomplete transformations associated with Cu–Sn system and little solubility of Sn in $\alpha$-Cu (~1 wt%) at room temperature could have produced unusable products.

The adaptation of cyclic quenching and tempering techniques like steels enabled the metalsmiths 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 was made in Jadavpur University to visualize the alloying problems faced by early Bengal metalsmiths in attaining this peritectic alloy, $\beta$-bronze[26,27].

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