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MECHANICAL PROPERTIES AND STRUCTURE OF CU-AL-SI-SN-MN SYSTEM NON-MAGNETIC CAST BRONZES

Purpose. To establish regularity of Cu-Al-Si-Sn-Mn system non-magnetic corrosion-resistant bronze chemical composition on structure and mechanical properties complex influence and to determine its rational composition in terms of suitability for manufacturing products by casting methods.

Methodology. For bronzes mechanical properties determination FP-100/1 technique and PSW-30 pendulum machine are used. Neophot-21 microscope is used to study microstructures. Chemical elements ratio in local areas of structural components determination is carried out with SEM-515 microanalyzer. Bronzes fracture surfaces fractographic analysis is performed visually and using Coxem EM-40 electron microscope. Bronzes relative magnetic permeability is measured with Magnetomat 1.790 magnetometer. Alloys chemical composition is determined using EXPERT 4L analyzer.

Findings. It has been established that Cu-Al-Si-Sn-Mn system bronze suitable for casting in sand molds should contain by weight 6.0–7.5 % Al, 1.0–2.5 % Si, 0.21–0.45 % Mn and 1.0–2.2 % Sn, and alloying chemical elements ratio and inevitable impurities, according to the formula: $K_R = (1-0.01\ nn)\ (Al\text{-}Si\text{-}Mn)/(1 + Sn)^2$, should be equal to 0.42–0.85. Bronze with $K_R > 0.85$ is low-strength, but ductile and, therefore, mainly suitable for manufacturing products from it by deformation methods. Bronze with $K_R < 0.42$ is low-strength and brittle and it is not suitable for manufacturing products by either casting or deformation methods.

Originality. For the first time, Cu-Al-Si-Sn-Mn system bronzes alloying elements complex influence on their mechanical properties and structure formation features has been determined. Cu-Al-Si-Sn-Mn system aluminum bronzes with K_R value from 0.42 to 0.85 mechanical properties levels increase with Cu-solid solution relative volume fraction in their structures decreasing, that is, with K_R value increasing.

Practical value. The data obtained can be used as a basis for new casting, corrosion-resistant non-magnetic bronzes development that have strength and density at the level of carbon steels or aluminum bronzes alloyed with nickel and iron.

Keywords: *bronze, aluminum, silicon, manganese, tin, strength, hardness, phase, structure*

Introduction. Bronzes belong to most popular nonferrous alloys today. That is why their production is large-scale in many countries around the world. According to European Union standard EN and industrialized countries of the world national standards (BS, DIN, NF, PN, CSN, JIS, ASTM, UNI, etc.), tin and aluminum bronzes have the largest grades variety. Among tin and aluminum bronzes, non-magnetic bronzes occupy the special place. Parts made of such tin and aluminum bronzes do not spark when knocked, do not create their own magnetic inductance during GPS navigation systems, MRT devices, telecommunications equipment, aircraft onboard magnetic sensors, electronic devices, etc. operation. At the same time, non-magnetic tin and aluminum bronzes standardized in world's industrially developed countries (see, for example, ASTM C90300, EN1982, DIN 17662, etc.) are characterized by low strength, high antifriction and acoustic properties, and relatively high corrosion resistance in various natural environments. Due to these properties complex, non-magnetic bronzes are used to make elements of measuring instruments and devices, compasses and telescopes, musical instruments, as well as air intakes, propellers, valves, fittings and other parts for marine and river floating vessels, elements of seawater desalination systems equipment, port infrastructure, mining and extraction machinery, etc.

The range of standardized non-magnetic bronzes also includes beryllium bronze –copper alloy with 0.5–3.0 % (by weight) beryllium. Beryllium bronze is characterized by high strength and elasticity with non-magnetic properties combination and sparking upon impact absence, high acoustic properties, due to which it is used for both metalworking and musical instruments production, springs, high-precision measuring devices, aerospace parts, etc. But beryllium is rather expensive metal (1 kg of Be cost is ~20 times higher than 1 kg of Cu cost and ~7 times higher than 1 kg of Sn cost), and beryllium and beryllium bronze specks are toxic for wildlife.

Aluminum bronzes, which are safe for human health and environment, widespread using in various industries is due to these alloys several indicators highest levels simultaneous combining possibility in these bronzes. These may include mechanical properties, thermal and electrical conductivity, biocide, wear resistance, spark resistance, corrosion resistance, resistance to cavitation and erosion, non-magnetism, good weldability and machinability with cutting tools, relatively low cost and alloying components non-scarcity, etc.

Today, among aluminum bronzes, single-phase aluminum bronzes (БрА5, БрА7, БрА7К2, etc.) are non-magnetic or weakly magnetic, and are mostly intended for products manufacturing from them by pressure processing (PP) of cast billets [1, 2]. Single-phase aluminum bronzes disadvantages as casting alloy are their significant linear and volumetric shrinkage, tendency to form hot cracks and grooving in castings, self-tempering during casting in casting mold slow cooling, grain growth upon heating, which makes them brittle [3, 4], relatively low strength and excessive plasticity in cast state and tendency to form trans-crystalline macrostructure in castings. At the same time, non-magnetic structural (foundry) aluminum bronzes standardized grades are currently absent.

Unlike parts made from tin bronzes, products made from stronger corrosion-resistant non-magnetic aluminum bronzes using will allow expanding modern equipment reliability, durability, technological and operational capabilities operating in difficult manufacturing conditions, in particular, in aggressive natural and technogenic environments, under high loads, elevated and lowered temperatures conditions, etc. Therefore, study and development of structural (foundry) non-magnetic aluminum bronze properties, which will be characterized by satisfactory plasticity and hardness, high strength and corrosion resistance in natural environments, is relevant challenge today. Solving this problem, already today, will allow expanding the possibilities of demanded materials choosing for modern high-technological and science-intensive industries.

Literature review. Most modern industrial foundry tin bronzes are multiphase corrosion-resistant non-magnetic or weakly magnetic alloys, cast products from which are usually not heat treated. According to Greshta V. L. (2014), Merkulova G. A. (2008), Arzamasov B. N. (2008) works, foundry tin bronzes are characterized by foundry and technological properties high level, but they have relatively low strength limit at rupture, as evidenced, in particular, by Table 1 data.

Tin bronzes relatively low tensile strength at rupture (σ_B = 147–345 MPa) significantly limits their application as structural material. Adding ~4 % Ni to tin bronze (Table 1) slightly increases its strength limit (bronze БрО8Н4Ц4С17). Adding ~1 % Ni while simultaneously reducing Sn content to 3 %, Pb to 5 %, and Zn to 7 % (bronze БрО3Ц7С5Н1) ensures bronze parts reliable operation in grease and fresh water. Ni content reducing to 1 % (bronze БрО3Ц7С5Н) allows bronze parts using for operation in seawater or water steam, etc. That is, multicomponent principle in alloying using allows tin bronzes implementation areas expanding from their resistance to chemical influence point of view. Nevertheless, despite cast tin bronzes multiphase structure, this does not allow their strength limit level and, accordingly, their industrial attractiveness as a structural material significant increasing.

Table 1

Tin bronzes mechanical properties at 20 °C before heat treatment (Greshta V. L., 2014)

Bronze grade	Mechanical properties (not less)		
	σ_B, MPa	$\delta_{0.5}$, %	*HB*, MPa
БрО19	–/295	–/4	–/1,570
БрО10	215/295	3/3	780/1,080
БрО10Ф1	215/245	3/3	800/900
БрО10Ц2	215/225	10/10	650/750
БрО5Ц5С5	147/176	6/4	600/600
БрО8Н4Ц4С17	265/345	14/16	785/785
БрО3Ц7С5Н1	174/206	8/5	600/600
БрО3Ц7С5Н	174/205	8/5	590/590

Notes: sand mold casting/chill mold casting

Unlike cast tin bronzes and single-phase aluminum bronzes, multiphase aluminum bronzes physical, mechanical, and operational properties levels can be significantly changed both by their appropriate additional alloying [5, 6] and by thermal and/or deformational treatment. In most corrosion-resistant cast aluminum bronzes, as a rule, improvements in their corrosion resistance levels could be achieved by Al, Ni and/or Mn content increasing. Strength level is usually increased by bronzes additional alloying with Fe, Ni, Mn, etc. Among such materials, for example, bronzes of brands БрА9Ж3Л, БрА10Ж4Н4, БрА11Ж6Н6, БрА9Ж4Н4Мц1, БрА10Ж3Мц2, БрА7Мц15Ж3Н2Ц2, etc. That is, bronzes properties specified levels complex changes are achieved through their multicomponent alloying.

According to Ukrainian foundries products expert evaluation results, among the known standardized aluminum bronzes used for various cast parts manufacturing, the most popular today is corrosion-resistant bronze of brand БрА9Ж3Л. БрА9Ж3Л brand bronze (fittings, antifriction parts) in as-cast state (without heat treatment) has strength limit (σ_B) of at least 392/490 MPa (sand casting/chill casting), elongation at rupture (δ_5) during stretching of at least 10 % and hardness H = 1,000 MPa [7]. Grades БрА9Мц2Л, БрА10Мц2Л bronzes (antifriction parts, fittings operating in fresh water, liquid fuel and steam up to 250 °C) are characterized by moderate strength ($\sigma_B \geq 490$ MPa), plasticity ($\delta_5 \geq 12$ %) and hardness HB = 1,100 MPa. Bronze БрА10Ж3Мц2 (reinforcement, antifriction parts) is characterized by moderate strength ($\sigma_B \geq 392/490$ MPa), plasticity ($\delta_5 \geq 10/12$ %) and hardness HB = 1,200 MPa [8, 9].

Bronze brand БрА7Мц15Ж3Н2Ц2 (antifriction parts, parts for marine use), which, additionally to Al and Fe, is also alloyed with Mn, Ni and Zn, is characterized by high strength ($\sigma_B \geq 605$ MPa), plasticity ($\delta_5 \geq 18$ %) and moderate corrosion resistance in various environments. Bronze БрА10Ж4Н4 (parts for the chemical and food industries, as well as parts operating at elevated temperatures, parts for marine use, etc.) is characterized by increased corrosion resistance in various environments, high strength ($\sigma_B \geq 587$ MPa), satisfactory plasticity ($\delta_5 \geq 12$ %) and hardness not lower than HB = 1,600 MPa. Bronze БрА11Ж6Н6 (reinforcement, antifriction parts, parts for marine use) has a high aluminum content, iron and nickel, which, among aluminum bronzes, gives it corrosion resistance in seawater, high strength ($\sigma_B \geq 587$ MPa) and hardness HB = 2,500 MPa highest levels but, at the same time, plasticity low level ($\delta_5 \geq 2$ %) [10].

As noted above, structural bronzes properties levels variability is achieved through their various alloying, which leads to multiphase structure of corresponding genesis formation in cast bronze. In particular, БрА9 bronze is single-phase corrosion-resistant material that has high wear resistance and good anti-friction properties in wrought state with following values (according to the data from industrial enterprises of Ukraine): $\sigma_B = 407$–455 MPa, $\sigma_{0.2} = 242$–269 MPa, $\delta_5 = 10$–17 %. At the same time, corrosion-resistant bronze БрА9Ж4Н5 ($CuAl_9Ni_5Fe_4$), according to [11], is characterized by corrosion rate in sea water within 0.025–0.076 mm/year, has values of $\sigma_B = 585$–760 MPa, $\delta_5 = 12$–20 %, HB = 1,600–1,900 MPa. That is, due to Ni and Fe alloying, БрА9Ж4Н5 bronze microstructure becomes multiphase and consists of α-phase – matrix in solid solution based on copper form, β-phase – copper chemical compound with system second main component, solid-phase transformations products, martensitic phases, etc.

Any bronzes magnetic properties are given by ferromagnets presented in them – Fe, Ni, Co. At the same time, Al or Mn certain amount presence in bronze also makes it weakly magnetic, since Al and Mn are paramagnetic materials [12, 13]. In addition, at Al and Mn in aluminum bronze certain concentration, magnetic intermetallic compound Cu_2AlMn may form, which also gives bronze magnetic properties. Therefore, Fe, Ni, Co (ferromagnets) presence in aluminum bronzes composition gives bronzes not only increased strength, compared to double aluminum bronzes, but also certain magnetic properties [13]. This is evidenced, in particular, by the data in Table 2.

From the data in Table 2 analysis, it follows that most durable multiphase bronzes have magnetic permeability of more than 1.05 H/m and, based on modern definitions about non-magnetism, are weakly magnetic or magnetic alloys [13].

According to Zhu, L., He, J., & Xie, S. (2008), among non-standardized non-magnetic corrosion-resistant materials, multicomponent copper alloy is known, containing by weight (%): 0.05–2.00 Ni; 2–15 Al; 0.5–8.0 Zn; 1–10 Sn; Cu – rest. This alloy significant disadvantage is instability and, accordingly, unpredictability of its properties levels. This uncertainty in properties levels is due to significant limits changes in mass fraction of alloying elements used in alloy. In particular, alloy with its alloying elements minimum amount will be single-phase, ductile, and suitable for products manufacturing from it only by pressure processing (PP) methods. Alloy with alloying elements maximum mass amount is multiphase, brittle material, poorly suited for casting and many PP methods. At the same time, depending on its alloying components content in such alloy combinations, alloy disadvantages will be those that are inherent in both bronzes and brasses. Based on this, it can be stated that alloy presented in work of Zhu, L., He, J., & Xie, S. (2008) is not suitable material for cast parts production of responsible or especially responsible level. That is, it has no significant practical significance.

From above it follows that achieving high strength and hardness in corrosion-resistant aluminum bronze by alloying it with ferromagnetic metals or manganese significant amount leads to structural high-strength corrosion-resistant bronze obtaining impossibility without it acquiring certain magnetic properties.

This contradiction solution lies in multicomponent aluminum bronze optimal chemical composition establishing, which includes:

- limited manganese content as an alloying component;
- ferromagnetic metals are absent or present in impurities small proportion;
- metal presence, which, according to "rule of four" (alloy alloying components mutual solubility four schemes), gives bronzes intermediate level of alloying and multiphase structure. Such bronze one of the bases is Cu-Al-Si-Mn system bronze, in which, for example, tin is present as metal according to "rule of four".

Currently, there is no information on Cu-Al-Si-Sn-Mn system corrosion-resistant bronzes structure, mechanical and magnetic properties levels in cast state.

Therefore, work aimed at finding rational composition of Cu-Al-Si-Sn-Mn system high-strength non-magnetic medium-alloyed aluminum bronze, that is, with properties set which is not inherent in aluminum bronzes of well-known brands, is relevant modern direction for scientific research and development.

Purpose. To establish regularity of Cu-Al-Si-Sn-Mn system non-magnetic corrosion-resistant bronze chemical composition on structure and mechanical properties complex influence and to determine its rational composition from suitability for manufacturing products by casting methods point of view.

Methodology. Study has been carried out on Cu-Al-Si-Sn-Mn system bronzes with mass content, %: Al = 5.0–7.9, Si = 0.85–2.95, Mn = 0.005–1.21, Sn – up to 3.3, undesirable impurities (nn) – up to 0.75.

For bronze melting, following materials have been used: cathode copper M2 (DSTU 3211-2009); aluminum Al99.7 (DSTU ISO 209-1:2002); silicon Кр1 (DSTU 2963-94); tin О1 (DSTU EN 610:2004); manganese metallic Мн95 (GOST 6008-90); silicomanganese МнС17 (DSTU GOST 16591.4:2009).

Bronze has been melted in induction furnace under charcoal layer. Bronze melts deoxidation has been carried out with Mn and/or silicomanganese. In 1–2 minutes after deoxidation, charcoal residues and slag formations has been cleaned from melt mirror and melt has

Table 2

Copper and some grades of aluminum bronzes magnetic permeability

Copper, bronze	μ_a, H/m	Bronze	μ_a, H/m	Bronze	μ_a, H/m
Copper	0.999 [14]	БрА6К2Ж	1.035 [15]	БрА11Ж4Н1,5Мц0,5	1.27 [18]
БрА7Ж2, БрА7Ж2О	1.01 [15]	БрА10Ж	1.07 [17]	БрА11Ж4Н4Мц3,5	1.32 [19]
БрА9Мц1,5	1.01 [16]	БрА9Ж2Н3	1.1 [15, 16]	БрА10Ж4Н5	1.5 [15]
БрА8Мц	1.03 [15]	БрА10Ж3Мц2	1.1 [15]	БрА10Ж5Н5	1.5 [16],1.6 [15]
БрА9Н7	1.03 [15]	БрА10Ж2, БрА11Ж4	1.2 [15]	БрА11Ж6Н6	1.75 [16]

been poured from crucible into a sand mold to obtain castings 16 × 16 × 120 mm. To produce cylindrical castings, casting molds here been used, which have been manufactured according to working method [20].

Castings in sand molds have been chilled for 24 hours. After cooling, bronze castings dimensions and their magnetic permeability have been measured, chemical composition has been determined, metallographic studies have been performed, and mechanical properties have been detected.

Bronzes free and absolutely hindered linear shrinkage have been measured according to work [20] methodology. Alloys chemical composition has been determined on EXPERT 4L analyzer, and magnetic permeability has been measured with Magnetomat 1.790 magnetometer.

Tensile tests have been performed at 20 ± 1 °C on FP-100/1 testing machine in accordance with DSTU ISO 6892-1:2019, impact strength has been calculated based on samples impact bending tests results, which have been carried out on PSW-30 pendulum machine in accordance with ISO 148-1:2016. Samples structure has been examined using Neophot 21 microscope.

β-phase (ϕ) relative share in bronzes structure has been determined by their microstructures images computer processing at magnification of 200 times.

Metals and alloys suitability for manufacturing products from them by metal processing methods such as metal pressure processing (PP) or casting has been assessed according to criterion *A* [20]

$$A = \frac{\alpha_{AH}}{\alpha_F}, \qquad (1)$$

where α_{AH}, α_F is cast metal (alloy), respectively, absolutely hindered and free linear shrinkage, %, and according to criterion B [20]

$$B = \frac{\delta_5 \cdot \sigma_B}{100 \cdot \sigma_{0.2}}, \qquad (2)$$

where δ_5 is elongation at rupture, %; σ_B, $\sigma_{0.2}$ are respectively, strength limit and yield stress during metal (alloy) samples stretching in as-cast state at temperature of 20 ± 1 °C, MPa; 100 is balance constant, %.

At the same time, the authors assume that work goal has been achieved and corrosion-resistant alloy (aluminum bronze) will be:

- foundry, if criterion B value is not more than 0.7, criterion *A* is not more than 0.5, and ratio $\sigma_{0.2}/\sigma_B$ is in the range from 0.5–0.6 up to 0.95 [20];
- structural, if its structure is multiphase, and strength limit is not less than that of БрА9Ж3Л bronze brand ($\sigma_B \geq 392$ MPa), and elongation at rupture is not less than that of БрА11Ж6Н6 bronze ($\delta_5 \geq 2$ %) brand, but not more than 30 %;
- non-magnetic if its magnetic permeability is not more than $\mu_a = 1.05$ H/m.

In order to determine the chemical composition synergistic effect on bronzes structure and properties, dimensionless criterion K_R have been adopted in following form [21]

$$K_R = \left(1 - \frac{nn}{100}\right) \cdot \frac{\text{Al} - \text{Si} - \text{Mn}}{(1 + \text{Sn})^2}, \qquad (3)$$

where nn, Al, Si, Sn, Mn are impurities, aluminum, silicon, tin and manganese mass content in bronze, respectively, %; 100 is balance constant, %.

Table 3

Bronzes cast in sand molds chemical composition, mechanical properties, volume fracture of other structural components (φ) except copper solid solution and criteria K_R, *A*, *B* values

Chemical elements mass content, %						Mechanical properties				K_R	φ, %	Criteria	
Cu	Al	Si	Mn	Sn	*nn**	σ_B, MPa	$\sigma_{0.2}$, MPa	δ_5, %	*KCU*, J/cm^2			*A*	*B*
89.2	5.08	2.87	0.555	2.03	0.265	140	140	0	0	0.18	–	–	0
90.1	5.06	1.09	0.990	2.24	0.520	422	418	1	3	0.28	–	0.307	0.01
87.2	7.66	1.63	0.054	3.30	0.156	206	205	0	5	0.32	–	–	0
88.2	6.28	2.92	0.010	2.18	0.410	434	434	0	0	0.33	–	–	0
88.7	6.10	2.49	0.257	2.10	0.312	310	295	3	6	0.35	59.1	0.305	0.032
89.1	6.00	2.33	0.487	2.00	0.112	362	350	4	10	0.35	59.1	0.312	0.041
86.8	7.84	1.90	0.376	2.66	0.424	320	306	7	4	0.41	56.8	0.321	0.073
89.2	6.32	1.07	1.030	2.17	0.210	421	284	13	18	0.42	56.1	0.324	0.193
88.2	6.71	2.50	0.232	2.01	0.348	456	390	5	12	0.44	54.7	0.333	0.058
87.8	7.12	1.24	0.960	2.26	0.620	465	332	10	19	0.46	53.1	0.338	0.14
89.0	6.37	2.50	0.297	1.54	0.318	482	350	9	20	0.55	43.8	0.340	0.124
88.8	6.00	1.33	0.373	1.64	0.354	475	350	11	22	0.61	36.5	0.343	0.149
89.8	6.00	2.00	0.402	1.31	0.447	492	285	17	23	0.67	29.1	0.385	0.293
88.6	6.70	1.79	1.070	1.23	0.610	504	275	19	28	0.77	18.4	0.392	0.348
91.4	5.84	1.12	0.010	1.37	0.260	479	250	28	34	0.84	13.3	0.393	0.536
89.1	6.68	1.75	1.210	0.67	0.590	459	206	35	40	1.33	12.8	0.457	0.344
91.8	6.09	1.08	0.010	0.55	0.470	348	138	47	139	2.07	11.6	0.644	1.185
92.06	5.70	0.87	0.650	0.10	0.490	342	128	55	255	3.45	6.2	0.762	1.47
92.6	6.06	1.18	0.010	0.005	0.145	350	115	54	280	4.81	0	0.783	1.643
91.9	6.76	1.00	0.002	0.001	0.337	345	110	55	299	5.73	0	0.78	1.725

Notes: * *nn* – impurities in bronze

Chemical elements ratio in samples structural components local areas determination has been performed using scanning electron microscope – X-ray spectral microanalyzer SEM – 515. To clarify the local features of phase components genesis and microstructure, hardware registration unit software capabilities have been used, which provided signal intensities recalculation and their further interpretation.

Samples fracture structure analysis has been carried out visually and by electron microscopic fractographic method. Impact specimens fracture surface has been studied using Coxem EM-40 scanning electron microscope.

Results. For Cu-Al-Si-Sn-Mn system bronzes, which have been cast in sand mold, in order to establish relationship between criterion K_R value, which has been calculated by formula (3), and their mechanical properties levels, relative volumetric amount of other structural components (φ) except copper solid solution, as well as criteria *A* and *B*, which have been calculated by formulas (1 and 2), experimental data presented in Table 3 have been used.

Indicators σ_B, $\sigma_{0.2}$, δ_5 and KCU dependences on K_R criterion value for studied Cu-Al-Si-Sn-Mn system bronzes, which are plotted according to the data in Table 3, are presented in Fig. 1, and criteria *A*, *B* and j dependences on K_R value for these bronzes are presented in Fig. 2.

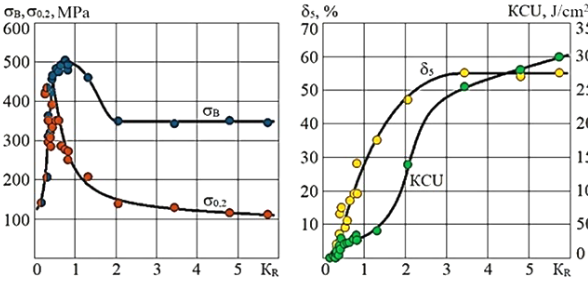
From the dependencies in Fig. 1 course analysis it follows that for bronzes, which have been cast in sand molds, indicators σ_B, $\sigma_{0.2}$ (Fig. 1, *a*) at, respectively, values $K_R \cong 0.42$ and $K_R \cong 0.85$ reach their maximum, after which they decrease and at $K_R \geq 2$ they practically do not change. At the same time (Fig. 1, *b*), with criterion K_R value rising, bronze plasticity indicators increase, reach their maximum value at $K_R \cong 3.5$ and changing slightly with K_R further increasing.

According to the curves in Fig. 2, *a* course, there is a certain correlation between criteria *A*, *B* and K_R. At the same time, according to dependencies in Fig. 2, *a*, with criterion K_R value increasing, criteria *A* and *B* values also monotonically increase. The reason for such regularities is the fact that all these criteria are in a certain dependence on other bronzes structural components relative volume fraction except copper solid solution, as indirectly evidenced by dependence in Fig. 2, *b* and dependence in Fig. 3, *a*.

Dependences in Figs. 2, *b* and 3, *a* courses comparison indicates their certain similarity, which confirms the direct criterion A value dependence on relative volume fraction of the initial b-phase in bronze structure. That is, for Cu-Al-Si-Sn-Mn system bronzes, which cast in sand mold, there is directly proportional linear relationship between criteria *A* and *B*, as evidenced by Fig. 3, *b*. It follows from this that criteria *A* and *B* values, in fact, depend exclusively on bronze structural components content other than α-solid solution and, accordingly, on K_R value.

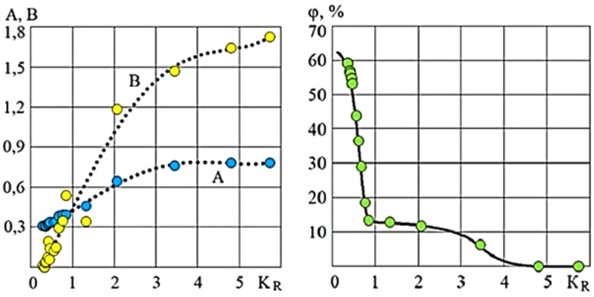
To identify bronzes brittle state region in studied interval of their K_R criterion changes, ratio $\sigma_{0.2}/\sigma_B$ dependence on K_R criterion value have been constructed, which is presented in Fig. 4.

From the dependencies in Figs. 3, *a* and 4 analysis it follows that bronzes with K_R from 0.42 to 0.85 according to criteria *A*, *B* and ratio $\sigma_{0.2}/\sigma_B$ are purely casting alloys, which in cold state are poorly suited for pressure processing. At the same time (Fig. 3) bronzes cast in sand casting molds with criterion K_R < 0.42 value are brittle alloys. In contrast, bronzes with K_R > 0.85 values are sufficiently ductile alloys for manufacturing from them products using known PP methods.



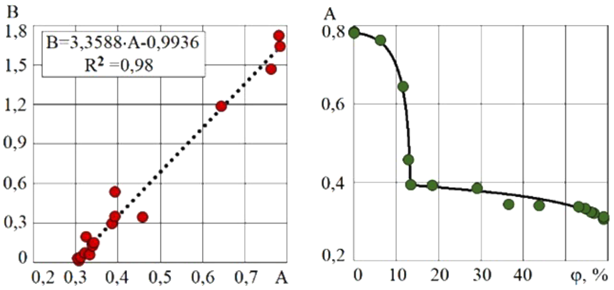
a *b*

Fig. 1. Cu-Al-Si-Sn-Mn system bronzes, cast in sand mold, indicators σ_B, $\sigma_{0.2}$ (a), δ_5, KCU (b) dependences on criterion K_R value



a *b*

Fig. 2. Cu-Al-Si-Sn-Mn system bronzes $A, B = f(K_R)$ (a) and $\varphi = f(K_R)$ (b) dependences



a *b*

Fig. 3. Cu-Al-Si-Sn-Mn system bronzes $A = f(\varphi)$ (a) and $B = f(A)$ (b) dependences

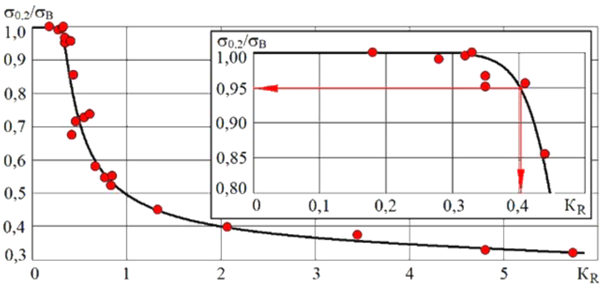


Fig. 4. Cu-Al-Si-Sn-Mn system bronzes cast in sand mold $\sigma_{0.2}/\sigma_B = f(K_R)$ dependence

Investigated cast bronze mechanical properties levels changes are due to differences in its microstructures according to K_R criterion, as evidenced by the images in Fig. 5.

From the images in Fig. 5, *a* analysis it follows that bronze with $K_R = 8.97$ has an α-Cu solid solution single-phase structure. With K_R value decreasing secondary phase appears in structure along solid solution boundaries (Figs. 5, *b*, *c*, *d*), which share and size increasing with K_R value decreasing (from $K_R = 4.81$ to $K_R = 2.07$). Similar change in structure formation nature has been observed by this work authors during primary and solid-phase transformations in БрО3А3 bronze according to mechanism eutectic-peritectic mixed transformation type realization.

According to bronze with $K_R = 2.07$ scanning electron microscopy and X-ray spectral microstructural analysis, which results are presented in Fig. 6, it follows that this continuous secondary phase is chemical compound with ratios (wt. %): Cu/Al = 85.58/8.35 and Cu/Al = 82.20/9.12. Such ratios correspond to stoichiometric formula Cu_3Al, i.e. β-phase, which is inherent in Cu-Al system.

At the same time, as evidenced by the data in Fig. 6, Table, β-phase, in this case, is significantly saturated with tin compared to α-Cu matrix (4.54 and 6.34 wt. % Sn in the β-phase versus 0.18 and 0.34 wt. % Sn in α-Cu matrix). This bronzes structural state provides with plasticity and ductility characteristics high level, but strength relatively low level, as evidenced by the data in Table 3 and the dependences in Fig. 1, *b*.

As K_R value decreases, strength increases and, to moderate value, plasticity decreases. This follows from Table 3 data. This pattern is associated with change in bronze microstructure, which is presented in Fig. 5, *e*. Difference between bronze with $K_R = 0.84$ microstructure and bronze with $K_R = 2.07$ microstructure is that in bronze with $K_R = 0.84$, in place of original β-phase, there is eutectoid structural component derived from it, which is solid-phase transformation $\beta \rightarrow \alpha + \gamma_2$ product.

According to bronze with $K_R = 0.84$ scanning electron microscopy and X-ray spectral microstructural analysis, which results are presented in Fig. 7, in bronze with $K_R = 0.84$ microstructure eutectoid structural component areas inherited from parent β-phase have been found, which also contain Sn large amount compared to

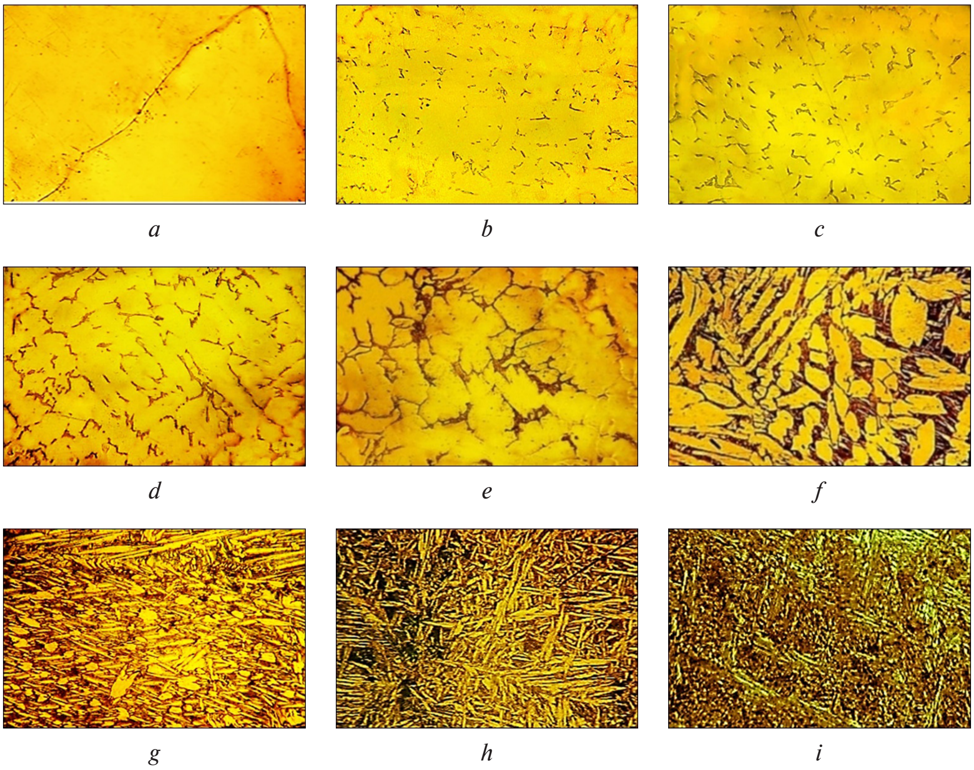
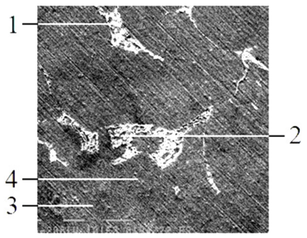


Fig. 5. Microstructures of Cu-Al-Si-Sn-Mn system cast bronzes which was cast in sand mold, with: $K_R = 8.97$ (a); $K_R = 4.81$(b); 3.45 (c); 2.07 (d); 0.84 (e); 0.68 (f); 0.46 (g); 0.41 (h); 0.35 (i), ×200

Chemical element	Chemical elements mass content at Fig. 6 bronze spectrums 1–4, %			
	1	2	3	4
Cu	85.59	82.21	92.01	92.47
Al	8.35	9.12	6.47	6.37
Si	1.44	2.19	1.11	0.9
Mn	0.08	0.14	0.07	0.08
Sn	4.54	6.34	0.34	0.18

Fig. 6. Bronze with $K_R = 2.07$ (×2,000) scanning electron microscopy image and X-ray spectral microstructural analysis results (Table) with local concentrations quantitate data



Chemical element	Chemical elements mass content at Fig. 7 bronze spectrums 1–4, %			
	1	2	3	4
Cu	77.66	78,53	91.09	91.59
Al	6.7	7.80	7.32	6.5
Si	1.67	1.41	1.1	1.25
Mn	0	0	0.09	0.03
Sn	13.97	12.26	0.4	0.63

Fig. 7. Bronze with $K_R = 0.84$ (×1,000) *scanning electron microscopy image and X-ray spectral microstructural analysis results (Table) with local concentrations quantitate data*

α-Cu matrix (12.26 and 13.97 wt. % Sn versus 0.4 and 0.63 wt. % Sn).

Alloys with $K_R = 0.68–0.42$ structure has signs of eutectic habitus two morphological types – simultaneously solidified coarse phases conglomerate (Fig. 5, *f*) or colonial structure (Fig. 5, *g*). In the latter case (Fig. 5, *g*) microstructure consists of primary α-Cu crystals and Cu-Al system α + β eutectic. In turn, eutectic origin β-phase in final structure is commonly represented by Cu-Al system eutectoid transformation products as $\beta \rightarrow \alpha + \gamma_2$ reaction result.

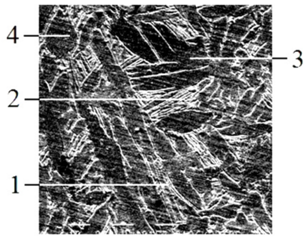
According to scanning electron microscopy and X-ray spectral microstructural analysis, whose results are presented in Fig. 8, it has been found that main elements content in primary and eutectic structural components in alloy with $K_R = 2.07$ is consistent with equilibrium concentrations characteristic of corresponding Cu-Al system alloys phase diagram three-phases horizontal.

That is, content of, for example, aluminum in primary α-Cu phase is 7.9 wt. % compared to 7.5 wt. % according to equilibrium diagram, while in eutectic component it is, for example, 8.25 wt.% versus 8.5 wt.%, respectively (Table in Fig. 8). According to Table in Fig. 8 data, in alloy with $K_R = 0.46$, in eutectic structural component tin concentration exceeds its content in primary α-Cu phase. However, this difference is smaller compared to the previous cases.

In multicomponent bronzes, present work analyzed, which have $K_R \leq 0.42$ values, structure formation by habitus similar to martensitic phases [4, 13] cases based on Cu-Al chemical compounds. Such microstructures are presented in Figs. 5, *h*, *i*. As an example, scanning electron microscopy image of bronze with $K_R = 0.35$ microstructure and Table with X-ray spectral microstructural analysis local concentrations quantitate data for this bronze are given in Fig. 9.

Cast bronzes according to K_R criterion differences in microstructure are accordingly reflected in appearance of its fracture surfaces, which can be assessed both by visual examination with naked eye (Fig. 10) and with scanning electron microscopic fractographic images (Fig. 11) using.

The images in Figs. 10, *a*, *b* clearly demonstrate the fact of bronzes with $K_R = 3.45$ and $K_R = 2.07$ ductile fracture. This is clearly evidenced by structural components break off ridges macrostructural presence in fractographic analysis area and even extra-destruction zone existence in Fig. 10, *b*. Bronze sample with $K_R = 2.07$ value fracture surface scanning electron microscopic fractographic image (Figs. 11, *a*, *e*) also confirms its viscous fracture intragranular nature. At the same time, on fracture surface there are characteristic configuration hollows, which location is naturally associated with intermetallic compounds presence areas.



Chemical element	Chemical elements mass content at Fig. 8 bronze spectrums 1–4, %			
	1	2	3	4
Cu	86.97	87.55	88.66	88.33
Al	8.23	8.25	7.67	7.69
Si	1.56	1.39	1.8	1.83
Mn	0.27	0.22	0.28	0.34
Sn	2.97	2.59	1.59	1.81

Fig. 8. Bronze with $K_R = 0.46$ (×1,000) *scanning electron microscopy image and X-ray spectral microstructural analysis results (Table) with local concentrations quantitate data*

Chemical element	Chemical elements mass content at Fig. 9 bronze spectrums 1–4, %			
	1	2	3	4
Cu	87. 49	87.34	90.62	90.64
Al	8.28	8.58	7.22	7.28
Si	1.36	1.29	1.12	1.11
Mn	0.53	0.48	0.31	0.32
Sn	2.34	2.31	0.73	0.65

Fig. 9. Bronze with $K_R = 0.35$ (×2,000) *scanning electron microscopy image and X-ray spectral microstructural analysis results (Table) with local concentrations quantitate data*

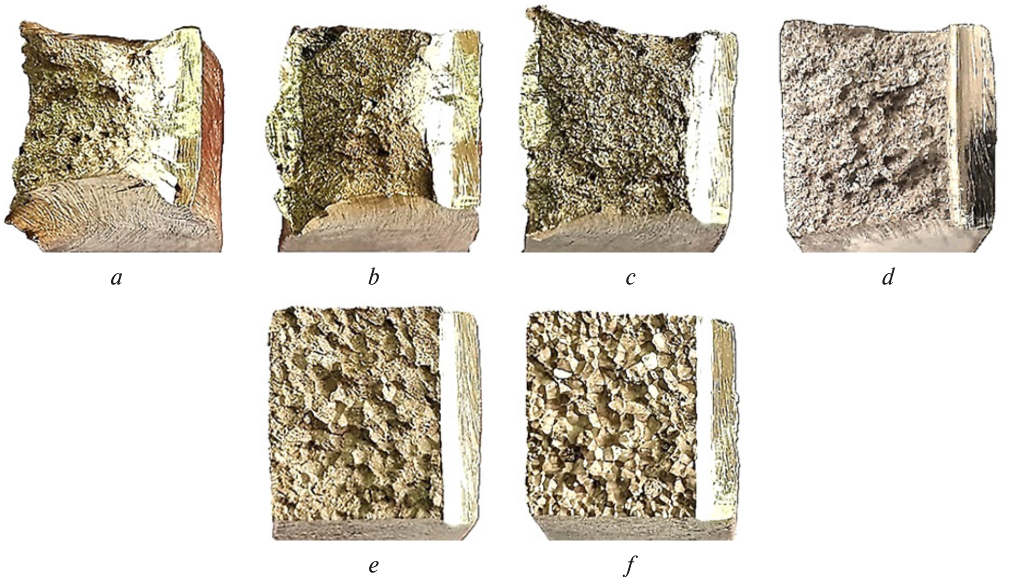


Fig. 10. Bronze cast in sand molds samples fracture surfaces appearance with: K_{Rm} = 3.45 (a); 2.07 (b); 0.84 (c); 0.71 (d); 0.46 (e); 0.35 (f), ×2.5

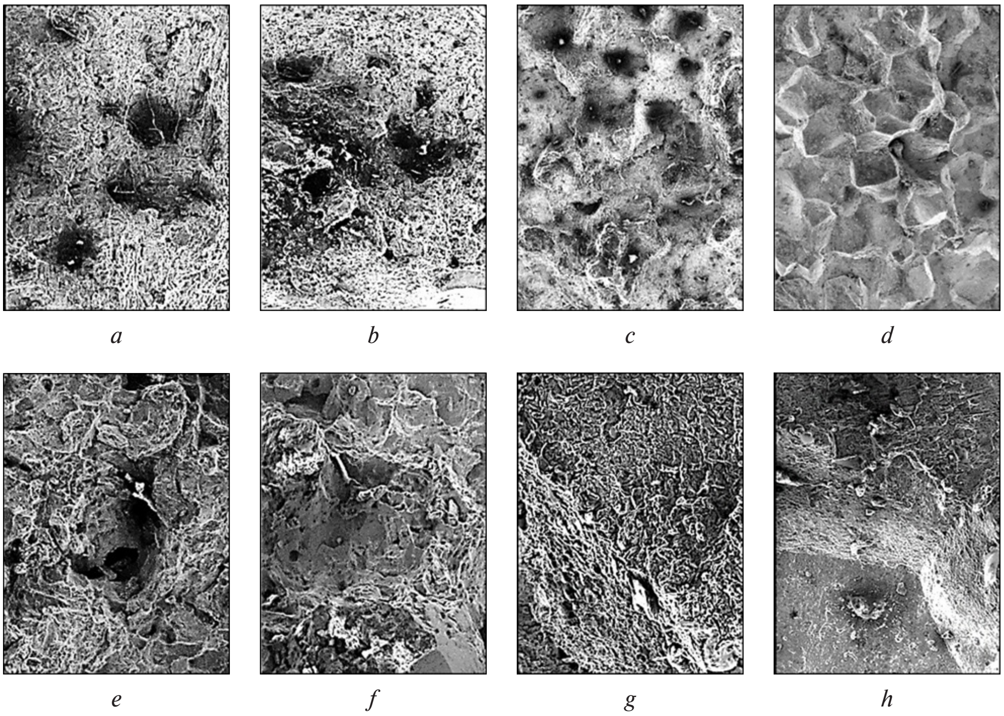


Fig. 11. Bronzes samples fracture surfaces scanning electron microscopic fractographic images with: K_R = 2.07 (a); K_R = 0.84 (b); K_R = 0.46 (c); K_R = 0.35 (d), ×50 and with values: K_R = 2.07 (e); K_R = 0.84 (f); K_R = 0.46 (g); K_R = 0.35 (h), ×500

With K_R value decreasing from 0.84 to 0.46 (Figs. 10, *b–e* and 11, *b*, *c*, *f*, *g*), bronze fracture nature changes to mixed brittle-viscous. Despite in image Fig. 10, *c* an extra-destruction zone presence, in alloy with $K_R = 0.84$ destroyed sample, nevertheless, in fractal zone, inter-crystalline fracture signs along grain boundaries already appear (Figs. 11, *b*, *f*). With K_R index in value decreasing, viscous structural component amount on studied bronze fracture surface decreases, and inter-crystalline brittle fracture areas number increases (Figs. 10, *c* → 10, *e*), which is confirmed by scanning electron microscopic fractographic analysis results (Figs. 11, *b*, *f* → 11, *c*, *g*).

Bronzes with K_R value less than 0.42 are brittle alloys (Figs. 1, *a*, *b*) with fracture surfaces characteristic macromorphology. In particular, sample with K_R = 0.35 (Figs. 10, *f* and 11, *d*, *h*) fracture surface appearance is fundamentally different from that of previously considered bronzes. In bronze with $K_R = 0.35$, ductile component of fracture is absent. Fractal zone macrostructure in this case is represented by polygonal grains smooth shiny faces, along which an absolutely brittle inter-crystalline fracture occurred with this phenomenon natural influence on mechanical properties indicators (Table 3).

As for Cu-Al-Si-Sn-Mn system bronzes with K_R value from 0.42 to 0.85 magnetic permeability, its value, as

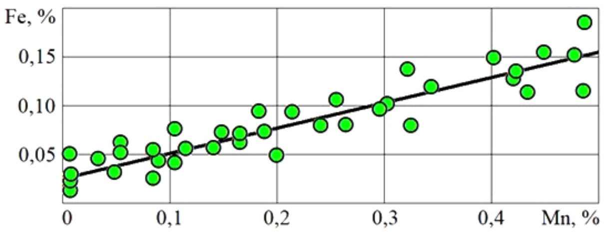


Fig. 12. Dependence between iron and manganese content in Cu-Al-Si-Sn-Mn system bronzes with $K_R = 0.42–0.85$

noted above (Table 2), mainly depends on iron content in them and, with Fe content ≤ 0.17. % by mass, does not exceed $\mu_a = 1.01$ H/m. In turn, iron content in studied bronzes depends on iron present amount as impurities in charge materials used in studies, in particular, in iron-containing silicomanganese, as evidenced by the dependence in Fig. 12.

From the dependence in Fig. 12 analysis it follows that:

- together with technical purity main charge materials, up to 0.07 % iron enters the studied bronze, the rest comes from iron-containing silicomanganese, in which iron content is 7–11 % by mass;
- studied bronze structure does not contain Cu_2AlMn intermetallics, which have ferromagnetic properties.

Therefore, when casting in sand molds, Cu-Al-Si-Mn-Sn system bronzes mechanical properties highest levels (σ_B = 421–504 MPa, $\sigma_{0,2}$ = 250–390 MPa, δ_5 = 5–28 %, KCU = 12–34 J/cm^2), according to their alloying elements mass content adopted in the studies limits, are achieved at K_R = 0.85–0.42, which, accordingly, corresponds to φ = 12–55 % values.

Conclusions.

1.The goal set in the work has been achieved by the fact that for cast products from structural non-magnetic corrosion-resistant bronze manufacturing, which is poured into sand casting mold, an melted alloy contains, wt., %: Al = 6.0–7.5; Si = 1.0–2.5; Mn = 0.21–0.45; Sn = = 1.0–2.2; Cu = 86.0–91.7 and inevitable impurities (nn) not more than 0.45. At the same time, in impurities composition, iron, nickel and cobalt total mass content is no more than 0.17 %, and alloying chemical elements and inevitable impurities ratio, which is determined by K_R criterion and calculated by formula: K_R = (1–0.01 nn) × × (Al-Si-Mn)/(1+Sn)^2, is from 0.42 to 0.85.

2. Adopted in research K_R criterion using allows, with sufficient accuracy for engineering calculations, to evaluate the complex influence of alloying components and impurities within their changes accepted limits on Cu-Al-Si-Sn-Mn system bronzes, which are cast in sand molds, mechanical properties.

3. Tin presence in Cu-Al-Si-Mn system multicomponent bronzes chemical composition in amount of more than 0.01 % ensures their existence with two-phase structure. At the same time, when poured into sand casting mold, bronze with K_R > 0.85 is low-strength, but plastic and, therefore, mainly suitable for products manufacturing from it using metal pressure processing methods (by deformation). Bronze with K_R = 0.85–0.42 is strong and sufficiently ductile, which makes it suitable for casting. Bronze with K_R ≤ 0.42 is low-strength and brittle, but, probably, if heat treated, can be used as a casting material.

4. Bronzes with K_R > 0.85 have two-phase structure consisting of copper based α-solid solution and chemical compound at the grain boundaries.

5. Bronzes with K_R = 0.85–0.42 are characterized by intermetallic phase continuity intragranular disruption presence due to its solid-phase transformations, which leads to chipped fracture areas appearance on fractograms of ruining.

6. In alloys with K_R ≤ 0.42 microstructure is represented by multiphase components complex, which is multistage transformations in liquid and solid states result during paired and more complicate components interactions in Cu-Al-Si-Sn-Mn system. Such structures are similar in habitus to martensitic phase formation cases.

7. In three established in the work K_R criterion intervals (K_R ≤ 0.42, 0.42 ≤ K_R ≤ 0.85, K_R > 0.85), change in bronzes structure formation nature has been recorded, which certainly affects their destruction mechanism specific nature and, as a result, mechanical properties indicators values.

8. Cu-Al-Si-Sn-Mn system aluminum bronzes with K_R value from 0.42 to 0.85 mechanical properties levels increase with Cu-solid solution relative volume fraction in their structures decreasing, that is, with K_R value increasing.

9. Cu-Al-Si-Sn-Mn system aluminum bronzes with K_R value from 0.42 to 0.85 are multiphase structural, corrosion-resistant, non-magnetic alloys mainly suitable for parts by casting methods manufacturing, which mechanical properties levels can be changed by castings heat treatment.

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Механічні властивості та структура немагнітних литих бронз системи Cu-Al-Si-Sn-Mn

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Мета. Встановити закономірності комплексного впливу хімічного складу на структуру й механічні властивості немагнітної корозійностійкої бронзи системи Cu-Al-Si-Sn-Mn і визначити її раціональний склад із точки зору придатності до виготовлення виробів способами лиття.

Методика. Для визначення механічних властивостей бронз використовували машину FP-100/1 і копер PSW-30. Для дослідження мікроструктур використовували мікроскоп Neophot-21. Визначення співвідношення компонентів у локальних ділянках структурних складових проводили на мікроаналізаторі SEM–515. Фрактографічний аналіз поверхонь руйнування бронз проводили візуально й на мікроскопі Coxem EM-40. Відносну магнітну проникність бронз вимірювали магнітометром Magnetomat 1.790. Хімічний склад визначали за допомогою аналізатору EXPERT 4L.

Результати. Встановлено, що придатна до лиття в піщані ливарні форми бронза системи Cu-Al-Si-Sn-Mn повинна містити за масою 6,0–7,5 % Al, 1,0–2,5 % Si, 0,21–0,45 % Mn та 1,0–2,2 % Sn, а співвідношення легуючих хімічних елементів і неминучих домішок, за формулою: $K_R = (1–0{,}01 \cdot nn) \cdot (\mathrm{Al–Si–Mn})/(1 + \mathrm{Sn})^2$, повинно дорівнювати 0,42–0,85. Бронза з $K_R > 0{,}85$ –маломіцна, але пластична й тому переважно придатна для виготовлення з неї виробів способами деформації, бронза з $K_R < 0{,}42$ – маломіцна, крихка й не придатна ані для виготовлення виробів способами лиття, ані деформування.

Наукова новизна. Уперше визначено комплексний вплив легуючих елементів бронз системи Cu-Al-Si-Sn-Mn на їх механічні властивості й особливості формування структури. Рівні механічних властивостей алюмінієвих бронз системи Cu-Al-Si-Sn-Mn з величиною K_R від 0,42 до 0,85 підвищуються зі зниженням відносної об'ємної долі Cu-твердого розчину в їх структурах, тобто зі зростанням величини K_R.

Практична значимість. Отримані дані можуть бути базовими для розробки нових ливарних, корозійностійких немагнітних бронз, що мають міцність і щільність на рівні вуглецевих сталей або алюмінієвих бронз, легованих нікелем та залізом.

Ключові слова: *бронза, алюміній, кремній, марганець, олово, міцність, твердість, фаза, структура*

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