Development of heat- and wear-resistant nanocomposite copper powder based material and technique of its obtaining used for plungers of die-casting machines

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Abstract. This paper presents the chemical composition, technology of manufacture and the basic properties of the nanocomposite Cu-Al-C-O copper powder based material for plungers of die - casting machines developed by the authors. The technology is based on the method of reactionary mechanical alloying in the attritor, which provides the formation of a dispersion-strengthened subgrain structure of the material containing strengthening particles $\gamma$-$\text{Al}_2\text{O}_3$ with an average size of 39±7 nm. Its recrystallization temperature is 1000 ± 20 °C, and the hardness in the test temperature range of (20-800 °C) exceeds the hardness of standard bronzes, in particular, CuBe2NiTi, CuAl10Fe4Ni4 and CuAl10Fe3Mn2, widely used in plungers of such foundry equipment. The developed material has a low wear intensity (3.20 ± 0.85)·10^{-11} and, in contrast to the above bronzes, it can be used at an extremely high (up to 115 MPa) pressure between the plunger and the steel pressing chamber.

1. Introduction
Die-casting is one of the high-performance and high-precision methods of mold casting used for metal products made of aluminum, magnesium and copper alloys, as well as zinc, tin and lead and weighing from several grams to 50 kg [1, 2]. Application of the process in practice shows that the use of the new materials for die molds and other parts of the die-casting machine that come into the contact with the molten metal being pressed provides the increase in the quality of casting as well as its cost reduction [3, 4]. Plunger of a die-casting machine (Figure 1) is considered to be one of these critical and wear parts. It pushes a portion of the molten metal out of the pouring bush into the pressing chamber and then into the die casting mold.

Figure 1. Types of plunger design for die-casting machine.
Along with this, moving inside the pressing chamber [1, 2, 5-7] the plunger simultaneously undergoes heavy specific loads, high temperature and significant friction forces. In particular, to obtain dense aluminum alloy castings, it is necessary to provide a pressing pressure of 35...85 MPa when the temperature of the molten metal reaches 720 °C [5]. The pressing pressure required to produce copper alloy castings increases up to 120 MPa (at a temperature of a molten metal, for example, brass - 960 °C) and in some cases it can reach 900 MPa [2, 6, 8, 9].

In case there is no «cold» space between the steel pressing chamber and the plate of a die-casting machine the contact pressure in the system «plunger-pressing chamber» can reach up to 250 MPa and if the «cold» space is 0.16 mm, the contact pressure falls down to 100 MPa. At such parameters of the contact pressure, according to [5], the coefficient of friction of the above tribosystem with a steel plunger is 0.39. Such a high value of the coefficient of friction indicates an extremely heavy interaction of tribosystem elements with each other that borders with possible seizure.

Based on the above investigation and the analysis of some published sources [2, 3-6, 10] we can make a conclusion that the promising material for a plunger must have high recrystallization temperature (more than 800 °C), high tensile strength (at least 800 MPa) and compressive resistance (at least 1000 MPa at standard temperature and at least 200 MPa at 800 °C), satisfactory thermal conductivity (at least 15% of the thermal conductivity of copper), low coefficient of linear thermal expansion (not more than 17·10⁻⁶ 1/°C at 20 ... 100°C and C 23·10⁻⁶ 1/°C at 700 – 800 °C), low wear intensity (not more than 5·10⁻¹¹). Along with this wear rate of the pressing chamber material must be much lower. Satisfying these requirements can provide the increase of the plunger service life by at least 1.5 times [11].

The absence of harmful impurities in the material and its complete technological reproducibility are also critical requirements.

Plungers are often made of various heat-resistant steels to be employed under these conditions. Since these steels have poor tribotechnical characteristics, the plungers made of them intensively wear out the pressing chamber of die-casting machines. At the same time, they wear out heavily themselves. To prevent wear of steel plungers in the source [12] it is proposed 1-3 rings made of ZrO₂-TZP based ceramic material and covered with Si-SiC material to be installed on them. In this case, the inner surface of a steel pressing chamber must be made of ZrO₂-TZP ceramic material containing TiO₂ and Al₂O₃ particles. MoS₂, BN or graphite is recommended as a dry lubricant. Because of high cost of the casting tool of this type this engineering solution was not widely used.

Russian enterprises, rather often use gray cast-iron for example, EN GJL-240 brand [13] with a tensile strength of 240 MPa, for the manufacture of plungers for die-casting machines. Due to a small coefficient of linear thermal expansion, the plungers made of this cast-iron brand can work when the gaps are relatively small, providing a good sealing with the pressing chamber. However, due to the low thermal conductivity of cast-irons, the bottoms of the plungers made of them heat rapidly up to 350-400°C. Heating to such temperatures is highly undesirable, as it results in large abrasive wear of the plunger working part forming fatigue cracks and scuffing [14].

Copper alloys containing beryllium, cobalt, nickel, titanium, bronzes such as EN CuCo2Be (CW104), EN CuBe2NiTi, CuBe1.7NiTi etc. [4, 11] are most widely applied for the parts exploited under cyclic loads at high temperatures, including plungers for die-casting machines. They are highly resistant to destruction, wear and corrosion. Beryllium contained in these bronzes effectively reduces the coefficient of linear thermal expansion. Such materials are technological: they can be worked by pressure and do not cause serious problems when cut. The mechanical properties of beryllium bronzes can be compared with those of special steels: heat treatment increases their strength and they retain good thermal conductivity even at high temperatures. However, when the plungers made of these bronzes are heated up to 350-450 °C, intensive wear occurs [4, 5]. At the same time, this hard-to-find and expensive beryllium component makes the material brittle. High cost of beryllium bronzes, short supply, and toxicity of beryllium itself call for the search or development of alternative materials to replace the bronzes used for plungers of die-casting machines.
Aluminum-iron bronzes, in particular, bronzes such as CuAl10Fe4 EN, EN CuAl10Fe3Mn2 found wide application as materials for plungers of die-casting machines. Due to their composition, these bronzes have high mechanical and anti-friction properties and corrosion resistance. The oxide film formed on their surface allows these bronzes to resist corrosion in active wet or gas media. Alloying iron additives improve the structure of bronze alloys. They increase their wear resistance, strength and resistance to abrasion. In spite of the fact, that these materials do not contain environmentally harmful and expensive beryllium the properties of these materials are not inferior to those of beryllium bronzes mentioned above. Along with this EN CuAl10Fe4 and EN CuAl10Fe3Mn2 bronzes are among the least expensive and the most affordable brands, because they do not contain expensive tin either. However, with the temperature increase up to 350 °C and higher, hardness of these bronzes decreases significantly, and therefore the use of these materials for heat-stressed and abrasion subjected parts and, in particular, for die-casting machines plungers is not always effective.

The above proves that precipitation hardening technique used for producing the bronzes mentioned above does not provide the required degree of heat and wear –resistance. It can be explained by the fact that finely dispersed precipitation phases dissolve in the copper matrix at high temperatures.

Unlike the precipitation hardened alloys the dispersion- strengthened materials contain finely dispersed refractory particles (dispersoids) as strengthening phases that neither dissolve in the copper matrix nor react with it right up to their melt temperature [15]. This phenomenon gives the highest strength to this type of materials at high temperatures. Moreover, the smaller the size of the dispersoids, the higher the recrystallization temperature [15].

The hardening coefficient (the ratio of the hardness of strengthened and non-strengthened copper) of copper dispersion-strengthened materials containing nanosized level dispersoids (less than 100 nm), is continuously increasing [15] with the temperature increase up to 0.90...0.95 of copper melt temperature. Besides the structure of these materials satisfies Georges Charpy principle according to which antifriction materials must have ductile base with regularly arranged hard particles.

On the bases of above there are all the reasons to consider that it is this nanocomposite copper material with dispersion-strengthened structure that can be successfully used for plungers of die-casting machines as a promising material. The present article is devoted to development and obtaining of this exact material of the system Cu-Al-C-O.

2. Experimental materials and methods

To obtain Cu-Al-C-O nanocomposite copper material the initial mixture was prepared of electrolyte copper powder PMS-1 (at least 99.5 wt.% of copper, average particle size -38 µm), aluminium powder PP-1 (at least 97.0 wt.% of aluminium, 75 µm) an pencil lead powder GK-3 (at least 92.0 wt.% of carbon, 40 µm). Carbon content varied depending on the quantity of aluminum in the powder mixture according to the following account: 1.0 wt.% fraction of aluminum should fit 0.1; 0.2; 0.3; 0.4 and 0.5 wt.% fraction of carbon, and aluminum content varied from 2.0 wt.% to 4.0 wt.%.

Reactionary mechanical alloying and certain operations of powder and granular metallurgy were used as methods for obtaining the required materials [16-18]. Reactionary mechanical alloying was performed in treating of 2 kg of powder mixture in the 15L attritor designed at the Chuvash State University. The mixture was worked for 1h in the chamber air medium at the attritor rotor rotation frequency 600 min⁻¹. The granules obtained in the attritor were cold pressed at a pressure of 600 MPa into briquettes with of 25 mm to 95 mm in diameter. Then these briquettes were put into technological steel capsules filled wood carbonizer and heated at 850 °C for 30-90 min depending on the briquette diameter. At that temperature the capsules were transported one by one to the container of the hydraulic press heated up to 450 °C where the heated briquette was taken out of each capsule and put into the press container to be extruded through a tapered extrusion die (angle of taper 120° at a ring height of 3 mm) into a bar 13-52 mm in diameter.

These bars were used to produce some samples to be tested according to the standard techniques in order to determine physical and mechanical properties of the obtained materials. Fine structure of the material was examined by X-ray diffraction analysis and transmission electron microscopy applying...
thin foils of this material and carbon replicas taken from its sections. Fine structure parameters (dispersoids, grains) were specified according to the technique mentioned in the source [19]. Methods of chemical analyses were also used.

Wear-resistance of the examined material was determined by friction test based on the system «pad-roller» using modernized friction machine SMZ-2, that provided contact pressure of 100 MPa and higher between the pad and the roller 100 mm in diameter made of hardened steel 42Cr4 with hardness of 52 HRC. The sliding speed of the roller over the pad was 5.3 m/s. Step loading of this simulative tribological system was performed with smooth increase in speed 0.03-0.09 MPa/s and specific load on the pad. Monitoring of the results of frictional torque and temperature of the pad was performed while testing. Load increment between the loading steps was 20 MPa. Testing was performed at every step of loading until the stable friction occurred or it was stopped in case the pad temperature was above 200 °C and / or some indication of system seizure appeared. For these reasons the testing was also stopped with load increasing. While rotating the roller was continuously lubricated with Isolat 128PP lubricant that is widely used for lubrication of plungers for die-casting machines.

Wear intensity of plunger material was determined as the ratio of linear wear of the pad to the length of its sliding path over the steel roller. Wear intensity of the roller material was determined as the ratio of the linear wear of the roller to the length of pad sliding path upon it. Along with this roller linear wear was determined by application of the well-known cratering method.

3. Test results and discussion

The test results of the Cu-Al-C-O material samples are shown in table 1.

**Table 1.** The properties of the tested Cu-Al-C-O system material.

| Aluminum content in the powder mixture, wt.% | Carbon content in the powder mixture, wt. % | Tensile strength, MPa | Relative elongation, % | Hardness HB5/250 | Thermoconductivity, % of copper thermoconductivity |
|---------------------------------------------|------------------------------------------|----------------------|----------------------|------------------|-----------------------------------------------|
| 2.0                                         | 0.0                                      | 772                  | 5.5                  | 206              | 22.9                                          |
| 0.2                                         | 0.0                                      | 756                  | 3.9                  | 216              | 28.5                                          |
| 0.4                                         | 0.0                                      | 767                  | 3.1                  | 225              | 25.3                                          |
| 0.6                                         | 0.0                                      | 772                  | 1.1                  | 235              | 23.4                                          |
| 0.8                                         | 0.0                                      | 838                  | 1.7                  | 243              | 19.6                                          |
| 1.0                                         | 0.0                                      | 814                  | 1.4                  | 237              | 19.5                                          |
| 0.3                                         | 0.0                                      | 790                  | 5.9                  | 219              | 18.0                                          |
| 0.6                                         | 0.0                                      | 816                  | 3.5                  | 230              | 22.9                                          |
| 0.9                                         | 0.0                                      | 830                  | 2.6                  | 224              | 18.7                                          |
| 1.2<sup>a</sup>                             | –                                         | –                     | –                     | 254              | 15.6                                          |
| 1.5<sup>a</sup>                             | –                                         | –                     | –                     | 244              | 15.4                                          |
| 3.0                                         | 0.0                                      | 782                  | 6.2                  | 223              | 16.4                                          |
| 0.4                                         | 0.0                                      | 822                  | 3.2                  | 243              | 18.1                                          |
| 0.8                                         | 0.0                                      | 850                  | 2.0                  | 260              | 15.2                                          |
| 1.2                                         | 0.0                                      | 841                  | 1.3                  | 268              | 13.5                                          |
| 1.6<sup>a</sup>                             | –                                         | –                     | –                     | 269              | 13.2                                          |
| 2.0<sup>a</sup>                             | –                                         | –                     | –                     | 244              | 13.1                                          |

Note: <sup>a</sup> this carbon content did not allow testing the samples because of extremely high brittleness of the material.

Table 1 shows that each given aluminum content has the best amount of carbon that gives the material highest thermoconductivity and hardness. In particular the maximum point of
thermoconductivity occurs when the carbon content in the amount of 0.1 wt.% per 1.0 wt.% of aluminum, and the maximum hardness—at 0.4 wt.% of carbon per 1.0 wt.% of aluminum.

The reason for these maximum values formation as shown in [16-18, 20] is the reduction of copper oxides by carbon and aluminium, that occurred while working the powder mixture in the attritor. Copper oxide occurs while working the powder mixture in the attritor.

As it follows from table 2 carbon additives presented in the bars made of the tested material result in reduction of both oxygen content (caused by carbon reduction) and aluminum content spent for forming its own oxide as well as for reduction of copper from oxides. Moreover, the results of X-ray diffraction analysis show that aluminum content in the copper lattice stays unchangeable with the introduction of carbon.

### Table 2. The results of chemical and X-ray diffraction analyses of the systems Cu-Al-O and Cu-Al-C-O materials.

| Material system | Initial content in the powder mixture, wt.% | X-ray diffraction analysis | Chemical analysis |
|-----------------|--------------------------------------------|----------------------------|-------------------|
|                 | Al  | C  | Lattice period, Å | Aluminum content in the lattice, wt.% | Aluminum content out of the lattice, wt.% | Oxygen content in the material, wt.% |
| Cu-Al-O         | 0.5 | 0  | 3.6177           | 0.2              | 0.35                      | 0.032                      |
|                 | 1.0 | 0  | 3.6200           | 0.5              | 0.80                      | 0.026                      |
| Cu-Al-C-O       | 0.5 | 0.15 | 3.6179          | 0.2              | 0.26                      | 0.025                      |
|                 | 0.5 | 0.25 | 3.6183          | 0.2              | 0.26                      | 0.030                      |
|                 | 1.0 | 0.30 | 3.6200          | 0.5              | 0.72                      | 0.011                      |
|                 | 3.0 | 0.90 | 3.6308          | 1.5              | 2.17                      | 0.017                      |

The analysis of the properties given in table 1 shows that the material samples shown in table 3 possess the best combination of such characteristics as tensile strength, hardness, relative elongation (characterizes technological properties of the material—ductility) and thermoconductivity.

### Table 3. The properties of the Cu-Al-C-O materials with different chemical properties.

| Identity code of a material sample | Initial content in the powder mixture, wt.% | Tensile strength, MPa | Relative elongation, % | Hardness HB50/50 | Thermo-conductivity, % of copper thermo-conductivity |
|-----------------------------------|--------------------------------------------|-----------------------|------------------------|-------------------|-----------------------------------------------|
|                                   | Al  | C  |                           |                        |                  |                                               |
| CAG2/08                           | 2.0 | 0.8 | 838                      | 1.7                    | 243              | 19.6                                          |
| CAG 3/09                          | 3.0 | 0.9 | 836                      | 2.5                    | 238              | 17.4                                          |
| CAG 4/09                          | 4.0 | 0.8 | 850                      | 2.0                    | 260              | 15.2                                          |

It goes without saying, that manufacturing a plunger of a glass shape (see figure 1) by turning the extruded bar will result in significant material loss. Therefore a work-piece for turning a plunger should resemble the final product in shape and in size as much as possible. Such a work-piece can be obtained by hot forming of the cylinder cut from the extruded bar. It’s clear that the higher the ductility of the material the easier the work-piece is hot formed.

Comparative analysis of the tested samples (see table 3) shows that the material with identity code CAG 3/09 possess the best ductility index. Because of the fact the further testing and investigations were performed over this material sample.
The performed tests showed that this material has an extremely high recrystallization temperature—1000 ± 20 °C, which is 0.92 of copper melt temperature and significantly exceeds all standard bronzes in this characteristic.

The analysis of the graphs (figure 2) shows, that the hardness the tested material is higher than that of the heat-resistant beryllium bronze EN CuBe2NiTi at the temperatures up to 420 °C and from 550 °C to 800 °C.

The hardness of the other two aluminum heat-resistant bronzes is lower than that of the tested material at the entire test temperature range. In this respect, the material CAG 3/09 can be classified as a heat-resistant material.

High heat resistance of this material is primarily due to the peculiarities of its fine structure. The photo of the foil (figure 3) shows that the material CAG 3/09 has clear subgrain structure of the nanosized level, indicating the absence of mechanically alloyed copper recrystallization when its granules hot (850 °C) extruded into a bar.

The presence of the corresponding rings on a microelectronic diffraction pattern taken of this foil, indicates that the fine structure of the material has a greater degree of polycrystallinity.

![Figure 2](image1.png)

**Figure 2.** Diagrams of «hot» hardness of the tested material and standard heat-resistant bronzes depending on the test temperature.

![Figure 3](image2.png)

**Figure 3.** The photo of the copper composite material CAG 3/09 foil, taken by a transmission electron microscope, x57000.
The interpretation of foils microelectronic diffraction patterns and the analysis of X-ray diffraction patterns of this material anode deposit showed that the main strengthening phases in it is aluminium oxide $\gamma$-Al$_2$O$_3$, which was formed as a result of mechanochemical synthesis of aluminium powder and oxygen of the attritor chamber. Copper oxide is not seen neither in microelectronic diffraction patterns nor in X-ray diffraction patterns. This proves that the function of carbon in this system is to be a reducing agent for copper from its oxides. Diffraction rings and lines resulted from graphite also appear both in electronic diffraction patterns and in X-ray diffraction patterns.

Stereological analysis of replicas (figure 4) showed that the average particle size of the strengthening phases ($\gamma$-Al$_2$O$_3$) is 39±7 nm.

![Figure 4](image.png)

**Figure 4.** Tracks of inclusions (replica) in a copper composite material CAG 3 / 0.9, taken by a transmission electron microscope, x 20000.

The above features of the material fine structure and of its components parameters make it possible to specify the tested material as a nanocomposite material, and the presence of finely dispersed free (residual) carbon in the amount of 0.69 - 0.7 wt.% together with the above physico-mechanical properties, should also add good working properties to this material. This assumption was confirmed by the results of comparative tribological tests the main technological stages of which were given above. These tests showed that the phenomenon of beryllium bronze EN CuBe2NiTi pad seizure with a steel roller was observed when the contact pressure between the pad and the roller reached 85 MPa. For the pad of aluminum bronze EN CuAl10Fe4Ni4, the ultimate contact pressure was 90 MPa. During the test of the Cu-Al-C-O material pads, the first signs of seizure were recorded at a contact pressure of 115 - 120 MPa. Therefore, the tests were stopped at a contact pressure of 110 MPa. The linear wear of the pad and the steel roller were measured, and the path taken by the friction pair was also determined. The average values of the wear intensity of the tested material and the steel roller were $(3.20 \pm 0.85) \cdot 10^{-11}$ and $(1.14 \pm 0.67) \cdot 10^{-12}$ correspondently.

The obtained values of the ultimate contact pressure in a friction pair and the wear intensity of its elements give reasons for classifying the tested material as antifriction material for heavy-duty friction pairs.

4. Conclusions

Comparison of the obtained values of the physical-mechanical, technological and working properties of the developed nanocomposite material of the Cu-Al-CO system (CAG 3/09) with the requirements for promising materials for plungers of die casting machines given here allows us to recommend this material for foundry equipment parts and especially for plungers that undergo the high specific loads, high temperature and considerable friction forces simultaneously while moving inside the pressing chamber.
At the same time, the main reason to recommend the material for this field of application is that it is superior conventional heat-resistant beryllium and aluminium bronzes currently used for the plungers of die casting machines in heat resistance and wear resistance.

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