Influence of modification by superdispersed powder of aluminum oxide on lead-tin bronze structure

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Abstract. Lead-containing tin bronzes are a good antifriction material. The area of their application is limited because of low strength properties. It is possible to enhance the strength properties by changing their structure using modification by nanopowders. This article presents data on the influence of admixtures of the aluminum oxide nanopowder on the structure of the cast bronze (with lead and tin). For the castings, containing different amounts of the prepared modifier based on aluminum oxide, metallographic studies and structural studies were undertaken. Based on the results of the work, the concentrations of the aluminum oxide nanopowder in the modifier, strongly influencing the structure of the castings, have been chosen. It has been shown that even small admixtures of the modifier (0.07-0.25%) based on aluminum oxide allow refining the casting grain, reducing the average size of lead inclusions and forming a dispersed network of eutectoid inclusions.

1. Introduction
It is known that the exploitation of bronze parts, wearing out under alternating and cyclic loads significantly, reduces their life cycle significantly [1, 2]. An important role in such parts belongs to stress concentrators, which are both a consequence of the design features and the peculiarities of the heterophase material of the parts. And if stress concentrators, caused by design features can often be quickly eliminated, the stress concentrators, caused by the structure of the material, are eliminated much more difficulty.

Increasing the fatigue life can be achieved by replacing bronze with a material that has enhanced strength properties, or by replacing with the similar bronze without stress concentrators – lead inclusions. But the most important practical property of such lead-bearing tin bronzes is their very low friction coefficient against hardened steel. At the same time, the low strength properties of these bronzes limit largely their application.

One of the promising areas of enhancing a set of service properties of metals at present is alloying them with nanopowders. The introduction of a small amount of them before the crystallization process into the melt makes it possible to substantially increase the strength properties of the castings [3, 4]. This kind of modification of copper alloys is promising simultaneously from several viewpoints. First, the nanopowders’ particles, introduced into the melt, will serve as crystallization centers. As a result, the microstructure of the castings will be more fine-grained. Such fine-grained structure will have
higher strength properties as compared to a conventional microstructure. Second, the introduction of additional particles of the nanopowder – grain nuclei - allows narrowing the temperature interval size of alloy crystallization. Thereby, the shrinkage porosity of the casting is reduced. The casting becomes denser with a less number of defects. This leads to enhancement of strength properties due to structural change. Third, the nanopowder particles of oxides and nitrides of metals have high melting temperature and high hardness. They will not dissolve in the casting’s volume and remain in the form of nanosized inclusions. In the process of plastic deformation, such inclusions will be an obstacle to dislocations glide. Thus, uniformly distributed particles will create dispersion hardening of the casting. In addition, an increase in the matrix strength can improve antifriction properties (a reduction of the friction coefficient and a decrease in wear).

2. Materials and Methods

2.1. Characteristics of used materials

The paper presents the research results of the influence of additives of aluminum oxide nanopowder on the structure and properties of lead-tin bronze of grade BrOS 10-10 (Alloy LB2, UNS C93700). This bronze consists of 10% mass. of lead, 10% mass. of tin and the rest is copper.

Aluminum oxide nanopowder has been chosen as a material for modifying bronze BrOS 10-10 since Al2O3 has high melting temperature, is insoluble in the melt of the base metal, and owing to the presence of several phases, it can contribute to realisation of not only grain boundary strengthening due to the grain refinement, but also dispersion hardening by Orowan mechanism [5]. Besides, SDP of aluminum oxide is inexpensive and widespread.

Modification of melts by nanopowders is associated with a number of problems. Refractory oxide particles are not wetted by the molten metal. This leads to the fact that the powder either comes to the surface of the melt, or is distributed non-uniformly throughout the casting. In this case, strength and tribotechnical properties are not enhanced. To solve this problem, it was decided to preprocess the powder in a ball planetary-type mill mixed with a copper powder. Such mechanical treatment will allow plating the SDP particles of aluminum oxide by copper and mills additionally the agglomerates of Al2O3 particles, increases surface energy due to formation of linear and point defects (dislocations, atomic and ionic vacancies, interstitial ions) and creates a positive charge on the particle surface [6-8]. Owing to this treatment, the particles will be wetted by the bronze melt, will not come to the surface and will be uniformly distributed throughout the entire volume [9, 8].

Superdispersed powders of aluminum oxide (average particle size is <1 μm), obtained by the plasmochemical method, and copper powder with an average particle size of ~ 0.07 mm were used for the studies.

To determine the phase composition of the nanopowder, its X-ray diffraction analysis was conducted. By its results, the following 5 phases of Al2O3 were identified (Table 1).

Mixing and cladding of the powders were carried out in the planetary ball mill "Activator-2SL". For the planetary disk, containing drums, the rotation frequency was 600 rpm. The total weight of the processed powders per one loading was 50 g. During activation, the processing time was 10 minutes. The mass ratio between copper powders and the nanopowder of aluminum oxide when preparing the modifier was 50% wt. of Al2O3 + 50% wt. of Cu. Activation of the powders did not lead to changes in their phase composition after mixing.
2.2. Methods of working the heat and pouring

The multicomponent bronzes under study were melted in high frequency induction furnace VCHG2-100/0.066 in crucibles and molds. The material of the crucibles is siliconized graphite. Melting was carried out using components of technical grade. The following was used as a charge: cathode copper of the M1k grade (GOST 859-78; 99.95% copper, the rest are admixtures); lead of sheet grade S-2 (GOST 3778-77; 99.95% lead, the rest are admixtures); bar tin of grade O1 (GOST 860-75; 99.9% tin, the rest are admixtures). The phosphorous copper alloy of the MF10 grade (GOST 4515-93; 9.5%-11.0% phosphorus, 99.8% copper + phosphorus, the rest are admixtures) was used as a deoxidizer. The powder-modifier was introduced into the melt, being preliminary placed in copper foil. Graphite molds were produced for ring and vertical castings. For ring castings, the outer diameter was 108 mm. Their internal diameter - 36 mm. The height of the rings was 13 mm, and the total mass of the ring was ~930 g.

2.3. Metallographic studies

The metallographic analysis of the structure was carried out using optical microscopes ZEISS AXIO Observer.A1m. The analysis of the obtained images was carried out using the program of autoprocessing of digital images "KOI System" [10]. This program allows calculating the inclusion volume fraction, the average size of particles using the photograph of the microstructure.

2.4. Scanning electron microscopy (SEM)

For microfractography, microscopes TM-3000 (“Hitachi” Company – Japan) and Carl Zeiss EVO 50, equipped with an EDS X-Act microanalyzer produced by Oxford Instruments Company, were used. Fractograms of fractures were made in the mode of reflected electrons - the main operating mode of the microscope.

2.5. X-ray diffraction analysis (XRD)

The studies were carried out using diffractometer Shimadzu XRD7000 X-ray (CuKα radiation, λ = 1.54060 Å), equipped with a graphite curved monochromator of radiation, Shimadzu SM-3121. Calibration of the diffractometer was carried out using a standard silicon etalon “Shimadzu standard silicon powder (99% of purity)”; at that, the error was about 20 ± 0.02-0.03 deg. The identification of crystalline phases (qualitative analysis) was carried out using the standard diffractometer software “PCXRD standard software” (ver. 7.00 Rel. 001), as well as PDF2+ databases. The size of the coherent-scattering regions was assessed by Debye Scherrer formula.

| Phase   | Formula     | Space group | Parameter of crystal lattice a, Å | Crystal system |
|---------|-------------|-------------|----------------------------------|----------------|
| α-Al₂O₃ | Al₂O₃       | R-3c        | 4.7587                           | Rhombic        |
| δ-Al₂O₃ | Al₂.67O₄   | P-4m2       | 5.599                            | Tetragonal     |
| σ-Al₂O₃ | Al₂.66O₄   | Fd-3m       | 7.948                            | Cubic          |
| γ-Al₂O₃ | Al₂.66O₄   | I41/amd     | 5.652                            | Tetragonal     |
| θ-Al₂O₃ | Al₂.423O₃.₆₄ | C2/m      | 11.854                           | Monoclinic     |

Table 1. The phase composition of the used aluminum oxide powder
3. Results and discussion
After processing the aluminum oxide powder in the ball planetary mill in the mixture with copper powder, it was introduced into the melt of bronze BrOS 10-10, having been wrapped in copper foil. The pouring was carried out into graphite molds at room temperature. The content of the modifier was 0.07; 0.15; 0.25; 0.5; 0.75 and 1.5% mass.

Proceeding from theoretical prerequisites, the main consequence of the introduction of nanopowders into the melt must be the refining of the macro- and microstructure since the powder particles must serve as nuclei of new grains. Fig. 1 and 2 show photographs of the macrostructure and the microstructure of BrOS 10-10, modified with and without nano-powder of aluminum oxide.

![Figure 1](image)

**Figure 1.** Microstructure of castings of bronze BrOS 10-10 with different contents of powder Al₂O₃: a – without powder; b – 0.07 % of powder Al₂O₃; c – 0.75 % of powder Al₂O₃; d – 1.5 % of powder Al₂O₃

Figure 3 and the data in Table 2 show that when a small amount (0.25% wt.%) of the modifier based on the aluminum oxide nanopowder is introduced, the distance between the axes of dendrites of the second order decreases 2.5 times, and the grain size decreases ~ 1.5 times. This indicates that a significant part of the particles of the Al₂O₃ powder served as effective crystallization centers. When the content of the Al₂O₃ nanopowder increases, the structure began to coarsen relatively the one that had been obtained with small powder concentrations. With 1.5% content of the modifier, the differences of the structure from the unmodified one are no longer so significant. This is related to coagulation of the Al₂O₃ powder particles with its sufficiently large (> 0.5 wt. % of the modifier) concentrations. It is necessary to note that the microstructure refining was uniform enough throughout the volume of the casting, which indirectly indicates that the distribution of the modifier was also fairly uniform and it did not come to the surface of the casting.
Figure 2. Etched microstructure of castings of bronze BrOS 10-10 with different contents of powder $\text{Al}_2\text{O}_3$: $a$ – without powder; $b$ – 0.07 % of powder $\text{Al}_2\text{O}_3$; $c$ – 0.75 % of powder $\text{Al}_2\text{O}_3$; $d$ – 1.5 % of powder $\text{Al}_2\text{O}_3$.

Figure 3. Dependence of distance between axes of dendrites BrOS 10-10 of the second order on modifier concentration.
Table 2. Dependence of sphericity coefficient of lead inclusions and average sizes of lead inclusions of BrOS 10-10 on modifier concentration

| Content of modifier based on nanopowder Al₂O₃, % | Average size of grain, μm | Sphericity coefficient of lead inclusions | Average size of lead inclusions, μm |
|-----------------------------------------------|---------------------------|----------------------------------------|-----------------------------------|
| 0                                            | 150                       | 10.2                                   | 6.9                               |
| 0.07                                         | 90                        | 2.2                                    | 5.1                               |
| 0.15                                         | 95                        | 2.8                                    | 7.3                               |
| 0.25                                         | 97                        | 2.6                                    | 9.3                               |
| 0.5                                          | 108                       | 3.5                                    | 9.5                               |
| 0.75                                         | 121                       | 4.1                                    | 15.8                              |
| 1.5                                          | 140                       | 6.9                                    | 18.2                              |

According to the X-ray diffraction analysis (Fig. 4), three structural constituents were successfully identified: α-solid solution of tin in copper, (α + δ) eutectoid and lead. A significant difference in the amount of eutectoid with different concentrations of the modifier was not found. By means of metallographic studies, it has been found that the change in the eutectoid content is not as significant as it was when the same bronze was exposed to different cooling rates. The maximum difference (a decrease from 15 to 10%) was found for a sample with a modifier content of 0.75%. At that, samples with additives of 0.75 and 1.5% of the modifier had such a mutibranched eutectoid morphology that it was impossible to determine the sphericity coefficient and the average size for them.

Table 3. Dependence of sphericity coefficient, content and average sizes of inclusions (α+δ) of eutectoid BrOS 10-10 on modifier concentration

| Content of modifier based on nanopowder Al₂O₃, % | Eutectoid content, % | Sphericity coefficient of inclusions (α+δ) | Average size of inclusions (α+δ) of eutectoid, μm |
|-----------------------------------------------|----------------------|-------------------------------------------|--------------------------------------------------|
| 0                                            | 15                   | -                                         | -                                                |
| 0.07                                         | 13                   | 8.2                                       | 20.1                                             |
| 0.15                                         | 12                   | 9.1                                       | 21.8                                             |
| 0.25                                         | 14                   | 11.3                                      | 16.7                                             |
| 0.5                                          | 13                   | 12.7                                      | 18.6                                             |
| 0.75                                         | 10                   | -                                         | -                                                |
| 1.5                                          | 13                   | -                                         | -                                                |

For lead inclusions, the following tendency was observed. With a decrease in the content of the modifier, they became more spherical (Table 3); the sphericity coefficient decreased approximately 3 times. As to their dimensions, it was found that with small concentrations of the modifier, lead
inclusions were 1.5 times larger than those in the unmodified sample, with medium concentrations comparable to them, and with high concentrations - 3 times coarser.

To determine the uniformity of distribution of the powder-modifier throughout the casting volume, an energy-dispersive X-ray spectrum analysis of the samples was carried out (Fig. 5 and 6). The research was carried out by comparing the near-surface regions of the samples with the regions located in the center of the casting, and the sections taken in the upper and lower parts of the casting were compared. The energy dispersion analysis showed macroscopically the uniform (i.e. along with the formation of small clusters, dispersed throughout the matrix volume) distribution of the modifier particles over both vertical and horizontal sections of the castings, which indicates that after treatment in the ball planetary mill, the nanopowder particles of aluminum oxide, cladded with copper, are wetted well with the bronze melt.

![Figure 4. X-ray diffraction analysis of samples BrOS 10-10 with additives: a – 1.25 % of powder Al₂O₃; b – 0.75 % of powder Al₂O₃; c – 0.25 % of powder Al₂O₃](image)

In the system of particle – cladding metal – melt, electrocontact interaction plays a key role in the interaction. In the general case, the potentials of the surface of two arbitrary phases will be different, and, consequently, their electrochemical potentials will be different. During close contact of phases, redistribution of charged particles occurs until a double charged layer is formed at the interface, due to which the surface potentials will change until the Fermi levels of the charged particles level off. The electric field in the melt in the vicinity of the system nucleus – cladded particle is caused by the electrocontact interaction of the layer of the cladding metal with the melt. A part of the area of particles, occupied by the fringes of crystal defects on the surface will contribution mainly to interphase energies. This statement remains true not only for the nanoparticle potential, but also for the
electrocontact interaction of the cladding layer. For metals that expand during melting, which is typical of the majority of metals and alloys, a good catalyst is a cladded particle-substrate, whose macro-potential (in the contact position) is greater than or equal to the average total potential value of the nucleus and the melt. Therefore, for the particle of the powder-modifier to be wetted in the melt and to serve as a catalyst for crystallization, the work function of the electron, cladding of the metal particle, must be greater or equal to the work function of the base metal of the melt [11]. In this case, the cladding of the aluminum oxide nanopowder with copper satisfies completely this condition.

Using energy-dispersive X-ray spectroscopy, it was found that with an increase of the concentration by more than 0.5 wt. % of the modifier, an active process of coagulation of its particles takes place (Fig. 5). The particle aggregates were located in pores ranging in size from several units to several tens of micrometers, formed as a result of the released gases, adsorbed on the surface of the aluminum oxide particles. It must be noted that the aggregates of particles were evenly distributed throughout the entire volume of the casting.
Figure 6. Mapping of distribution of powder-modifier throughout casting volume (data of energy-dispersive analysis): a – 0.75% Al₂O₃; b – 1.5% Al₂O₃.

4. Conclusions
After the undertaken studies of the properties of tin bronze of grade BrOS 10-10, it is possible to conclude that the modification with superdispersed powders influences greatly its structure. This is especially typical for small concentrations of the modifier (up to 0.26%).

When introducing a small (0.06-0.26%) amount of the aluminum oxide nanopowder, the distance between the axes of the second order dendrites decreases 2.5 times, and the grain size decreases 1.5 times. This indicates that a significant part of the powder particles is effective centers of crystallization. With an increase of the nanopowder content, the structure begins to coarsen relatively that obtained with low concentrations of the powder.

The content of the eutectoid does not undergo such significant changes. The maximum difference (decrease from 15 to 10%) was found for a sample with a modifier content of 0.75%. At that, the samples with 0.75% and 1.5% of the modifier had such a multibranched morphology of the eutectoid that it was impossible to determine the sphericity coefficient and the average size for them.

With a decrease in the modifier content, lead inclusions became more spherical; the sphericity coefficient decreased approximately 3 times.

The data of the energy-dispersive X-ray spectral analysis showed that when the modifier concentration increases over 0.25% (wt.), an active coagulation process of the powder particles of alumina oxide starts, which is accompanied by emission of the gas, adsorbed on the surface of the particles, and by the formation of gas pores. In these pores, the aggregates of the modifier particles are predominantly located.

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