STRUCTURAL FORMATION REGULARITY OF Cu-Sn-Si SYSTEM LOW-TIN «SINGING» BRONZE

Uzlov K. I., Mazorchuk V. F., Dziubina A. V.

INTRODUCTION

Bell bronzes traditionally consist of copper and an increased amount of tin to $18...25\%^{1}$. Author² claims that the optimal alloy for these items is bronze with 20% tin and 80% copper. Only one normative document for this products type is GOST 8117-74 «Ship's bells. Specifications» literally establishes the following: «... bell bodies manufacturing is allowed from bell tin bronze with following chemical composition: copper 78-80%, tin 20-22% with impurities of lead 0.15%, phosphorus 0.10%, zinc, etc. – up to 0.75%».

Sacrificial singing bowls from Nepal modern studies³ indicate (Table 1) main components similar ratio in the presence of about 1% (mass) impurities.

Table 1

Chemical composition of singing bowls					
Nos.	Chemical element	Mass %	Atomic %		
1	Cu	75,82	85,15		
2	Sn	23,15	13,92		
3	Zn	0,20	0,22		
4	Sb	0,25	0,15		
5	Ag	0,22	0,15		
6	Pb	0,04	0,01		
7	Fe	0,29	0,37		
8	Ni	0,03	0,04		

Chemical composition of singing bowls

¹ Савега В.С. Благовіст: Історія дзвонів, дзвонового литва, дзвіниць та дзвонової бронзи. Дніпропетровськ: Пороги. 2000. С. 294

² Лапшин А.В. Некоторый опыт литья колоколов. *Литейное производство*. 1996, № 6. С. 56.

³ Jabłońska M., Maciąg T., Nowak M. [et al.] Thermal and structural analysis of high-tin bronze of chemical composition corresponding to the composition of the singing bowl. *Journal of Thermal Analysis and Calorimetry* (2019) 137. P. 735

This nature of alloy main components correspondence is due to casting bronze structure formation⁴ with eutectoid stable transformation products – δ -phase⁵ or even metastable martensitic transformation products formation. In general tin bronzes with satisfactory strength demonstrate high indicators of corrosion resistance and antifriction properties. They are characterized by low friction coefficient, high wear resistance, and low sensitivity to stress corrosion. At the same time, they are characterized by low fluidity⁶ due to the fact that they have a large crystallization interval of 150...200°C⁷. This is the reason with that author⁸ associates the tendency of tin bronze castings to scattered shrinkage porosity.

Nickel, zinc, lead and phosphorus are usually purposefully added as alloying elements to bronze⁹.

In addition, common impurities in tin bronzes are As and Sb at 0.01% and 0.002%, respectively. With chemical composition within specified limits industrial regulation, these impurities are located in solid solution without residue or any consequences for alloys structural state and properties.

From the point of view of alloying components effect on tin bronzes acoustic properties estimation, author¹⁰ established that Pb, P, Zn, Al, Fe have «detrimental» influence on sound. It is indicated that Al, Bi, As are acoustics «fierce enemies». That is, silicon does not belong to acoustically undesirable alloying elements category. According to generally accepted provisions, in order to reduce tin bronzes cost, in them expensive tin should be replaced with cheaper alloying elements.

Taking into account tin preciousness and scarcity and the fact that there are no contraindications of silicon in products for acoustic purposes using,

⁴ Богуслаєв В.О., Реп'ях С.І., Могилатенко В.Г. [та ін.] Ливарні властивості металів і сплавів для прецизійного литва. Запоріжжя: АТ «МОТОР СІЧ». 2016. С. 388.

⁵ Шашкина Т.Б., Чумаченко А.А., Лященко А.Б. О фазовом строении звучащей бронзы. Известия ВУЗов. Цветная металлургия. 1983, №2. С. 86.

⁶ Колачев Б.А., Ливанов В.А., Елагин В.И. Металловедение и термическая обработка цветных металлов и сплавов. Москва: Металлургия. 1981. С. 290.

⁷ Гуляев Б.Б. Теория литейных процессов. Ленинград: Машиностроение. 1976. С. 42.

⁸ Осинцев О.Е., Федоров В.Н. Медь и медные сплавы: Справочник. Москва: Инновационное машиностроение. 2021. С. 78.

⁹ Попова Е.Н., Сударева С.В., Романов Е.П. [и др.]. Влияние легирования на структуру бронзы с повышенным содержанием олова. *Физика металлов и металловедение*. 2007, Том 103. № 2. С. 165.

¹⁰ Евтихеев С.В. Литье колоколов. Возрождение традиций. *Литье и металлургия*. 2000, № 4. С. 101.

authors¹¹ proposed as bell bronze copper alloy in which Sn is completely replaced by Si. According to authors¹² data, alloys BrSi5FeZnPb (5.0-5.5%wt.Si) and BrSi6Mn (5.5-6.0%wt.Si), which are additionally alloyed with Mn, Zn, Fe, Pb are effective substitutes for scarce and expensive tin bronzes with damping capacity higher than classical bell bronze.

Based on the same task of acoustic bronzes containing about 20%Sn cost reducing, the aim of economically alloyed bronze composition developing with expensive tin replacement with silicon has been formulated in the present work.

1. Ternary Cu-Sn-Si system alloys structural formation regularity microstructural investigation

There is an established opinion¹³ that of all impurities present in bronzes, aluminum and silicon have the most harmful effect on properties. This view about negative influence of doping bronze with silicon caused strict regulatory limitation of this component amount in tin bronzes. DSTU 3474-96 «Casting bronzes in pigs. Specifications» sets Si concentration limit: 0.02 ... 0.05%, DSTU GOST 5017:2007 «Wrought tin bronzes. Grades» – 0.002 ... 0.005 wt.%, depending on bronze grade. According to GOST 8117-74 «Ship's bells. Specifications» requirements, total amount of impurities, including silicon, cannot exceed 0.75%. Due to such normative and industrial limitation and, as a result, lack of professional pragmatic interest, authors of this work could not find three-component copper-tin-silicon system state diagram in general use reference sources. Therefore, in these studies, assessment of ternary Cu-Sn-Si system alloys structural formation regularity has been carried out on the basis of own microstructural analysis according to requirements of ASTM E3 -11(2017) «Standard Guide for Preparation of Metallographic Specimens» results. At the same time, isolated information about silicon influence on tin bronzes structural formation peculiarity has been taken into account.

¹¹ Пат. 2265894 РФ, МПК7 G10К 1/00. Материал для изготовления колоколов и звучащих элементов ударных музыкальных инструментов / О.Б. Лисовская, В.А. Лисовский; заявл. 07.07.04; опубл. 10.12.05// Бюл. 2005. №34. С.4

¹² Лисовский В.А., Лисовская О.Б., Кочеткова Л.П., Фавстов Ю.К. Экономнолегированные колокольные бронзы с повышенными характеристиками механических свойств. *Металловедение и термическая обработка металлов.* 2007, №5 (623). С. 23

¹³ Курдюмов А.В., Пикунов М.В., Чурсин В.М. Литейное производство цветных и редких металлов. Москва: Металлургия. 1982. С. 295

Authors¹⁴ suggested that in Si esence, initial β -phase and, as a result, Cu-Sn alloys $\alpha+\delta$ eutectoid change their composition. This assumption has been confirmed by studies¹⁵.

According to these studies results, it has been established that at silicon content increasing tin bronze hardness sharply increases up to 5.0 wt.%Si, despite an insignificant increasing in α -solid solution microhardness. That is, according to work main reason for tin bronze hardness sharp increasing when alloyed with silicon is primary β -phase and, as a result, derived eutectoid structural component doping with silicon increasing accompanied its microhardness achievement of 3200...3500 MPa. Indicative in this case is the fact that Cu-Si system alloy eutectoid itself has a much lower microhardness: 2000 MPa (at 2.0wt.%Si) and 2700 MPa (at 5.0wt.%Si).

In addition, during Cu-Sn-Si system alloys microstructures identification, authors proceeded from theoretical provisions that logically follow from Cu-Si and Cu-Sn binary diagrams analysis.

1. In both diagrams copper corners ($T_{meltCu}=1084^{\circ}C$), after primary α -Cu dendrites crystallization, first peritectic transformation takes place L+ α -Cu $\rightarrow \beta$. Peritectic equilibrium temperatures are: in Cu-Sn system 798°C and in Cu-Si system (according to various authors) 852...785°C, i.e., they are practically the same. This leads to conclusion that liquidus surface in copper corner of Cu-Sn-Si ternary system is completely shared between Cu-Si and Cu-Sn axes. Two-phase spatial region L+ α is located below it. Liquid phase composition naturally depends on components in alloys concentration. Further during cooling peritectic reaction L+ α -Cu $\rightarrow \beta$ occurs. Composition of β -phase obviously depends on initial phases' composition, primarily – liquid phase. Important in this case is the facts that in both systems β -phases are crystallographically similar – BCC (Im $\overline{3}m$) with almost identical lattice parameters – 0.2981 nm in Cu-Sn system and 0.2854 nm in Cu-Si system¹⁶.

¹⁴ Лебедев К.П., Райнес Л.С., Шеметев Г.Ф., Горячев А.Д. Литейные бронзы. Ленинград: Машиностроение, 1973. С. 82.

¹⁵ Комков В.Г., Стариенко В.А. Физико-механические свойства легированных меди и оловянной бронзы. Электронное научное издание «Ученые заметки ТОГУ». 2013, Том 4. № 4. С. 1322 URL:http://ejournal.khstu.ru/media/2013/TGU_4_254.pdf

¹⁶ Диаграммы состояния двойных металлических систем: Справочник в 3-х томах /Под ред. Н.П. Лякишева. Москва: Машиностроение. 2001. Т. 2. С. 323.

It follows from above that in Cu-Sn-Si ternary system: peritectic reaction product is β -phase of variable chemical composition, according to components totality in alloy.

Eutectoid transformations subsequent kinetics is naturally determined by initial β -phase doping degree.

That is, in final bronze structure, it is reasonable to expect eutectoid component formation with different doping degree of chemical compound that is its part, or various intermediate phases' presence, or doped high-temperature β -phase stabilization at room temperature without transformation, or even two peritectic reactions of Cu-Sn and Cu-Si systems products simultaneous existence. Such phases, in order to prevent confusion with previously used designations of martensitic phases¹⁷, are conventionally accepted in present work – $\beta_{(Cu-Sn)}$ for Cu-Sn system and $\beta_{(Cu-Si)}$ for Cu-Si system.

2. Due to significant difference in melting temperatures of copper (T_{meltCu}=1084°C) and tin (T_{meltSn}=231.9°C), researchers of threecomponent system Cu-Sn-Al¹⁸ provide information about existence in diagram tin corner extended region of immiscibility gap of two liquid phases L' and L'' with corresponding monotectic equilibrium below it. Based on this position, for alloy with fixed copper concentration of 10%, phase equilibrium temperatures of diagram corresponding polythermal section has been given: immiscibility curve is 587°C, monotectic horizontal is 558°C, eutectic equilibrium with solid phases participation is provide 523.8°C. Authors¹⁹ information high-temperature on transformations of Cu-Sn-Al system alloys at solidification first stages. First reaction during cooling is $L' \rightarrow L'' + \beta$ at temperature of 785°C. It is followed by $\beta + \gamma CuSn \rightarrow L' + CuSn$ at 642°C.

It is clear that it is impossible to unambiguously translate these regularities to another diagram of Cu-Sn-Si system, but it is useful to take into account fact of solid phase initial crystallization from liquid and subsequent crystallization kinetics according to three-phase reaction of different composition liquid phase transformation. Metallographic studies

¹⁷ Исайчев И. Превращения в эвтектоидных сплавах Cu-Sn. Журнал технической физики. 1939, Т.9. № 14. С. 1286.

¹⁸ Kotadia H.R., Patel J.B., Fan Z. [et al.] Processing of Al-45Sn-10Cu Based Immiscible Alloy by a Rheomixing Process. *Solid State Phenomena*. 2008, Vols. 141-143. P. 529.

¹⁹ Mircovic D., Grober J., Schmid-Fetzer R.. Liquid Demixing and Microstructure Formation in Ternary Al-Sn-Cu Alloys. *Materials Science & Engineering*. 2008, A 487. P. 456.

of Cu-Sn-Si system alloys with total Sn+Si content up to 5% by mass demonstrate three-component bronzes single-phase structure presence. Illustration of this regularity is presented by several examples in Figure 1.



a, c - ×400; b, d - ×200 Fig. 1. Microstructure of three-component Cu-Sn-Si system alloys with Si and Sn components ratio: 0.618wt.%Si + 0.649wt.%Sn (a), 0.732wt.%Si+3.186wt.%Sn (b), 1.124wt.% Si+0.989wt.%Sn (c), 2.469wt.% Si +1.946wt.%Sn (d)

Exceeding this specified concentration (5wt.%Si+Sn) leads to Cu-Sn-Si alloys single-phase structure losing and to formation in alloys β -phase and/or its products of solid-phase decomposition according to eutectoid transformation mechanism additionally to primary copper-based solid solution dendrites α -Cu^I (Figs. 2-4).

It has been established that, in this case, silicon amount in threecomponent alloy composition has fundamental effect on final structure.

Figures 2 and 3 shows microstructure examples of alloys with silicon up to 4wt.% and various tin amounts.

Specified group test samples microstructures metallographic analysis demonstrates (see Fig. 2 a \rightarrow d) tendency to original β -phase in bronze

eutectoid decomposition products amount increasing with tin content in alloys increasing.



a, b, d - ×200; c - ×400 Fig. 2. Microstructure of three-component Cu-Sn-Si system alloys with Si and Sn components ratio: 2.312wt.%Sn + 3.934wt.%Si (a), 4.044wt.%Sn + 1.889wt.%Si (b), 9.560wt.%Sn + 1.389wt.%Si (c), 10.173wt.%Sn + 3.993wt.%Si (d)



a, b – ×1000; c – ×500

Fig. 3. Microstructure of three-component Cu-Sn-Si system alloys with Si and Sn components ratio: 2.312wt.%Sn + 3.934wt.%Si (a), 4.044wt.%Sn + 1.889wt.%Si (b), 10.173wt.%Sn + 3.993wt.%Si (c)

At the same time, Figure 3 evidences that in all cases of this concentration range alloys, β -phase underwent eutectoid transformations after solidification upon further cooling in solid state. In addition, in all cases (see Fig. 3 a, b, and c), significant amount of residual original β -phase has been recorded. That is, solid-phase transformations for Cu-Sn-Si system alloys take place in difficult manner and not until high-temperature phase decomposition completed.



Figure 4 Microstructure of three-component Cu-Sn-Si system alloys with Si and Sn components ratio: 4.188wt.%Si + 3.662wt.%Sn (a), 4.950wt.%Si + 2.080wt.%Sn (b), 5.355wt.%Si + 1.282wt.%Sn (c, d)

Different structure formation kinetics has been observed in Cu-Sn-Si system alloys with silicon content of more than 4% by mass.

This phenomenon is illustrated on several alloys examples with silicon content of 4.59 wt.%, 4.95 wt.%, and 5.35 wt.% in Figure 4. In this case (see Fig. 4), initial β -phase is stabilized by silicon and does not undergo low-temperature eutectoid transformations in solid state.

2. Scanning electron microscopic, X-ray spectral microscopic, energy dispersive spectral, X-ray structural phases and metallographic investigations of Cu-Sn-Si alloys of optimized composition

Metallographic microphotograph (Fig. 5) shows the structure of alloy with component ratio of 4,950wt.%Si+2,080wt.%Sn, which corresponds to optimal concentration range (silicon within 4.5...5.5%, tin -2...5% at mass ratio Si/Sn≥1)²⁰. Optimization procedure according to values of acoustic indicators, taking into account this publication data, was realized in works²¹.



Fig. 5. Microstructure (×500) of three-component Cu-Sn-Si alloy with ratio 4,950wt.%Si + 2,080wt.%Sn

Microstructure in Figure 5 analysis shows that such an alloy structure is two-phases, that is, copper solid solution and intermediate phase in continuous form, without traces of solid-phases transformations. This compound look like thin thread branched in α -Cu solid solution body. Taking into account the fact that this phase is chemical compound with lattice parameter of 0.2981nm, and its surroundings (α -Cu) have another lattice with parameter almost 1.5 times larger – 0.3608nm, it is obvious that their interfacial boundary is internal structural stresses zone of II type.

²⁰ Патент України № 146989 / Узлов К.І., Реп'ях С.І., Мазорчук В.Ф., Дзюбіна А.В., Кімстач Т.В. Спосіб виготовлення дзвонів та звукових елементів музичних інструментів ударного типу: заявл. 16.11.2020; опубл. 31.03.2021, Бюл. № 13.

²¹ Патент України № 147278 / Узлов К.І., Реп'ях С.І., Дзюбіна А.В., Мазорчук В.Ф., Кімстач Т.В. Спосіб виготовлення бронзи музичної: заявл. 05.10.2020; опубл. 28.04.2021, Бюл. № 17.

Scanning electron microscopic studies²² (Fig. 6) of alloy close in composition to optimal concentration interval clearly show that this chemical compound is continuous in entire casting volume. That is, this is continuous resonator («string»).



Fig. 6. Studied sample surface scanning electron microscopic images of three-component Cu-Sn-Si alloy with the ratio: 4.188wt.%Si + 3.662wt.%Sn in secondary (a) and scattering (b) electrons

Figure 5 analysis shows that this structural system has one more structural stresses internal element – segregated α -Cu phase with well-defined boundary between two microstructural zones of differently saturated with main components copper solid solution. Such separation boundary indicates different regularities of copper matrix microstructure certain sections formation – primary crystals α -Cu^I and α -Cu_{react} – residual reactive.

It is obvious that, due to insufficient silicon stabilizer of hightemperature phase amount, in bronze with 4.188wt.%Si + 3.662wt.%Sn chemical compound structure (Fig. 6) includes single and undeveloped, germinal areas of eutectoid transformations.

²² Кальнер В.Д., Зильберман А.Г. Практика микрозондовых методов исследования металлов и сплавов. Москва: Металлургия. 1981. С. 67

Color map of X-ray spectral²³ microscopic analysis (X-raySMA) results is presented in Figure 7.



Fig. 7. X-ray spectral microscopic presentation of elements distribution in three-components Cu-Sn-Si alloy with components ratio 4,950wt.%Si + 2,080wt.%Sn (electron image and characteristic radiations)

X-raySMA results (see Figure 7) demonstrate the fact that copper is naturally an element that is uniformly located on the surface of test sample in all phases. Similar to copper is silicon localization. According to characteristic radiation image data (see Figure 7), its distribution is also uniform across specimen section.

Another picture occurs in Sn characteristic emission (see Figure 7). In this case, chemical component Sn distribution characteristic clearly shows that chemical compound is a phase with tin increased content.

Quantitative assessment of components content in intermediate phase has been carried out using energy dispersive spectral (EDS) analysis (Figure 8 and Table 2).

²³ Приборы и методы физического металловедения [Текст]: Пер. с анг. / Под ред. Ф. Вейнберга. М.: Мир, 1974. Выпуск 2. С. 221



Fig. 8. Electron microscopic image (in secondary electrons) of threecomponent Cu-Sn-Si alloy with component ratio of 4.950wt.%Si + 2.080wt.%Sn research sample surface (Spectrum 5 – chemical compound)

Figure 8 shows one of three EDS analysis cathode ray points examples («Spectrum 5»). Quantitative data (three measurements) of components in intermediate phase local concentrations are presented in Table 2.

Table 2

EDS analysis results of main elements content in three-component Cu-Sn-Si alloy with ratio of 4.950wt.%Si + 2.080wt.%Sn intermediate phase determination

Alloying component	SiKa, atomic %	CuLa1_2, atomic %	SnLa1, atomic %
Spectrum 5	7,06	79,26	13,62
Spectrum 4	6,55	79,21	14,18
Spectrum 3	6,61	79,76	13,51
Average	6,74	79,41	13,77

Quantitative EDS analysis (see Table 2) results indicate that intermediate phase is chemical compound containing an average of 79.41at.% copper and 13.77at.% tin, which in terms of atomic ratio corresponds to \sim 5/1. That is, based on obtained result, this chemical compound is peritectic genesis Cu-Sn system phase of Cu₅Sn. Certain amount (~6.74at.%) of dissolved silicon is also observed in this phase.

In addition, concentration of dissolved components in α -Cu solid solution has been determined by EDS analysis method.

Cathode ray positions when determining the local chemical elements concentrations are presented in α -Cu_{react} and α -Cu^I as «Spectrum 1» and «Spectrum 2» in Figure 9, respectively.



Fig. 9. Electron microscopic images of three-component Cu-Sn-Si alloy with ratio 4,950wt.%Si + 2,080wt.%Sn sample research surface (Spectrums 1, 2 – α-Cu solid solutions)

EDS analysis quantitative results of α -Cu solid solutions are shown in Table 3.

 Table 3

 EDS analysis results of three-component Cu-Sn-Si alloy with ratio of

 4.950wt.%Si + 2.080wt.%Sn main components* content

 in a Cu solid solutions (according to Fig. 9)

In a-Cu solutions (according to Fig. 9)						
Alloying	SiKa, %		CuLa1_2, %		SnLa1,%	
component	Weight	Atomic	Weight	Atomic	Weight	Atomic
Spectrum 1	4,55	9,75	94,61	89,67	0,59	0,30
Spectrum 2	9,91	12,56	91,68	86,12	2,22	1,12

*) data presented are average of at least five measurements for each «Spectrum 1» and «Spectrum 2»

Analysis obtained data in Table 3 confirm significant difference of components concentrations in α -Cu_{react} and α -Cu^I solid solutions. It has been determined that reaction origin solid solution α -Cu_{react} (see Table 3 – «Spectrum 1») is two times less saturated with silicon than original α -Cu^I solid solution (see Table 3 – «Spectrum 2») – 4, 55wt.%Si vs. 9.91wt.%Si.

Similar situation has been observed with tin solubility in α -Cu solid solution. In this case, tin solubility in α -Cu_{react} (see Table 3 – «Spectrum 1») is 0.59wt.%Sn. At the same time, in α -Cu^I solid solution (see Table 3 – «Spectrum 2») this amount is 2.22 wt.% Sn. Difference is almost four times.

That is, fact of significant (in multiples) liquation in copper solid solution at the same time of both components is confirmed quantitatively. As mentioned above, presence of primary α -Cu^I crystals and residual reactive α -Cu_{react} with dissolved components fundamentally different

amount creates another structural stresses system in castings body and acts as one more acoustic resonator.

Intermediate phase nature has been additionally studied by X-ray structural phase analysis²⁴. Three-component Cu-Sn-Si alloy with ratio of 4.950wt.%Si + 2.080wt.%Sn typical diffractogram is presented in Figure 9.

Identification results of X-ray diffraction spectrum diffraction maxima in Figure 9, using reference literature sources²⁵, are presented in Table 4.

According to X-ray structural phase analysis results, it has been confirmed that intermediate phase in this optimal chemical composition alloy is Cu_5Sn . That is β -phase – subject of peritectic formation nature in two-component Cu-Sn system.

As shown by existing work comprehensive analysis data, this hightemperature phase is preserved at room temperature stabilized by silicon and does not undergo solid-phase transformations with eutectoid structural states formation.

Cu-Sn-Si three-component system optimal concentration alloy typical microstructure final identification results on example of bronze with ratio of 4,950wt.%Si + 2,080wt.%Sn are presented in Figure 10.



Fig. 9. Three-component Cu-Sn-Si alloy with component ratio of 4.950wt.%Si + 2.080wt.%Sn sample X-ray diffraction spectrum

²⁴ Миркин Л.И. Рентгеноструктурный контроль машиностроительных материалов. Москва: Машиностроение, 1979. С. 107

²⁵ Горелик С.С., Расторгуев Л.Н., Скаков Ю.А. Рентгенографический и электроннооптический анализ. Москва: Металлургия. 1970. С. 60

Table 4

Three-component Cu-Sn-Si alloy with ratio of 4.950wt.%Si +			
2.080wt.%Sn experimental data on X-ray structural phase analysis			
results identification			

i cours racintification						
№	d _{hkl} , Å experimental	d _{hkl} , Å reference	Ι	Phases	(hkl)	
1	2,21	2,23	1,0	β-Cu ₅ Sn	110	
2	2,08	2,08	1,0	α-Cu	111	
3	1,8	1,798	0,86	α-Cu	200	
4	1,51	1,58	0,29	β-Cu ₅ Sn	200	
5	1,27	1,271	0,71	α-Cu	220	
6	1,18	1,117	0,17	β-Cu ₅ Sn	220	
7	1,08	1,083	0,86	α-Cu	311	
8	1,06	1,000	0,29	β-Cu ₅ Sn	310	
9	1,04	1,038	0,56	α-Cu	222	



Fig. 10. Ternary Cu-Sn-Si alloy with ratio of 4.950wt.%Si + 2.080wt.%Sn phase components microstructural (×200) presentation

3. Functional advantages and innovation of scientific – technical work solutions

In addition to acoustic characteristics optimization, in present work, in order to compare mechanical properties and impact resistance, similar plates and samples for mechanical tests have been also made from bronze according to chemical composition optimized in previous sections of this investigation.

The average values of investigated bronzes («classic» bell bronze and own elaboration) 15 mechanical properties measurements are shown in Table 5.

	Tal	bl	e	5
--	-----	----	---	---

Sample	UTS, MPa	δ, %	KCU, J/cm ²
«Classic» bell bronze	260-290	6-9	31-34
Innovative	310-405	4-7	56-83

Mechanical properties of innovative and «classic» bronzes

From obtained data analysis (see Table 3.1), it follows that, with comparable relative elongation values, in terms of strength and impact toughness, innovative bronze exceeds similar indicators of «classical» bell bronze by $\sim 1.5...2.5$ times.

This evidences that, compared to «classic» bell bronze, cast bronze products with developed optimal chemical composition are characterized by greater reliability and durability during operation within its application specified area.

Innovative bronze acoustic parameters have been evaluated on cast plates of small diameter. At the same sound volume, harmony, same or greater sound prolongation, plates made of innovative bronze, like plates made of «classical» bell bronze, have three overtones, which manifest themselves in wider frequency range than «classic» bell bronze (Fig. 11).



Fig. 11. Plates from «classic» bell and elaborated bronzes sound frequency diagram

At the same time, tone pitch varies with plate size and shape, bronze composition or, if necessary, appropriate product²⁶ heat treatment.

Innovative bronze using will make it possible to manufacture not only new types of cast musical instruments acoustic elements, bells and chimes,

²⁶ Мазорчук В.Ф., Репях С.И., Узлов К.И. [и др.] Поющая бронза. Матеріали науково-технічної конференції: Х Міжнародна науково-технічна конференція «Нові матеріали і технології в машинобудуванні-2018», 24...25 квітня 2018 р. Київ: КПІ ім. Ігоря Сікорського. 2018. С. 116

but also, practically, entire range of well-known musical instruments elements, including cymbals such as Crash, Ride, Sizzole, Splash, etc.

Present work innovative solutions on methods of making musical bronze, obtaining bronze castings and making bells and percussion musical instruments acoustic elements are covered by intellectual property protection documents.

CONCLUSIONS

1. In the present work, three-component system Cu-Sn-Si copper corner of conodes triangle alloys phase transformations regularities have been established due to structure formation metallographic studies results:

– in Cu-Sn-Si system alloys with total Sn+Si content of up to 5% by mass, single-phase α -Cu structure of three-component bronzes creates;

- Sn+Si in tin-silicon bronze total concentration excess by more than 5wt.% leads to formation in alloys, in addition to copper-based solid solution (α -Cu^I) primary dendrites, also β -phase and/or its solid-phase decomposition products;

– at the same time, for alloys with Si content of up to 4 wt.%, trend towards the amount of original β -phase eutectoid decomposition products increasing in bronze was recorded with tin content in alloys increasing;

– another structure formation kinetics is observed in Cu-Sn-Si system alloys with silicon content of more than 4 wt.% – in this case, initial β -phase is stabilized by silicon and in solid state does not undergo low-temperature eutectoid transformations with small (up to 4 wt.%Sn) tin amount in bronze.

2. Results regarding silicon content lower limit in amount of 4.5% by mass accuracy was confirmed by electron microscopic analysis method. It has been demonstrated that in tin-silicon bronzes with smaller Si (4.0...4.5% by mass) amount, eutectoid transformations embryonic areas are observed in chemical compound structure – isolated and undeveloped. But they also turn out to be significant from the point of view of such material structurally sensitive characteristic as sound duration.

3. For the first time, with comprehensive using of scanning electron microscopic, X-ray spectral, energy dispersive, X-ray structural phase and metallographic studies of Cu-Sn-Si alloys with optimized composition (silicon 4.5...5.5% by mass and tin 2...5% by mass at mass ratio Si/Sn \geq 1), tin-silicon bronzes with main components optimal ratio structural formation regularities are established. This structure consists of peritectic origin β -phase (chemical compound Cu₅Sn) and matrix. At the same time, matrix consists of α -Cu phase with clear segregation demarcation

boundary of different genesis solid solution areas: primary α -Cu^I crystals and residual reactive α -Cu_{react}. with fundamentally different dissolved components amounts.

4. According to the work results, idea of silicon alloying influence on tin bronze has been further developed. It was established that, with optimal components ratio in investigated bronzes, silicon, as alloying component of high-temperature β -Cu₅Sn phase, stabilizes this chemical compound in metastable temperature region with constant further labile existence, even after normative castings low-temperature tempering.

5. It was established that this «singing» bronze structural state is the basis for two systems of structural stresses in castings body existence, which act as acoustic resonators in products material. These systems are: α -Cu solid solution liquated areas of different genesis and interphase boundary α -Cu $\leftrightarrow\beta$ -Cu₅Sn, which causes occurrence of II type internal structural stresses between α -Cu and chemical compound Cu₅Sn, which are fundamentally dissimilar in nature.

6. According to investigation results, elaborated new bronze for bells and percussion musical instruments. It is in terms of strength and impact toughness, exceeds «classical» bell bronze indicators by ~1.5...2.5 times with comparable relative elongation values. This evidences that, compared to «classic» bell bronze, cast bronze products with developed optimal chemical composition are characterized by greater reliability and durability during operation within its application specified area.

7. From functional point of view, at the same sound volume, harmony, same or greater sound prolongation, plates made of innovative bronze, like plates made of «classical» bell bronze, have three overtones, which manifest themselves in wider frequency range than «classic» bell bronze

8. Present work innovative solutions on methods of making musical bronze, obtaining bronze castings and making bells and percussion musical instruments acoustic elements are covered by intellectual property protection documents

9. Innovative bronze using will make it possible to manufacture not only new types of cast musical instruments acoustic elements, bells and chimes, but also, practically, entire range of well-known musical instruments elements, including cymbals such as Crash, Ride, Sizzole, Splash, etc.

SUMMARY

Based on the task of acoustic bronzes containing about 20%Sn cost reducing, the aim of economically alloyed bronze composition with

expensive tin replacement by silicon developing has been formulated in the present work. Three-component system Cu-Sn-Si bronzes structure formation has been studied and conodes triangle copper corner alloys phase transformations regularities were determined. It was established that in Cu-Sn-Si system alloys with Si content more than 4wt.%, original βphase is stabilized by silicon and in solid state does not undergo lowtemperature eutectoid transformations with small (up to 4wt.%) tin amount in bronze. It is shown that this «singing» bronze structural state is the basis for two systems of structural stresses in castings body existence, which act as acoustic resonators in products material. These systems are: α-Cu solid solution liquated areas of different genesis and interphase boundary a- $Cu \leftrightarrow \beta$ -Cu₅Sn, which causes occurrence of II type internal structural stresses between α -Cu and chemical compound Cu₅Sn, which are fundamentally dissimilar in nature. For the first time, with comprehensive using of scanning electron microscopic, X-ray spectral, energy dispersive, X-ray structural phase and metallographic studies of Cu-Sn-Si alloys with optimized composition (silicon 4.5...5.5% by mass and tin 2...5% by mass at mass ratio Si/Sn≥1), tin-silicon bronzes with main components optimal ratio structural formation regularities are established. New bronze for bells and percussion musical instruments in terms of strength and impact toughness exceeds «classical» bell bronze indicators by ~1.5...2.5 times with comparable relative elongation values. This evidences that, compared to «classic» bell bronze, elaborated cast bronze products with developed optimal chemical composition are characterized by greater reliability and durability during operation within its application specified area. Present work innovative solutions on methods of making musical bronze, obtaining bronze castings and making bells and percussion musical instruments acoustic elements are covered by intellectual property protection documents.

BIBLIOGRAPHY

1. Савега В.С. Благовіст: Історія дзвонів, дзвонового литва, дзвіниць та дзвонової бронзи. Дніпропетровськ: Пороги, 2000. 461 с. URL: https://nmetau.edu.ua/file/hudozhne_litvo_ta_yogo_rol_v_ istoriyi.pdf

2. Лапшин А.В. Некоторый опыт литья колоколов. Литейное производство. 1996, № 6. С. 56-57.

3. Jabłońska M., Maciąg T., Nowak M. [et al.] Thermal and structural analysis of high-tin bronze of chemical composition corresponding to the composition of the singing bowl. *Journal of Thermal Analysis and*

Calorimetry (2019) 137. P. 735–741. URL: https://doi.org/10.1007/s10973-01908015-z

4. Богуслаєв В.О., Реп'ях С.І., Могилатенко В.Г. [та ін.] Ливарні властивості металів і сплавів для прецизійного литва. Запоріжжя: АТ «МОТОР СІЧ». 2016. 474 с. URL:

http://195.20.96.242:5028/khportal/TopicDescription?topic_id=KhH AI.Topic.14276

5. Шашкина Т.Б., Чумаченко А.А., Лященко А.Б. О фазовом строении звучащей бронзы. Известия ВУЗов. Цветная металлургия. 1983, №2. С. 86-90

6. Колачев Б.А., Ливанов В.А., Елагин В.И. Металловедение и термическая обработка цветных металлов и сплавов. Москва: Металлургия. 1981. 416 с. URL: https://www.bukinist.in.ua/books/ view/12597

7. Гуляев Б.Б. Теория литейных процессов. Ленинград: Машиностроение. 1976. 216 с. URL: https://www.twirpx.link/file/ 43620/

8. Осинцев О.Е., Федоров В.Н. Медь и медные сплавы: Справочник. Москва: Инновационное машиностроение. 2021. 360 с. URL: https://tech.edu-lib.com/tehnicheskie-zhurnaly/osincev-fedorovlitejnye-mednye-splavy-prilozhenie-k-inzhenernomu-zhurnalu-1-2003

9. Попова Е.Н., Сударева С.В., Романов Е.П. [и др.]. Влияние легирования на структуру бронзы с повышенным содержанием олова. Физика металлов и металловедение. 2007, Том 103. № 2. С. 165-179.

10. Евтихеев С.В. Литье колоколов. Возрождение традиций. *Литье и металлургия*. 2000, № 4. С. 101-107. URL: https://lim.bntu.by/jour/article/view/2843

11. Пат. 2265894 РФ, МПК7 G10К 1/00. Материал для изготовления колоколов и звучащих элементов ударных музыкальных инструментов / О.Б. Лисовская, В.А. Лисовский; заявл. 07.07.04; опубл. 10.12.05// Бюл. 2005. № 34. С. 4. URL: https://www.dissercat.com/content/issledovanie-i-razrabotka-

kolokolnykh-bronz-s-uluchshennymi-funktsionalnymi-kharakteristikam

12. Лисовский В.А., Лисовская О.Б., Кочеткова Л.П., Фавстов Ю.К. Экономнолегированные колокольные бронзы с повышенными характеристиками механических свойств. *Металловедение и термическая обработка металлов.* 2007, №5 (623). С. 23-25.

13. Курдюмов А.В., Пикунов М.В., Чурсин В.М. Литейное производство цветных и редких металлов. Москва: Металлургия. 1982. 353 с. URL: https://www.twirpx.com/file/1640277/

14. Лебедев К.П., Райнес Л.С., Шеметев Г.Ф., Горячев А.Д. Литейные бронзы. Ленинград: Машиностроение, 1973. 312 с.

15. Комков В.Г., Стариенко В.А. Физико-механические свойства легированных меди и оловянной бронзы. Электронное научное издание «Ученые заметки ТОГУ». 2013, Том 4. № 4. С. 1322 – 1329. URL: http://ejournal.khstu.ru/media/2013/TGU_4_254.pdf

16. Диаграммы состояния двойных металлических систем: Справочник в 3-х томах /Под ред. Н.П. Лякишева. Москва: Машиностроение. 2001. Том 2. 1024 с. URL: https://www.twirpx.com/file/106147/

17. Исайчев И. Превращения в эвтектоидных сплавах Cu-Sn. Журнал технической физики. 1939, Т.9. №14. С. 1286-1292

18. Kotadia H.R., Patel J.B., Fan Z. [et al.] Processing of Al-45Sn-10Cu Based Immiscible Alloy by a Rheomixing Process. *Solid State Phenomena*. 2008, Vols. 141-143. P. 529-534. URL: https://www.researchgate.net/publication/239059111_Processing_of_Al4 5Sn10Cu_Based_Immiscible_Alloy_by_a_Rheomixing_Process

19. Mircovic D., Grober J., Schmid-Fetzer R.. Liquid Demixing and Microstructure Formation in Ternary Al-Sn-Cu Alloys. *Materials Science* & *Engineering*. 2008, A 487. P. 456-467 doi:10.1016/j.msea.2007.10.043, URL: https://scholar.google.com.ua/scholar?q=Materials+Science+% 26+Engineering.+2008,+A+487.+P.+456-467&hl=uk&as_sdt=0&as_ vis=1&oi=scholart

20. Патент України № 146989 / Узлов К.І., Реп'ях С.І., Мазорчук В.Ф., Дзюбіна А.В., Кімстач Т.В. Спосіб виготовлення дзвонів та звукових елементів музичних інструментів ударного типу: заявл. 16.11.2020; опубл. 31.03.2021, Бюл. № 13.

21. Патент України № 147278 / Узлов К.І., Реп'ях С.І., Дзюбіна А.В., Мазорчук В.Ф., Кімстач Т.В. Спосіб виготовлення бронзи музичної: заявл. 05.10.2020; опубл. 28.04.2021, Бюл. № 17.

22. Кальнер В.Д., Зильберман А.Г. Практика микрозондовых методов исследования металлов и сплавов. Москва: Металлургия. 1981. 216 с. URL: https://www.twirpx.com/file/1688965/

23. Приборы и методы физического металловедения [Текст]: Пер. с анг. /Под ред. Ф. Вейнберга. М.: Мир, 1974. Выпуск 2. 364 с. URL: https://www.twirpx.com/file/2840641/

24. Миркин Л.И. Ренгеноструктурный контроль машиностроительных материалов. Москва: Машиностроение, 1979. 134 с. URL: https://ar.b-ok.global/book/2751756/ffc3df

25. Горелик С.С., Расторгуев Л.Н., Скаков Ю.А. Рентгенографический и электроннооптический анализ. Москва: Металлургия. 1970. 366 с. URL: https://ru.scribd.com/doc/119745141/B7

26. Мазорчук В.Ф., Репях С.И., Узлов К.И. [и др.] Поющая бронза. Матеріали науково-технічної конференції: Х Міжнародна науковотехнічна конференція «Нові матеріали і технології в машинобудуванні-2018», 24...25 квітня 2018 р. Київ: КПІ ім. Ігоря Сікорського. 2018. С. 116-118 URL: http://metalcasting.kpi.ua/ index/schedConfs/archive

Information about the authors: Uzlov Kostiantyn Ivanovych,

Doctor of Technical Science, Professor at the Materials Science and Heat Treatment of Metals Department Ukrainian State University of Science and Technology 4, Gagarina Ave., Dnipro, 49600, Ukraine

Mazorchuk Volodymyr Fedorovych,

Candidate of Technical Science, Associate Professor at the Foundry Department Ukrainian State University of Science and Technology 4, Gagarina Ave., Dnipro, 49600, Ukraine

Dziubina Alina Valentynivna,

Postgraduate Student at the Materials Science and Heat Treatment of Metals Department Ukrainian State University of Science and Technology 4, Gagarina Ave., Dnipro, 49600, Ukraine