Development of copper dispersion-strengthened composite material with increased indexes of high-temperature strength and wear resistance for thermally loaded friction pairs

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Abstract. The article presents the chemical composition, technology and general properties of copper dispersion-strengthened composite material developed by the authors based on Cu-Al-C-O system with increased indexes of high-temperature strength and wear resistance for parts of thermally loaded friction units and, first of all, for valve guides of highly forced internal combustion engines and plungers of die-casting machines. This material containing 0.9 wt % aluminum, 0.3 wt % carbon has recrystallization temperature of 1000 °C and has higher tribotechnical properties comparing with standard materials. In particular, the wear out intensity of the developed material is 2.9 lower comparing to gray cast iron Gh 1051, which is used for valve guides. At the same time, wear of coupled element is also became 2.8 times less. The technology of new material is based on the method of reactionary mechanical alloying in the attritor, which provided the material with dispersion-strengthened subgrain structure with γ-Al2O3 reinforcing nanodisperse particles.

1. Introduction
It is known [1-3] that interaction of machine parts and mechanisms which are in moving contact with each other is always accompanied with friction and wear out. However the wear out intensity depends on many factors, where the main ones are contact pressure between parts of the friction unit, surface roughness, presence or absence of lubrication, heating temperature of the contact surface and etc. Significant contact pressure can arise in friction couplings of technical devices very often. Coupled with sliding, they cause significant temperature changes in contact area of the coupling parts. As a result the specific stress-strain behaviour arises in the parts of the friction unit, which causes their rapid wear [2, 4].

In the case where parts of the friction unit work in the conditions of reciprocating motion the load for the friction pair will be sign-variable [4, 5]. This cause the additional increasing of the total load and fatigue deformation of the material in micro- and macro-volumes. Areas that are the closest to the contact surfaces are especially strongly subjected to deformation. When one part of the friction unit is skewed, areas with loosed and stronged contact appear. Because of such tight contact interaction plastic deformation of parts material occurs. This often leads to damage to the surfaces of parts and their adhesion [2, 3].
In the conditions of reciprocating motion, the details of many friction units of cutting machine (guides and support), pumps (plunger and cylinder), press equipment (guides and traverses), textile and weaving machines (guides and runners), electric knife switches (knife and pressure contact) work and etc [5]. But there are a lot of friction units where their linear relative motion takes place not only with high contact pressure, but also in high temperature conditions and in aggressive environment. Such friction couplings can include, for example, «piston – cylinder liner», «valve – valve guide» of the internal combustion engines (especially high-powered engines), «plunger - casting chamber» of die-casting machines [6-13].

The valve guide is used to provide valve motion totally coaxial to its seat, which gives proper bearing of valve head to the seat. Valves rapidly reciprocate into valve guides holes and provide direct supply of the specific portion of fuel-air mixture or only air to the cylinders and release exhausted gases. The operating temperature of the valves of the internal combustion engines with positive ignition exceeds the 1000 ° C [6]. At the same time, large temperature differences occur (700...800 C° and 150 C ° in the head and rods, respectively) [7], which reduce the mechanical strength of the material of both the valve itself and its guide, and moving gas flows cause corrosion and gas erosion surfaces of exhaust valves and, accordingly, valve guides. The main part of the temperature loads from the valve is taken over by the valve guide, in connection with which it can be heated to 0.9, the valve heating temperature. Thus, the materials for valve guides should have, first of all, high resistance to both wear and high temperatures, low friction coefficient, high hardness and good thermal conductivity [6,7,9,10].

The plunger of the die-casting machine is used to push the melt (plastic, non-ferrous metals and alloys) from the casting chamber into the mold. Since the plunger of the injection molding machine reciprocates along the inner surface of its casting chamber, and the piston heating temperature can reach 800 °C, the material from which the piston of the foundry equipment should be made should be, first of all, heat-resistant [11, 13]. Due to the fact that significant axial specific loads affect to the plunger which can reach 900 MPa [14], the plunger material must also have high strength characteristics, including at high temperatures. Since the radial pressure in the contact of the plunger with the casting chamber can reach 100MPa or more [15], the plunger material must have good antifriction properties and, first of all, have a low tendency to seize with the mating material of the casting chamber. At the same time the materials used for the plungers of foundry equipment must have high thermo-conductivity.

It appears from the above that operation conditions of these parts are similar: parts work in reverse motion conditions, extremely high temperatures and lubrication deficiency in the friction area. That is why the requirement for these materials are the same. For that matter it seams advisable to use the same material for both parts.

Gray cast irons are frequently used for production of the parts, which work flat out in high temperature conditions. These parts are strong enough and wear-resistant. But their drawback is their low thermo-conductivity. More over, it is not recommended to heat grey cast irons to 400 °C and higher as it leads to their large wear [9, 11]. It should also be noted that when using cast iron as a material for friction units, such an extremely undesirable phenomenon is observed as abrasive wear of the friction surfaces of the coupled element. In addition, in this case, fatigue cracks and scores often occur.

For parts operating under cyclic loads at high temperatures, including valve guides and pistons of foundry machines, copper alloys such as beryllium bronzes (e.g. CuBe2NiTi), aluminum bronzes (e.g. CuA19Fe3), nickel silicon bronzes (e.g. CuNi2Si) are widely used. These bronzes are highly resistant to destruction, wear and corrosion. They also have satisfactory thermo-conductivity. However, it should be noted that heating of contact parts from these bronzes to such temperatures as 350...450 °C leads to their softening and rapid wear [8, 17]. In this regard, the use of such materials in heat-stressed friction units cannot ensure their high resource.

Nevertheless, the use of copper as a metal with high thermal conductivity as the basis of the required materials is the most optimal solution. However it is necessary to increase the temperature of
copper material recrystallization to 900 °C and more. This cannot be achieved with dispersion hardening of copper material, achieved by isolating the dispersed inclusions during the heat treatment. These dispersion inclusions dissolve in copper base at high temperatures and do no prevent the coarsening of the grain of the material [17].

Unlike the above dispersion hardening copper alloys, dispersion-strengthened copper-based materials can have high mechanical properties at high temperatures. The interface boundary in such materials is always incoherent. This means that for mating of different phases transition lattice and grain boundary dislocations are required. The most optimal conditions for inhibition of dislocations are provided when the particle size is less than 10 nm, and the distances between particles do not exceed 100 nm [18]. When dispersion strengthening, such solid particles (dispersoids) that increase the strength of the material, and do not dissolve in the copper matrix and do not interact with it until it gets the melting temperature [10-14]. Besides, the structure of such materials meets the well-known G. Charpy Rule (solid particles are evenly distributed in a ductile base), due to which they also should have good anti-friction properties [2, 3].

The method of reactionary mechanical alloying with powdery and granule metallurgy is now the most effective and perspective way of production of dispersion-strengthened materials [18-20]. This method has approved very useful for development and production of copper dispersion-strengthened DISCOM® [21, 22] materials with high indexes of electrical conductivity (85…92 % IACS) and recrystallization temperature (800…830 °C). The main system of these materials is the Cu-Al-C-O system, which ensures the formation of dynamically thermostable γ-Al2O3 particles of the nanodispersed level in the ready material and the creation of a subgrain fine structure [18, 22, 23]. The aluminum content in these materials does not exceed 1.0 wt. Obviously, in order to be able to use this system and to obtain material for the valve guides of valves and plungers of die-casting machines, it is necessary to increase the content of aluminum. Due to this, the number of strengthening nanoparticles γ-Al2O3 in the material will increase, which will provide an increase in the mechanical properties of the material at elevated temperatures. Moreover, it is necessary to increase the content of carbon in the material, part of which will play the role of dry lubricant.

Thus, this article is devoted to implementation by the authors of the above technical solutions in order to create a dispersion-strengthened composite material of the Cu-Al-C-O system for parts of heat-loaded friction pairs and, first of all, for valve guides of valves of high-powered internal combustion engines and plungers of die-casting machines.

2. Experimental materials and methods

To obtain experimental samples of the developed copper dispersion-strengthened composite material of the Cu-Al-C-O system, the following were used:
- copper, in the form of copper powder PMS-1 (average particle size - 38 μm);
- aluminum, in the form of PP-1 aluminum powder (average particle size -75 μm), the content of which ranged from 2 wt% to 4 wt%;
- carbon, in the form of a powder of pencil lead GK-3 (average particle size of 40 μm), which was taken from the following calculation: so that 0.1; 0.2; 0.3; 0.4 and 0.5 weight parts of carbon accrued to 1 weight part of aluminum.

To develop the required material, we used the method of reactionary mechanical alloying in the attritor and operations of powder and granular metallurgy:
- making an initial powder mixture by joint mixing of dosed powder quantities of these powders in powder mixer with 40 l capacity for 1 h;
- treatment of initial powder mixture in the air atmosphere of the attritor working chamber of 15 l for 60 min (rotor rotation speed - 600 min⁻¹, degree of working chamber filling - 0.7);
- cold pressing of granules obtained in the attritor in a rigid matrix into briquettes with 54 mm diameter (pressure is 600 MPa);
heating of briquettes in a furnace in shielding atmosphere to the 850°С, hold for 15..20 min and further hot extrusion into bars from the press container heated to 450°С through a conic draw die (extrusion coefficient is 17).

Straightening bars in the subpress die and cutting of the defective first part of the bar and its discard.

During the works physical and mechanical properties of obtained materials were determined by standard samples testing using corresponding methods. The microstructure was analyzed by means of a microscope with 1200x magnification. The fine structure of the materials was analyzed using the X-ray diffraction method and transmission electron microscopy (TEM), samples for which were thin foils and extraction carbon replicas.

As shown above, the main factor that affects to the greatest extent the performance of friction units is the wear. Since the operating conditions of guide valves and pistons of die-casting machines are similar, wear tests for the friction pair «valve guide – valve» should be sufficient to conclude that it is advisable to use the developed material as well for pistons of die-casting machines. The valve guides for the tests were made of the studied copper dispersion-strengthened composite material and which was widely used in such parts of gray cast iron engines Gh 1051. The inner diameter of the valve guides was 8,033 mm, its length was 42 mm.

Tribotechnical tests were carried out on a special stand simulating the work of a friction pair «valve guide – valve». Exhaust steel valve with an ion-nitrated rod and an initial roughness $R_a = 0.92...1.25$ μm were used as a coupled element. Dosing of the lubricant was carried out as in a real engine with serial valve stem seals. The lubricant temperature was maintained at the level of 121±0.5°С. The movement of the valve in each direction was 11 mm. The valve's reciprocating frequency was 1500 cycles/min. The test duration for one pair was 12 h, i.e. the friction path that the valve passed through the hole of the guide sleeve was the same for each of the tested friction pairs and amounted to 23.76 km. The weight wear of the guide sleeve and valve were determined. Then, based on weight wear, assuming uniform wear of the contacting surfaces of these parts, their linear (radial) wear was calculated. By dividing the linear wear by the friction path, the wear rate of both parts of the friction coupling was determined.

3 Experimental results and their discussion
The materials for tests were obtained with different contents of aluminum and carbon (but with the same oxygen content - not more than 0.02 wt%) and, accordingly, with different physical, mechanical and operational properties. Figure 1 shows a graph of the relative thermo-conductivity of the obtained materials on the content of carbon and aluminum in the initial powder mixture.

![Figure 1. Dependency diagram of the relative thermo-conductivity of the materials under analysis from the carbon content at different aluminum contents in the initial powder mixture.](image-url)
As follows from figure 1, the maximum relative thermo-conductivity of the materials under analysis is achieved with a carbon content of 0.1 mass fractions per 1 mass fraction of aluminum. But the maximum hardness is achieved when 0.4 mass fractions of carbon accounted for 1 mass fraction of aluminum (figure 2).

![Figure 2. Dependency diagram of Vickers hardness of the materials under analysis from the carbon content at different aluminum contents in the initial powder mixture.](image)

Due to the fact that the optimal values of certain properties of the materials under analysis are obtained for different chemical compositions, when choosing the most suitable ones, preference was given to those materials that have the best combination of such characteristics as relative thermo-conductivity, hardness and elongation, which characterizes the plastic properties of materials. The last characteristic is very important, because to obtain blanks of valve guide in the form of hot extruded tubes, a sufficiently good ductility of the material is required.

In accordance with this approach, the selected materials are given in table 1.

**Table 1.** Properties of materials under analysis with the most optimal chemical composition

| Conventional designation of material | Initial content in powder composition, wt % | Elongation, % | Thermo-conductivity, % from copper thermo-conductivity | Ultimate tensile strength, MPa | HV hardness |
|------------------------------------|--------------------------------------------|---------------|--------------------------------------------------------|-------------------------------|-------------|
| 2/08                               | 2.0                                        | 1.7           | 19.6                                                   | 838                           | 2380        |
| 3/09                               | 3.0                                        | 2.5           | 17.4                                                   | 836                           | 2330        |
| 4/08                               | 4.0                                        | 2.0           | 15.2                                                   | 850                           | 2540        |

The material with the symbol 3/09 is most preferable, since its elongation (and therefore ductility) is higher than that of the materials designated as 2/08 and 4/08. This allows to obtain parison tubes from this material, which is especially important from the point of view of its development in production.

Therefore, guide valves were made from this material, they were tested in comparison with the same guide valves from standard gray cast iron Gh 1051.

Table 2 presents the results of tribotechnical tests of a friction pair «valve guide – valve».

From Table 2 it follows that the wear out intensity of the guide valves from the developed dispersion-strengthened material with the symbol 3/09 is 2.9 times lower than that of the guide valves from gray cast iron Gh 1051. At the same time, the wear rate of the valve itself has become 2.8 times less.
Table 2. Average values of wear and wear out intensity of valve guides from developed material, gray cast iron Gh 1051 and steel ion-nitrided valves.

| Valve guide material | Weight wear (measured), mg | Linear wear (designed), micron | Wear out intensity for valve guide | Wear out intensity for valve |
|----------------------|-----------------------------|-------------------------------|----------------------------------|-----------------------------|
| Testing material 3/09| 0.81                        | 0.226                         | 0.067                            | $1.12 \times 10^{-11}$     | $0.28 \times 10^{-11}$    |
| Grey cast iron Gh 1051 | 2.13                      | 0.769                         | 0.185                            | $3.24 \times 10^{-11}$     | $0.78 \times 10^{-11}$    |

The higher wear resistance of the developed material is explained not only by a suitable chemical composition, but also by the presence of a macrostructure oriented in the direction of friction from discrete microfibers elongated in this direction (figure 3), between which there is residual carbon ($0.70...0.73$ wt%), playing the role of dry lubricant.

![Figure 3](image1.png)

**Figure 3.** Longitudinal (a) and cross (b) thin sections of the bar of the developed material manufactured by hot pressing (extrusion) with a drawing coefficient of 17 (x30).

In addition, the increased wear resistance is also facilitated by the fine structure of the developed material, which fully complied with G. Charpy's rule, which is confirmed by a photograph of the carbon replica from this material (figure 4, a). It follows that solid particles of the hardening phase with an average size of 36 nm are uniformly distributed in a soft copper matrix. The amount of these particles is about 15%. As shown by X-ray diffraction analysis, these solid particles are $\gamma - Al_2O_3$. The presence of these dynamically thermostable particles and a well-developed subgrain structure (figure 4, b) with nanodisperse subgrain sizes also provide this material with high mechanical properties at elevated temperatures.

![Figure 4](image2.png)

**Figure 4.** TEM - photos of a carbon replica (a, x 20000) and foil (b, x57000) obtained from a developed dispersion-strengthened composite material.
In particular, it has a recrystallization temperature of 1000 °C, which is higher than the heating temperature of both the valve guides of the valves of internal combustion engines and the plungers of die-casting machines. The decrease in hardness of this material during heating to a temperature of 900 °C does not exceed 75%, which is significantly lower than the decrease in hardness at this temperature for the above bronzes CuBe2NiTi, CuA19Fe3, CuNi2Si. The above allows us to attribute this material to the class of heat-resistant materials. The material has a thermo-conductivity of 18% of the thermo-conductivity of copper, and has a low coefficient of linear thermal expansion (17.4 · 10⁻⁶ 1/°С at 20 ... 100 °С and 22.9 · 10⁻⁶ 1/°С at 800...900 °C).

4. Conclusions
The developed copper dispersion-strengthened composite material of the Cu-Al-CO system, containing 0.9 wt% aluminum and 0.3 wt% carbon, due to its a significant high-temperature strength, good thermo-conductivity, high wear resistance, is a good alternative to modern copper-based antifriction heat-resistant materials (for example, CuBe2NiTi, CuA19Fe3, CuNi2Si) and to iron-based materials (for example, Gh 1051) used in heat-loaded friction units such as valve guides of valves of internal combustion engines and plungers of die-casting machines.

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