Analysis of bell materials: Tin bronzes

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Abstract: The present study was set up to examine the effect of alloying elements (including harmful elements) on metallurgical features (material properties and qualitative parameters) of tin bronzes, with particular reference to church bells from Middle Ages to Current times. A driving force of this study was to identify and demonstrate features related to the quality of church bells made in different centuries. The findings have been derived via metallographic and chemical analysis of specimens of bells from various parts of Australasia and Europe. The bell materials consisted of a mixture of the α phase and the ($\alpha+\beta$) eutectoid essentially, in proportions determined by tin content and mould materials during casting. The samples from the 15th century to the one from the 20th century showed a progressive increase in hardness, ranging from the minimum of ~280 VHM_{20g} to a maximum of ~470 VHM_{20g} for the ($\alpha+\beta$) eutectoid, and ~160 VHM_{20g} to ~230 VHM_{20g} for the α phase. The investigation also shows that the sound decay of the bell decreased with lowering the wt.% of tin and increasing the wt.% of lead and silver. This information is expected to provide an additional interesting knowledge into manufacturing practices and their significance in the quality of church bells over past centuries.

Key words: tin bronzes; bell material; church bells; microstructure; chemical composition; material properties; quality

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The success of bell materials in bell making applications has to date largely been based on tin bronzes [1-6]. It has been recognised that tin bronzes (Cu-Sn) vary widely in composition. Traditionally, bell materials consist of a wide variety of other elements such as Pb, Zn, Bi, Ag, Sb, As, Ni, Fe, P, S and Si [2, 3, 5-7]. Some of these elements (e.g. Pb, Zn, Ni, Fe, Ag, Sb) were used for alloying purposes, whereas others such as S and P were impurities entering the bronze liquid through the process of melting with coke and charcoal. Bell materials differ in both number of alloying elements and their amount. This is because through the centuries the bell makers have been searching for 'best' tin-bronze composition that would satisfy: (a) melting/casting requirements, (b) expectations in high quality of cast bell, (c) good bell material properties, (d) long service life, and (d) nice bell sound. It is therefore not surprising that the knowledge associated with preparation of a bell material mixture was closely guarded secret in different bell foundries.

In the present study, the effects of individual elements on different type bell materials was investigated qualitatively – assessed by material properties, casting properties, service life, and bell sound. Different bell materials produced from the Middle Ages to Current times were included for comparison.

1 Effects of bell material composition on qualitative measures of bells: reported data

An extensive literature survey has been carried out on different bell material compositions, their properties and effects on various qualitative/performance measures. The most important findings are summarised in Table 1 with references to different literature sources [2-17].

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From Table 1 it is evident that the most appropriate bell material characteristics (such as cast ability, tensile strength, hardness, wear resistance, cast quality, sound, cost etc.) can probably be obtained by having a type bronze composition as: ~20wt.%Sn, < 2wt.%Ni, < 1.5wt.%Pb, ~0.01wt.%P, < 1wt.%Sb, with balance of Cu.

Table 2 from ref. [5] shows the composition of a standard 'modern and current' bell material produced in France, Switzerland, former Czechoslovakia and Germany.

Table 2 indicates that the quantitative recommendations of weight percentage of the main elements (as a whole) in tin bronze materials are incomplete and vary in detail for each reference. Incomplete quantitative recommendations contribute to the lack of knowledge about this popular and common bell material. Furthermore, it is also anticipated that large variations in bell material composition may occur in practice because of different bell manufacturers' knowledge/experience/preference as reported in the reference [2-11]. Therefore, it is necessary to determine the quality of different bell materials by metallurgical and chemical analyses, including the measurement of mechanical properties (e.g. microhardness) whenever possible due to small size of specimens.

2 Experimental apparatus and methods

Properties and characteristics of different types of original bell materials ranging from a Gothic to Current Eras were investigated using chemical and microstructural analyses prior

Table 1 Number and amount of alloying elements in tin bronze bell materials and their possible effects on qualitative parameters of church bells

Alloying element(s), wt.%											Variables effected	Reference(s)
Sn	Pb	Zn	Bi	Ag	Sb	As	S	Ni	Fe	P		
10–20		~5									Tensile strength increases	[2, 3, 6–10]
10–20	yes		yes			yes					Tensile strength decreases	[2, 3, 6, 8, 10]
Max. 23		Max.5			~1		yes		yes		Hardness increases	[2, 3, 6, 10]
>23			yes		>1	yes					Brittleness increases	[2, 3, 6, 10]
	yes							yes	yes		Wear resistance increases	[10]
		up to 5									Ductility increases	[2, 3, 7, 10]
<5											Ductility decreases	[2, 5]
~20											Elastic limit increases	[2, 5, 6, 7]
>23											Elastic limit deceases	[2, 5, 6, 7]
									yes		Abrasion resistance increases	[11]
Yes											Toughness increases	[2, 5, 6]
									yes		Toughness decreases	[2, 5, 6]
								yes			Fatigue resistance increases	[12]
yes	yes										Fluidity increases	[5, 7, 10]
								>2			Fluidity decreases	[5, 7, 10]
					~1					0.01	Acts as a deoxider	[5]
								yes			Reduces deformation	[13]
									yes		Rust resistance decreases	[2, 3, 14]
>15											Crack resistance decreases	[2, 5]
yes											Changes the colour of castings	[2, 5, 7, 15]
		yes									Crystallisation interval is reduced	[2, 3, 5, 10, 15]
			yes			yes					Cast-ability decreases	[2, 3, 5–7, 10, 15]
yes	yes						yes				Machinability improves	[2, 3, 5, 6, 10, 15]
									yes		Machinability decreases	[2, 3, 5–7]
<10											Porosity increases	[2, 3, 5, 7, 15]
								0.4-5			Porosity decreases	[16, 17]
								0.5-2			Structure softens	[7, 16, 17]
								2-4			Structure stabilises	[7, 16, 17]
20–23					~1						Sound quality improves	[2, 3, 5–8]
	>1.5	>1.5		yes							Sound quality decreases	[2, 3, 5–8]
yes	yes	yes									Melting temperature decreases	[2, 3, 5–8]
yes				yes							Cost increases	[2, 3, 5–8]
	yes										Cost decreases	[2, 3, 5–8]

Table 2 Composition of a standard ‘modern and current’ bell material produced in France, Switzerland, former Czechoslovakia and Germany

Country	Bell material composition, wt.%					
	Sn	Ag	P	Fe	Zn	Cu
France	26.5	1.5	0	--	--	Balance
Switzerland	25	0	0.5	--	--	
Former Czechoslovakia	20.25	0	1.5	0.25	--	
Germany	22–26	0	Max.1	0.3	0.5	

to the microhardness tests and sound measurements.

2.1 Chemical analysis

A Perkin Elmer 2380 atomic absorption spectrometer was used to determine the metal elements present in 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 [18]. The process was as follows:

Firstly the debris was obtained from the bell specimens, then they were dissolved in a solvent mixture of H_2O_2 and HCl and sprayed as an aerosol towards the air-acetylene flame. Because of the burning solution in a cathodic lamp, the light source created by the free atoms of an element being determined 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 transformed into the electric signal by a special photodiode situated in the output 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 in the bell material was calculated.

It needs to be noted that sulphur levels could not be determined by the Perkin Elmer apparatus so it was done by an iodometric method. The iodometric method involves burning the bronze debris in an oxygen environment. After burning, sulphur and oxygen reacts to form SO_2 gas that can be easily absorbed in water. This solution is then mixed with excessive iodine for quantitative analysis of sulphur after back filtration.

2.2 Microscopical observations and microhardness tests

An optical microscope was employed to carry out the metallographic analyses on the selected specimens. The specimens taken had a prismatic shape of approximately 3 mm^3. They were mounted with 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 s to reveal internal microstructure. In addition, a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) was also used to quantify and map individual phase in the microstructure. The EDS system only provides quantitative measurement of element once its concentration is greater than 0.1wt.%. Therefore, Perkin atomic absorption spectrometer was necessary for analysing tracing elements in the bronze debris.

The microhardness measurements were carried out using a Vicker microhardness tester under an indentation load of 20 g. The investigated areas were the α phase, the $(\alpha+\delta)$ eutectoid, and inclusions.

2.3 Sound measurements and analysis

The sound of bells was recorded on a tape recorder and the sound frequencies were analysed using a computer equipped with Types Snap Master and Math-Cad softwares. The patterns were plotted in a way to allow recognising one whole complete sound signal and the beginning part of the next beating. The frequency charts were presented in a pattern of voltage output/time graphs to give (1) overall information about the tone decay (sound duration) and (2) to plot the real width of frequency sound charts.

3 Features of the experimental bell materials

3.1 Chemical composition of specimens

The results from chemical analyses are given in Table 3. In the 'Gothic' bell materials investigated the amount of tin varied from 7 to 12 wt.%. This sort of bell-material has a solidification range of about 180℃ [5-7], so such bronzes are inclined to develop a high level of inter-dendritic porosity. For the 'Empire' bell materials the amount of tin varied in the range of 12wt.% to 15.5wt.%. The 'Modern' bell material showed tin levels in the range of 18 wt.% to 20wt.%, while the

Table 3 Experimental data on chemical analysis of world-wide bell materials produced in different centuries

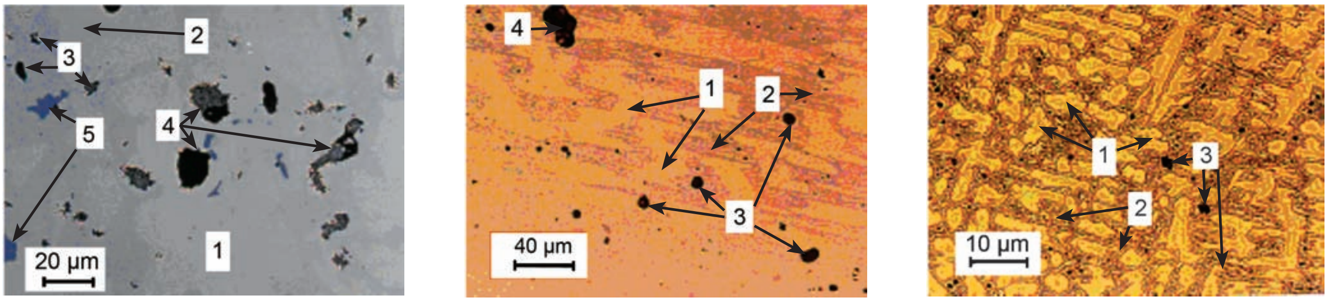
wt.%	Sn	Pb	Zn	Bi	Ag	Sb	As	S	Ni	Fe	Cu	Era date
min.	7	2	0.02	0.026	0.2	3.2	0.48	0.09	0.27	0.2	balance	Gothic
max.	12	3	0.17	0.038	0.9	3.94	0.79	1.44	0.39	0.7		1150–1560
min.	11	1.5	0.14	0.017	0.15	0.32	0.13	0.08	0.05	0.11	balance	Renaissance
max.	12	1.7	0.47	0.021	0.16	1.34	0.54	1.3	0.32	0.2		1420–1620
min.	11	1.5	0.17	0.018	0.11	0.28	0.12	1.1	0.31	0.03	balance	Baroque
max.	14	1.8	0.23	0.02	0.2	1.2	0.45	1.2	0.42	0.15		1620–1750
min.	10	0.8	0.5	0.012	0.03	1.25	0.49	0.4	0.09	0.09	balance	Rococo
max.	15	1.74	0.64	0.033	0.11	3.62	0.8	0.6	0.41	0.76		1720–1800
min.	12	0.3	0.47	0.001	0.006	0.25	0.33	0.3	0.025	0.12	balance	Empire
max.	15.5	0.81	0.62	0.026	0.028	0.27	0.84	0.8	0.096	0.82		1800–1870
min.	18.57	0.25	0.06	0.008	0.004	0.21	0.05	0.41	0.028	0.34	balance	Modern
max.	20.86	0.32	0.1	0.011	0.007	0.35	0.1	0.63	0.029	2.4		1900–1950
min.	23.2	0.3	--	--	--	0.8	--	0.02	--	0.15	balance	Current
max.	25	1.5	--	--	--	1.2	--	0.06	--	0.26		1950–

Note: Silicon in amounts of about 0.21wt.% was observed from a specimen taken from a bell cast in Italy in the early Middle Ages. In addition, phosphorus, in amounts of about 0.01wt.% was obtained from several specimens taken from the Modern and Current Bells.

'Current' bells contained about 20wt.% to 24wt.% tin. These data clearly show that the weight percentage of tin in church bells increased from about 12wt.% in the Middle Ages to about 25wt.% in the Modern Era. Further, chemical analysis of such bell-materials has also indicated that the bronze alloys also contained other elements like Ni, Zn, Fe, Pb, As, Sb, Ag, S and Bi as shown in Table 3 which adopted from ref. [5]. The most important feature relevant to the wt.% of other elements in bell materials from the Middle Ages to Current times is an increasing trend in the wt.% of alloying elements of Ni, Zn and Fe, decreasing trend in the elements of Ag and Pb, and stabilizing trend in the volume of other elements (Bi, Sb, S, P and As) which may easily became negative/harmful when their amount increases over certain level (e.g. more than 1wt.% for Sb and more than 1.5wt.% for Pb, as shown earlier in Table 1).

3.2 Microstructure of specimens

Figure 1 shows three different types of microstructures observed from the bell-materials produced in the Gothic, Modern and Current Eras.



(a) Polished, but un-etched (b) Polished and etched (c) Polished and etched

1-α phase; 2-(α+δ) eutectoid; 3-Pb; 4-porosity; 5-CuS inclusion

Fig. 1 Optical micrographs of tin bell materials from bells cast in Gothic (a), Modern (b), and Current (c) eras

The above micrographs show that the bell materials consisted essentially of a mixture of the α phase and the (α+δ) eutectoid, in proportions determined by tin content and mould materials during casting. These latter affect the cooling rate, which in turn, influences the grain size and the nature of the α phase (copper-tin solid solution) – the extent of coring – as well as the amount of the (α+δ) inter-dendritic eutectoid, as depicted in Fig. 2. Figure 2 shows the photo-micrographs of eight different microstructures observed from the bell materials produced in the Empire, Modern and Current Eras. The mechanical properties of such alloys are crucially influenced by their microstructural features. During cooling, the solidified alloy undergoes a number of eutectoid reactions (as indicated in Cu-Sn alloy phase diagram) resulting in the microstructure of α solid solution and (α+δ) eutectoid. The δ phase is an inter-metallic compound of $Cu_{31}Sn_8$. Increased amounts of δ phase in the microstructure will cause the bell artefact brittle. In order to reduce the amount of δ phase in the final microstructure, one can either reduce tin content and/or increase cooling rate to suppress equilibrium-like microstructures.

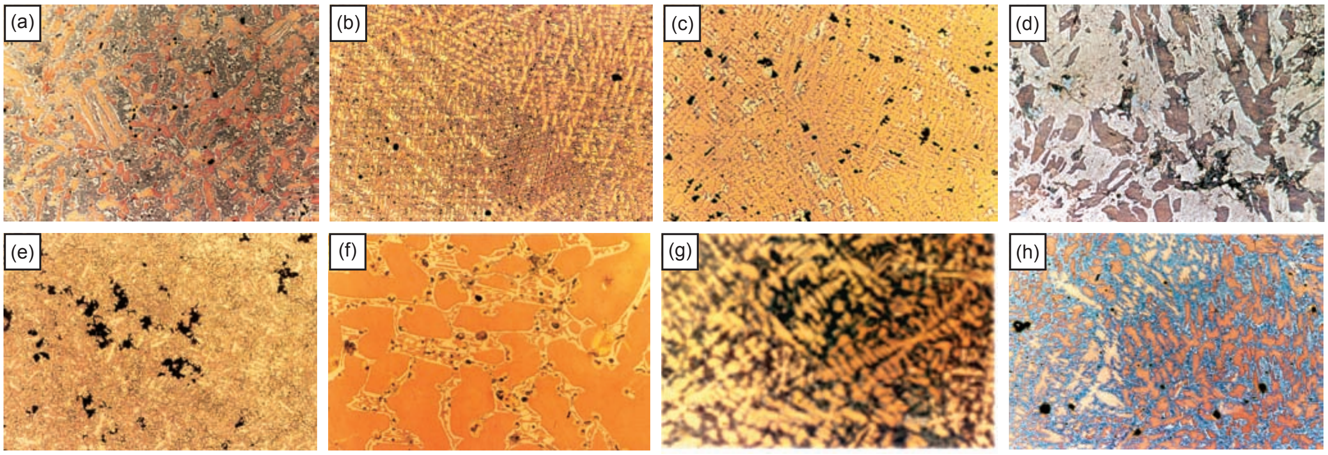


Fig. 2 Optical micrographs showing a wide variety of microstructures of different bell materials from different eras: 1846 (a); 1851 (b); 1856 (d); 1858 (e); 1921 (f); current (g) and (h)

Figure 2 also shows that variability in microstructures is largely due to cooling rate. When the cooling rate was low the final microstructures usually showed larger grain size and smaller amount of cracks and internal porosity.

3.3 Microhardness of specimens

As a matter of interest it was decided to measure the variations in micro-hardness of ten specimens. Their chemical compositions are shown in Table 4, and the trend in microhardness data is depicted in the form of a histogram shown in Fig. 3.

Generally, there were some differences in the hardness relating to the α phases (average of 180.3 VHM_{20g} and standard deviation of 21.7 VHM_{20g}), oxide inclusions (average of

Table 4 The wt.% of individual elements in the bell specimens produced from the 15th century to the 20th century being chosen for microhardness measurements

Bell material	Composition, wt.%									
Era	Sn	Pb	Zn	Bi	Ag	Sb	As	S	Ni	Fe
15th Century	7.9	2.2	0.2	0.03	0.15	1.72	0.51	1.3	0.41	0.8
16th Century	11.5	2.1	0.02	0.04	0.16	3.8	0.9	0.08	0.25	0.2
16th Century	12.1	0.52	0.04	0.02	0.03	0.31	0.15	1.1	0.06	0.32
17th Century	14.7	1.4	0.25	0.02	0.07	1.6	0.63	0.07	0.4	0.22
18th Century	15.2	1.5	0.15	0.19	0.07	1.5	0.52	0.1	0.32	0.15
19th Century	10.2	1.8	0.52	0.41	0.11	3.72	0.92	0.09	0.45	0.12
19th Century	18.4	0.32	0.09	0.007	0.003	0.22	0.06	0.15	0.03	0.56
20th Century	19.9	0.37	0.12	0.008	0.003	0.23	0.07	0.2	0.03	0.39
20th Century	20.8	0.29	0.08	0.013	0.003	0.3	0.1	0.12	0.027	0.56
20th Century	21.5	2.4	0.1	0.04	---	0.3	---	0.02	---	0.12

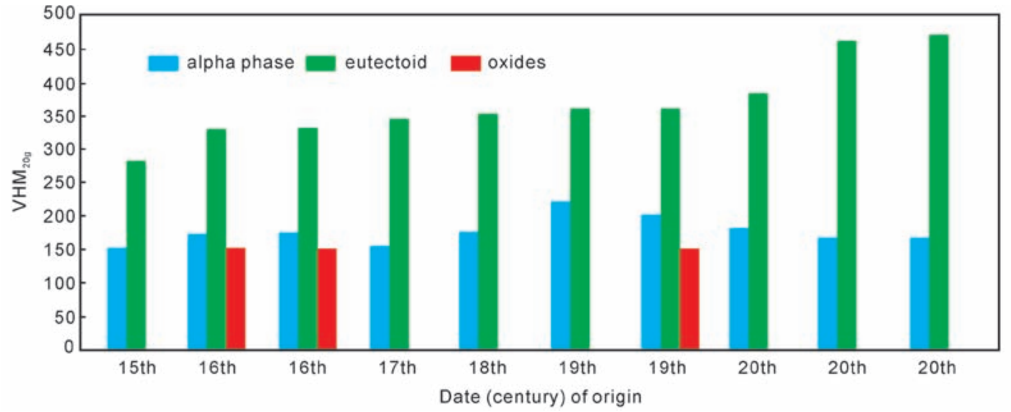


Fig. 3 Histogram summarising the measured variations in microhardness of various experimental bell materials investigated

162.6 VHM_{20g} and standard deviation of 2.1 VHM_{20g}), and eutectoid (average of 369 VHM_{20g} and standard deviation of 52.3 VHM_{20g}) when comparing sample by sample as well as bell-material by bell-material. Following the age/origins of the bell-materials there was a progressive increase in average hardness, sample from the 15th Century to the one from the 20th Century, ranging from the minimum of ~280 VHM_{20g}, to a maximum of ~470 VHM_{20g} for the ($\alpha+\delta$) eutectoid, the levels which probably reflected the higher amounts of tin and antimony in bells cast after the 18th century.

3.4 Sound of bells

As bell materials, it is critical to examine the impact of chemical composition/microstructure on the quality of bell sound considered from frequency and duration perspectives. Referring to Table 1 it appears that in Cu-Sn bronze alloys the tin element (up to 23wt.%) improves the bell sound quality, whereas the Pb (over 1.5wt.%), Zn (over 1.5wt.%) and Ag in any quantity have a negative effect on the sound in terms of time existence. Figure 4 adopted from reference [6] indicates that there was an increasing trend in the wt.% of Sn, and decreasing trend in the wt.% of potentially harmful elements particularly Pb and Ag in different bell materials produced from the 16th century to modern times.

Figure 5 shows the frequency-sound charts of two geometrically similar bells made of different Cu-Sn alloys. The bell (a), contained ~15.2wt.% of Sn, ~1.57wt.% of (Pb+Ag),

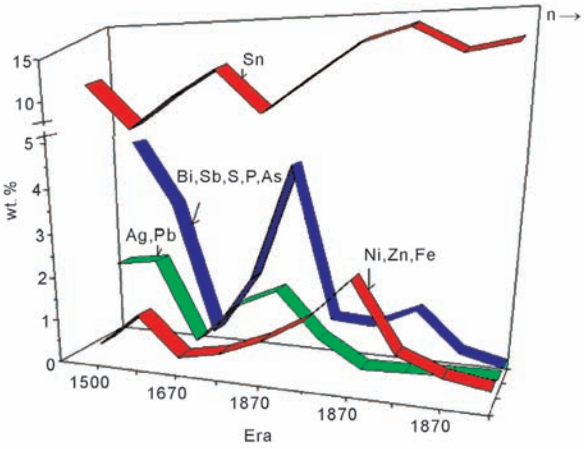
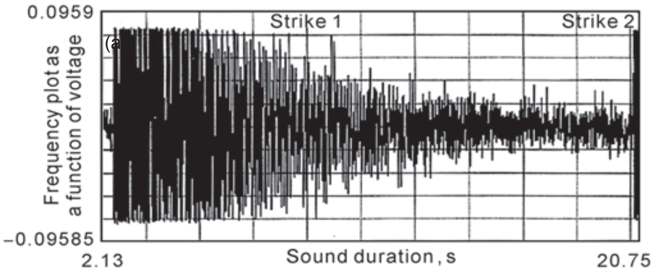


Fig. 4 A plot showing concentrations of elements found in different bell bronze materials produced from the 16th to the 20th century



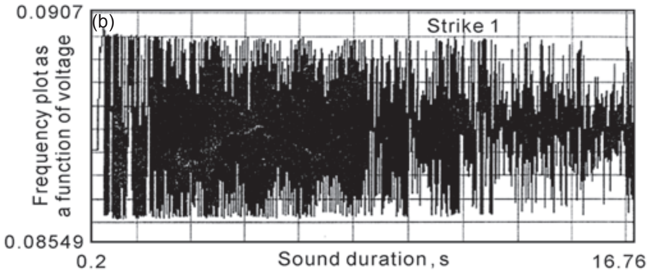


Fig. 5 The out-put frequency/sound charts of two geometrically similar bells cast of different bell-materials

~2.93wt.% of (Zn+Bi+Sb+As+Ni+Fe), with balance of Cu. The bell (b), contained ~20.8wt.% of Sn, ~0.293wt.% of (Pb+Ag), ~1.2wt.% of (Zn+Bi+Sb+As+Ni+Fe), with balance of Cu.

The patterns are plotted in a way that one can recognise one complete sound signal and discrete the end of first beating and the beginning of the next beating. The frequency charts are presented in a pattern of voltage out-put/time graphs to give (1) overall information about the tone decay (sound duration) and (2) the real width of frequency sound charts. By comparing plots 5 (a) and 5 (b), one might conclude that the sound decay decreased with lowering the wt % of tin and increasing the wt.% of lead and silver.

4 Conclusions

Traditionally bells have been manufactured by casting, and several hundred years ago skill and know-how were such that bells, often with complex bell material composition, could be created. Through metallurgical analysis of the alloys most commonly used, namely tin bronzes, the high level of 'metallurgical' skill (in melting, alloying and casting) becomes more evident, to be able to produce intricate castings free from defects such as cracks and porosity. Because of the lack of this metallurgical understanding the compositions of the alloys used in earlier centuries are substantially different from those in use today. Metallographic examination of bells fabricated through the century reveals significant differences in microstructure, which brought about by compositional variations in the alloys, as well as through differing melting and casting techniques. Also, the use of purer constituent elements, and improved melting practices, have reduced the levels of undesirable impurities such as phosphorus and sulphur, rendering the bell less susceptible to cracking and fatigue when struck by the clapper. Also the bells of better sound quality can be obtained by proper selection of alloying elements and optimum balance of their individual weight percentages in Cu-Sn alloys.

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References

[1] Derry T K, Williams T J. *A Short History of Technology: From the Earliest Times to AD 1900*. Oxford, Clarendon Press, 1960.

[2] Audy J. *Bells Evaluation from Buchner Workshop from Casting Point of View*. Engineering Thesis, The Technical University in Kosice City, Czechoslovakia, June 1988.

[3] Audy J, Cech J, Beno J. Composition and microstructure of medieval bells. *Practische Metallography*, 1992, 29(2): 74–84.

[4] Hua J. The sound of chime bells of 2400 years ago. *Endeavour*, 1993, 17:32–37.

[5] Audy K. *The* Metallurgy of Ancient Artefacts. *Ph.D Thesis*, University of South Australia, 1999.

[6] Audy K, Audy J. Analysis of bell-making process from the middle ages to recent times. *Practische Metallography*, 2006, 43(6): 271–291.

[7] Strafford K N, Newell R, Audy K, Audy J. Analysis of Bell Material from the Middle Ages to the Recent Time. *Endeavour*, Elsevier Science, 1996, 20(1): 22–27.

[8] Buchner A. *Workshop Diary and Recipes (1884-1975)*. Collection of Slovak Technical Museum (STM), Item Number HU 1384/193/84, Kosice City, Slovakia, 1984.

[9] Sarudyova M. Work of A. Buchner - the Bell-maker and Art black-Smith (1884-1975). *Collection of Slovak Technical Museum (STM)*, Brochure of Permanent Museum Exhibition, Kosice, 1987.

[10] Grigerova T. *Metallurgy of Casting Alloys of Nonferrous Materials*. Technical University (VST) Kosice, Slovakia, 1986.

[11] Vilcko J, Slovak S. *Casting Technology*. SNTL Bratislava, Slovakia, 1987.

[12] American Society for Metals: *Casting Design Handbook*, McGraw Hill Inc, USA, 1958.

[13] American Foundrymen's Society: *Pattern-makers' Manual*, McGraw Hill Inc, USA, 1953.

[14] Schubert R, D' Egidio S M. The surface composition of copper with indoor exposures ranging from 3 to 47 years. *Corrosion Science*, 1990,30(10): 999–1008.

[15] Borland D W. *The Structure of Materials*. The University of Melbourne, Australia, 1989:24–25.

[16] Heine R W, Loper C R and Rosenthal P C. *Principles of Metal Casting*. McGraw Hill Inc, USA, 1967.

[17] Zeuner F. *Dating the Past*. Methuen & Co. Ltd, London, USA, 1970.

[18] *Analytical Methods for Atomic Absorption Spectrophotometry. Brochure*, Perkin Elmer, Norwalk, 1982.

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