EFFECTS OF MICROSTRUCTURE AND CHEMICAL COMPOSITION ON STRENGTH AND IMPACT TOUGHNESS OF TIN BRONZES

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The present study is concerned with examining metallurgical features and their significance on strength and impact toughness of tin bronzes, with particular reference to bells. It has embraced a number of interrelated aspects – alloy types – composition, constitution and properties, fabrication technology, service life and effects of environmental/working conditions on strength and impact toughness of bell materials from Gothic, Modern and Recent Eras. The results are discussed in terms of qualitative assessment of microstructural features of these different cast tin bronzes examined in destructive tests. The observations considered are the variations in ultimate tensile strength values, impact toughness, and hardness data with respect to microstructural features of the above mentioned three different types of bell materials. The influence of alloying and harmful elements on the mechanical properties and qualitative parameters of bronze casts is also discussed.

Keywords:
Tin Bronzes, Microstructure, Chemical Composition, Strength and Impact Toughness.

1. Introduction

It is generally accepted and well acknowledged that bronzes play a significant role in shaping the origins of human history. Literature sources [Clark 1961], [Clark 1970], [Piggot 1968], [Powell 1983] suggest that Sumero-Arkadians and Egyptians invented, and later Grecians mastered, methods for casting non ferrous materials such as gold and silver, and later (around 2500 years B.C.) bronzes [Audy 1999] – alloys of copper, tin and other additive elements such as iron, antimony, zinc and lead – more or less independently. Reported evidence in the literature sources [Derry 1960], [Kranzeberg 1967] indicates that early workers understood that a high content of tin made the bronze alloy harder, and less tin made a soft bronze alloy. With this knowledge, bronzes with varying content of tin were produced for different purposes – tools, chandeliers, sculptures, and later canons and bells.

When people realised that bells cast in such a way are able to generate a pleasant sound, the tin bronzes formed the basic bell material. In 1978, Chinese archaeologists discovered 65 ancient bells in the North of Hubei Province in China. A Chinese researcher, Hua Jueming [Hua 1993], analysed the material composition of these bells and reported that they were cast from a bronze alloy containing copper as a base material and additives such as Sn up to 14 %, and Pb ranging from 2 to 4 %. Over centuries, foundry workers tried, mostly by trials and errors, to determine the most favourable composition of tin bell materials and improve the quality of their bells through controlling the chilling rate of their casts by using a wide variety of clay forming mixtures involved in preparation of the casting moulds. It has been known since ancient times that tin increases the strength of copper and that lead improves fluidity of the cast. Despite the fact that the most suitable alloy was not determined until some time in the middle of the twentieth century, there is strong evidence in the literature sources [Audy 1988], [Audy 1992], [Audy 1999], [Strafford 1996a], [Strafford 1996b] to say that the weight percentage of tin in the structure of bells systematically increased from as low as about 10 wt % in ancient times to about 20 wt % at the present. This increase coincided with decreasing amount of harmful elements (such as sulphur, bismuth and silver) from about 2.5 wt% in ancient times to about 0.5 % at present. However, it should be noted that apart from the generally recognised and widely accepted Cu-Sn diagram/system that allows to link the weight percentage of tin with different phase structures and corresponding strength and elongation to rupture for tin bronzes, the influence of additional alloying elements such as iron (Fe), nickel (Ni), antimony (Sb), silver (Ag), bismuth (Bi), zinc (Zn), phosphorus (P) and sulphur (S) on the final quality of bell materials and their effects on the mechanical properties including failure and fracture of tin bronzes has only scarcely been studied and rarely reported.

Therefore, in this paper the effects of microstructure and chemical composition on mechanical properties of tin bronzes were studied from different types of bell materials produced in Gothic, Modern and Recent Eras. An investigation was made into the effects of weight percentage of tin (and other elements in Cu-Sn diagram/system) on the material structure and mechanical properties. Different types of mould forming mixtures, clay in ancient times and green sand (bentonite) at present, were used in the study for comparison of different types of microstructures formed due to different cooling rates. A number of specimens were prepared for, and examined in, destructive tests for studying performance characteristics and failure patterns of tin bronze bell materials as affected by composition, a type of microstructure and casting defects.

2. Experimental details

Properties and characteristics of three different types of original bell material from a Gothic, Modern and Recent eras were investigated using chemical and microstructural analyses prior conducting tensile, hardness and impact toughness tests. The experimental procedures and relevant equipment are described in the following subsections.

Chemical Analysis

A Perkin Elmer 2380 Atomic Absorption Spectrometer was used to determine the metal elements present in the bell material of the bells investigated. The experimental conditions used for atomic absorption tests were selected from the recommendations described in a manual of the Perkin Elmer Device [Brochure 1982]. The process was as follows: firstly the debris were obtained from the bell specimens, then they were dissolved in a solvent created by mixing H_2O_2 with HCl and sprayed as an aerosol towards the air-acetylene flame. The light source created by the free atoms of an element being determined was developed in a cathode lamp because of the burning solution, and it was carried through the absorption environment to a monochromator. The later was used to isolate the selected narrow spectral band from the spectrum of the light source. The light signal was transferred to the electric signal by a special amplifier situated in the out put of the monochromator. The absorption level of the element being investigated was determined from the level of this electric signal. From this signal the weight percentage of a particular element present in the bell material was calculated.

It needs to be noted that sulphur levels could not be determined in the Perkin Elmer apparatus so it was done by an iodometric method. This method involved burning the bronze debris in an oxygen environment. After burning, sulphur and oxygen created SO_2 which was absorbed in water. This solution was then mixed with excessive iodine which after back filtration allowed analysis of the weight percentage of the sulphur in particular bell specimens.

Microscopy Procedure

Both optical and scanning electron microscopes were employed to carry out the metallographic analyses on the selected specimens. For the optical analyses the specimens taken had a square shape of approximately 3 mm^3. They were set in epoxy resin and polished to a 1 micron finish. Optical examination was performed prior to etching to identify inclusions, porosity, and other casting defects, as well as cracks. The specimens were etched in a 2% acid ferric chloride solution for about 10 seconds to reveal internal structure. The details from the fracture faces of the specimens broken in the tensile and impact toughness tests were examined using a scanning electron microscope (SEM). The SEM fitted with an Energy Dispersive Spectrometer (EDS) was also used to photograph and analyse the individual phases visible within the structure. It should be noted that the EDS system provided only semi-quantitative results because of its ability to detect elements greater than 0.1 wt%. Therefore, whenever more detailed chemical analysis was required, the bronze debris were investigated using Perkin atomic absorption spectrometer as described earlier.

Tensile, Impact Toughness and Hardness Tests

Tensile, toughness and hardness tests were conducted on specimens taken from damaged bells. Figure 1(a) shows one such piece from a Gothic bell material cast in the middle of the 16th century. Figure 1(b) shows the shapes and dimensions of specimens prepared for examinations by destructive tests. Rounded specimens were used for measurements of ductility using an Instron testing machine set up in slow strain rate (0.1 cm.min^{-1}) mode. The notched specimens were used for measurements of toughness using a Charpy hammer impact testing machine. Additionally, microhardness tests were conducted on each type of bell material specimen investigated in this study. This was done on polished and etched specimens prepared for optical microscopy. Experiments were made using a diamond pyramid pushed into the test material with the load equal to 20 grams for 20 seconds.

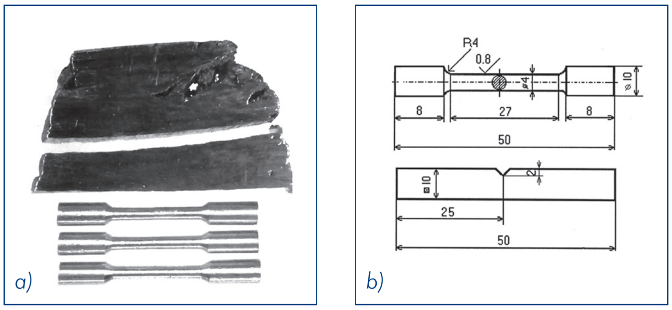
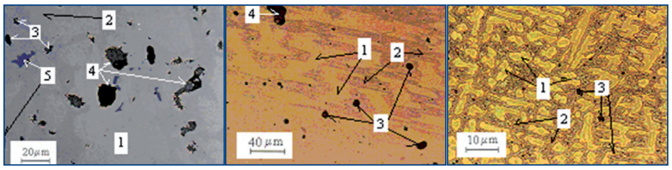


Figure 1. *A rare piece from a damaged Gothic bell with specimens for tensile tests (a), and sketches showing dimensions of specimens for destructive tests, (b).*



a) polished, but unetched *b) polished and etched* *c) polished and etched*

Figure 2. *Optical micrographs of the tin bell materials from bells cast in Gothic a), Modern b), and Recent c), eras.*

3. Results and discussion

Chemical Content and Microstructural Observations

The chemical compositions and microstructures of the studied tin bronze bells are shown in Table 1. and Figure 2., respectively.

From Table 1 it is evident that the weight percentage of tin in the three different type bell materials increased from about 7 wt % in the Gothic Era to about 20 wt % in the Modern and Recent Eras. Furthermore, the chemical analysis confirmed that these bronze alloys also contained different weight percentages of other elements like Pb, Zn, Sb, Fe, P and S. Traditionally, ancient bells ***eg*** that from Gothic era (specimen A) were cast into clay moulds [Audy 1992], [Audy 1999], [Hua 1993], [Strafford 1996a], [Strafford 1996b], whereas the modern (Type B) and most recent (Type C) bells were cast into green sand (bentonite) moulds. The chemical composition coupled with different chilling rate affected the microstructural formation in the following way. The microstructures of these three bell materials, pictured in Figure 2, are created by both the a phase and eutectoid (a+d). The high percentage of tin (at around 20 wt %) in modern and recent bell materials was responsible for creation of a greater amount of eutectoid in the microstructures, that were formed at more favourable solidification range than, for example, the one belonging to the ancient (Type A) specimen. It was because this Gothic bell material with its low content of tin (at around 7wt %) was sensitive to crack formation and showed a greater level of porosity than other two bell materials, as evident from Figure 2. Low content of tin is a feature of this gothic bell material. The solidification range for this tin content is approximately 130 °C. This tin bronze is disposed to segregation (both crystalline and ribbon) and crack formation as a consequence of the width of solidification range. Microstructures with 16, and greater, weight percentage of tin are created by a solid solution and by eutectoid (a+e) when cooling under equilibrium [Audy 1992]. In fact, phase transformations are controlled by metastable diagram as drawn by interrupted lines in Cu-Sn diagram/system pictured in Figure 3 (a). Therefore, two phase-structure a+(a+d) occurred in the gothic bell-material. In addition, this a+(a+d) structure may also exist under much lower content of tin too, as documented by 7wt% of tin in Specimen A. It was caused by low diffusion rate of Sn in Cu, no eutectoid decomposition occurred in this case. Therefore, the bell material specimens studied in this paper were built up by a solution and eutectoid (a+d). An unstable amount of eutectoid is probably a result of differences in chemical composition, and heat transfer associated with types of molding mixtures used in preparation of casting molds. In detailing, especially the grain size, of the alpha phase and the nature of the

Table 1. Chemical composition of examined tin bronze bell materials

	Composition of Bell Materials in wt%								
Specimen	Sn	Pb	Zn	Sb	Fe	P	S	Cu	Era
A	7	2	--	3	0.2	NA	0.095	balance	Gothic
B	20	0.3	0.1	0.2	0.3	0.5	---		Modern
C	20.25	0.9	1	1.1	0.25	0.1	---		Recent

Note: Specimen A (Gothic era) belongs to a bell cast in the Middle Ages in the second half of the 16th century;
Specimens B (Modern era) and C (Recent era) are the bell materials similar to those cast in the 1960's and 1990's.

(a+d) eutectoid were evidently determined by chilling rates of these casts. The green sand moulds used for casting the modern and recent bells removed the heat quicker than the clay moulds used in ancient times. Because of this, the size of grains in the microstructure of the modern (Type B) and recent (Type C) bells was smaller than that (Type A bell material) manufactured in the Gothic era. Therefore, the bell materials both types of B and C were expected to be harder than the ancient (Type A) one. Moreover, the microstructural differences were also influenced by the alloying additions of Pb, and particularly Fe and Sb, also governing the variations in the mechanical properties of these three different bell materials as set out later in this paper. Lead is not soluble in Cu-Sn diagram/system [Audy 1988], [Audy 1992], [Audy 1999], therefore it appeared in globular form on polished surfaces of the bell material specimens pictured in Figure 2. The bright particles visible only on the micrograph of the Gothic specimen (A), in Figure 2(a), were observed as CuS inclusions.

The following studies [Audy 1992], [Audy 1999], [Strafford 1996a], [Strafford 1996b] indicated that the final quality of bronze casts depends closely on the chemical composition, structural features and casting errors of a particular solid. It has been shown experimentally [Audy 1999] that hardness, impact toughness and tensile strength are three major variables representing the mechanical properties of church bells. As such, these variables are crucially dependent on the right selection and weight percentage of individual elements present in tin bronzes, as it is documented, for example, in the following Figure 3 which shows the Cu-Sn diagram/system and the mechanical properties – strength (s_{pt}) and elongation to rupture (A) versus different content of tin in Cu-Sn diagram/system – bronze alloys.

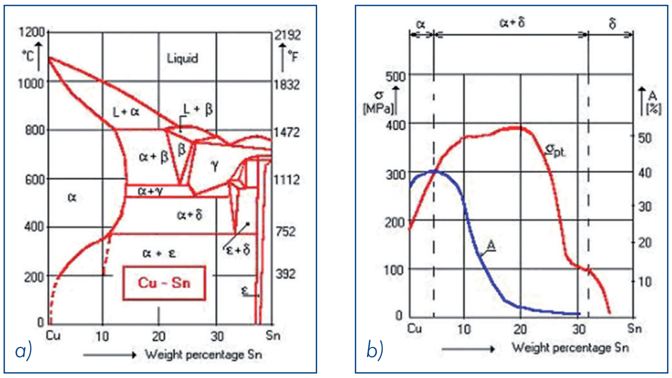


Figure 3. *Cu-Sn diagram/system (a), and Strength (spt) and Elongation at Rupture (A) for tin bronzes (b); after ASM, 1973:298-330 [14].*

From Figure 3 (b) it is evident that the bronzes containing up to about 20 wt % of tin (similar to both Modern and Recent Bell materials) have the highest ultimate tensile strength of about 380 MPa. Tin addition has a tendency to lower the melting temperature of the melt, and to improve the sound of bells due to its ability to increase the hardness of bell materials. However, the tin content over 20 wt % is not recommended because both the strength and elongation at rupture are expected to decrease rapidly, as shown in Figure 3(b). In the middle ages the tin was expensive therefore some medieval founders used both the lead and antimony in more or less excessive amounts. However, in the 19th century it was recognised that the lead in concentrations greater than 1 wt % was responsible for reducing the sound quality of bells. Thus, the Pb content in the Modern and Recent bell materials usually did not exceed the level of 1 wt %, as also evident from Table 1. Zinc up to about 5 wt % was reported [Audy 1999] to increase the tensile strength, hardness and ductility, to reduce the crystallisation interval, and to lower the melting temperature of tin bronzes. However, in the bell materials the zinc is tolerated up to only about 1.5 wt% otherwise it reduces the sound quality of cast bells. Phosphorus in the wt% of about 0.1 is acceptable because it acts as a deoxider in tin bronze melts. Finally, the sulphur is represented by some hundreds of wt % in the Gothic bell material. This element is usually responsible for creation of brittle eutectics that causes chipping of the bell material around the bell mouth – a phenomenon observed in the first half of the 20th century when some bells were driven with 'mechanical ringers' without respect to the frequency of swinging. Some examples of typical fatigues and fractures with respect to casting conditions and service life are presented in literature sources [Audy 1992], [Strafford 1996b] and as such they are not included in this paper.

Experimental Observations from Hardness Measurements and Destructive Tests

The results from microhardness measurements ($HV_{0.02}$), hardness measurements ($HG_{150kgf–1/16'' \text{ ball indenter}}$), and mechanical characteristics from destructive tests conducted on three different type bell materials investigated in this study are presented in the following Table 2.

When looking at the microhardness of a Type Gothic bell material (A) and comparing it with modern (B) and recent (C) types of bell materials it is evident that the hardness values of both the alpha phase (94.5 $HV_{0.02}$) and the eutectoid (142 $HV_{0.02}$) were significantly lower than those measured from other two bell materials investigated in this study. Interestingly, both bell materials – type B and C exhibited very similar hardness values of ($\alpha+\delta$) eutectoid that was around 300 $HV_{0.02}$. Referring to microstructural observations it is interesting to note that the bell material specimens B and C had more eutectoid in their structure than specimen A. It was because of the greater amount of tin ***i.e.*** about 20 wt % for specimens B and C compared to about 7 wt % of tin for specimen A. These results indicated that the hardness of the bell materials increased with the weight percentage of both tin and antimony additives. Although hardness data also increased because of two different types of forming mixtures used, variations in these variables for a given section of a particular bell were caused mainly by the different cooling rates.

Destructive experiments conducted on the three bell material specimens produced in the Gothic, Modern and Recent eras showed clearly that the tensile strength values of recent tin bronze specimen C were as about 1.4 (=340 MPa/242 MPa) times greater than those obtained from Modern era (Specimen B) and about 1.65 (=340 MPa/206 MPa) times greater than those produced by the Gothic bell material (Specimen A). Similar trends were observed in the values associated with the energy required to break these specimens employing a Charpy hammer. The current bell material showed the highest toughness values than both the modern and gothic bell ma-

Table 2. Microhardness and Mechanical Characteristics of 'experimental' tin bronze bell materials.

Specimen	Hardness Data ($HV_{0.02}$)			HG_{150kgf}	Mechanical Characteristics		
(Era)	Alpha phase	($\alpha+\delta$) eutectoid	CuS inclusions	1/16'' ball indenter	Tensile Strength [MPa]	Elongation [%]	Fracture Toughness [J]
A (Gothic)	94.5	142	192	$49.4^{\pm1.6}$	206	1.2	3
B (Modern)	152	322	NA	$58.6^{\pm0.7}$	242	2.7	5
C (Recent)	228	321	NA	$56.9^{\pm0.95}$	340	4.2	8.5

terials. The energy required for breaking the gothic bell material specimen was 1.6 times lower than that for the modern bell material and about 2.8 times lower than that for the current bell materials. It is believed that the reduction of mechanical properties of the original gothic bell material was associated with its relatively high amount of antimony (cca 3 wt %), as well as porosity. This sort of experimental results confirmed that the mechanical properties of tin bronzes closely related to the microstructural features, and internal defects, of a particular cast. The effect of chilling rate on the final structure of the bronze casts examined in destructive tests was investigated from a number of photographs showing the topography of the actual broken surfaces associated with the specimens tested. Further discussion is carried out with respect to observations concerning the microstructural features of tin bronzes examined using Charpy Hammer and using Tensile Testing Instron Machine.

Figure 4. (a to d) and Figure 5. (a to d) depict a number of details photographed from the fracture faces of both the modern (Type B) and recent (Type C) bell materials examined after toughness test.

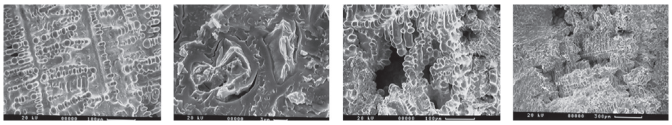

a) b) c) d)

Figure 4. *SEM micrographs photographed from the fractured faces of the modern specimen B showing inter-dendritic shrinkage (a), secondary cracks bordering brittle fracture (b), high level of porosity (c-d) after toughness test.*

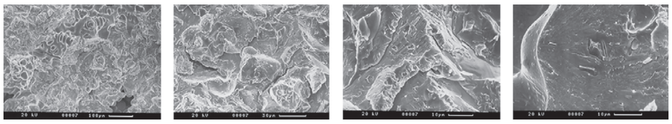
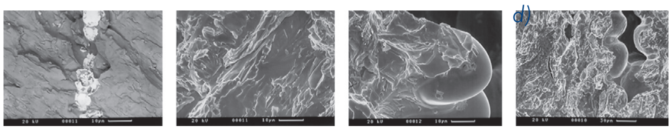

a) b) c) d)

Figure 5. *SEM micrographs photographed from the fractured faces of the recent specimen C showing defect sites, some shrinkage (a), quite brittle fracture with secondary cracks (b), few areas exhibiting ductile behaviour – very brittle transcrystalline fracture with some intergranular fractures (c), and small ductile particles surrounded by a crack (d) after toughness test.*

Figure 6. (a to d) and Figure 7. (a to d) depict a number of details photographed from the fracture faces of both the modern (Type B) and recent (Type C) bell materials examined after tensile test.



a) b) c) d)

Figure 6. *SEM micrographs photographed from the fracture faces of the modern specimen B showing a lead inclusion (a) very brittle crystallographic pattern (b), the end of a dendrite with smooth areas and ductile dimples (c), and porosity (right) which was probably reason for the development of secondary crack (left) in the structure (d) after tensile test.*

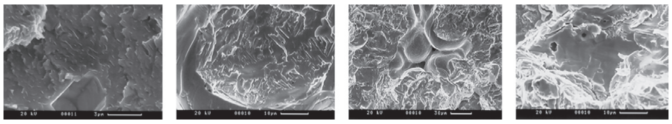

a) b) c) d)

Figure 7. *SEM micrographs photographed from the fracture faces of the recent specimen C showing a sand inclusion surrounded by microductile particles (a), brittle fracture with ductile areas (b and c), brittle fracture with flat surface in the middle (d) after tensile test.*

4. Conclusions

Tin bronzes for bell materials were CuSn alloys with the tin content ranging from as low as 7 wt % in Gothic bells and as high as 20 wt % in Modern and Recent bells. The structure was therefore created by the alpha phase (influenced by the wt % of Cu) and a type (a+d) eutectoid (influenced by the wt % of tin, and cooling rate). Metallographic examinations conducted in this study on the bell materials (Type A to C fabricated through the centuries) revealed significant differences in microstructures, brought by compositional variations in the alloys, as well as through different casting techniques. The use of purer constituent elements and improved melting practices in specimens from Modern and Recent eras, for example, eliminated the presence of brittle CuS inclusions rendering the bells less susceptible to cracking and fatigue when struck by the clapper. Additionally, the use of green sand moulds in the 20th of century increased the cooling rates and influenced in a positive way the nucleation, growth, and shape of grains, mostly the (a+d) eutectoid, and hence the whole mechanical properties (mainly the hardness and sound qualities) of the bell. For a particular cast, chilling rate and chemical composition there was a progressive increase in the hardness, for specimens A to C. The Gothic – type A – bell material cast into clay moulds had significantly lower hardness values of both the alpha phase and (a+d) eutectoid in comparison with modern – Type B and recent – Type C bell materials that both exhibited the similar hardness of (a+d) eutectoid of about 300 $HV_{0.02}$. These differences in the hardness values were probably caused by the high amount (2 wt %) of Pb and the low amount (7 wt %) of Sn in the Gothic bell material compared to the low amount (0.3 wt % and 0.9* wt %) of Sn and the high amount (20 wt% and 20.25*wt %) in the modern and recent* bell materials. Consequently, the ultimate tensile strength values and the fracture toughness data also showed definite patterns and confirmed the existence of a strong correlation between the microstructure, mechanical properties and type of failures of tin bronze bell materials. The trend in tensile strength, for example, was 206 MPa for the Cu-7 wt % tin (Gothic alloy-Type A), 242 MPa for the Cu-20 wt % tin (Modern alloy-Type B), and 340MPa for the Cu-20.25 wt % tin (Recent alloy-Type C).

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