Heat - and Wear-Resistant Nanocomposite Material Based on Copper Powder for Valve Guides of High-Forced Engines

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Abstract. The article presents the results of the development of heat - and wear -resistant nanocomposite material based on copper powder Cu-Al-C-O system, which due to the optimally selected chemical composition and dispersion-strengthened structure with a strengthening phase $\gamma$-Al$_2$O$_3$ of nanodispersed range has a set of physical, mechanical and operational characteristics, at its level significantly higher than the similar characteristics of the standard bronze CuNi2Si F65 DIN 17666, used by a number of engine companies for the valve guides of powerful and high-forced internal combustion engines. In particular, the wear resistance coefficient for the valve guide made of this material is 17 times higher than for the guide made of this standard bronze. In this case, the coefficient of score-resistance of the bushings of the new material is 2.54 times higher than the same index for the bushings of bronze. Moreover, it also provides the least wear not only of the guide bushing but also of the valve, i.e. of the entire pairing as a whole.

1. Introduction

It is known [1, 2] that a significant number of failures of internal combustion engines occur due to valve failures. The valve provides direct supply to the cylinders of a certain portion of the fuel-air mixture or only air and also releases exhaust gases. In this regard, the heating temperature of the heads and valve stems (especially exhaust valves) is respectively 700 ... 800 °C and 150 °C [2].

The important role in ensuring reliable operation and high service life of the valve is played by its guide bushing (Fig. 1), since the reciprocating movement of the valve can cause mechanical wear of the bushing hole and even sticking of the valve in the bushing, which leads to the failure of the entire engine.

The occurrence of such defects is primarily due to the wrong selection of material for the guide bushing. The temperature at the height of the guide bushing is reduced and is 80...90% of the heating temperature of the valve. In this regard, in the upper part of the guide bushing adjacent to the valve seat area, its temperature can reach 720 °C. It should be added that the guide bushings work in an aggressive environment of gases heated to more than 700 °C, moving at a speed of 400…600 m/s [3].
In connection with the above, it is obvious that the material for valve guides should have, above all, high wear resistance and resistance to scoring, low friction coefficient, the stability of properties at high temperatures, good thermal conductivity, and low linear thermal expansion coefficient.

Depending on the required properties and operating conditions, the engine valve guides are made of gray pearlitic and bleaching cast iron, complex-alloyed steels. Recently, sintered composite materials based on iron, copper and even aluminum have found widespread use.

For example, gray cast iron Gh1051 brand (3.65wt% C; 2.65wt% Si; 0.45…0.75wt% P; 0.55wt% Mn; S ≤ 0.155wt%; Fe-res.), which in recent years has been less and less used. It is also known the use of solid special cast iron with the structure of the cane and c carbide inclusions. But they are distinguished by the complexity of the chemical composition and low adaptability. As follows from the source [4], in Japan, well-known cast iron is also a thing of the past, and instead, they come sintered composite materials, which already occupy more than 70% of the domestic market in the production of valve guides. For example, in [5] it is proposed to use iron powders based on high-speed steel HSS to obtain a sintered framework of the valve guide, which is then impregnated with molten copper. The experience of [6] using sintered materials of the Fe-Cu-C system for valve guides is also known. However, it should be noted that when using iron-based materials under cold start conditions, when the viscosity of the oil is high and there is not enough lubrication, there is increased wear on both the valve stem and the bushing itself. In addition, due to the high linear thermal expansion coefficient, the gap between the valve stem and the bushing guide is reduced, which in turn causes the valve to sticking in the guide. Also, these materials are quite porous, which in turn complicates their machining.

For powerful engines with a high level of afterburner in their guide bushings valves are often used copper-based alloys obtained using the method of dispersion hardening. So, in the guide bushes of the engines of Russian high-speed cars based on the LADA model, the complex-alloyed brass CuZn40Al2 PTL2101 was used. In a powerful and uprated engines companies are Motoren- und Türenbien Union Friedrichshafen G. m.b.H. and PORSCHE AG widely used alloys CuNi2Si F65 (1.6…2.5 wt %Ni; 0.5…0.8 wt %Si; Mn≤0.8 wt %; Cr≤0.04 wt %; Cu – res.) with hardness 180…220HB, also alloys of Thermo-Hedul FS-15 (10.0…12.0 wt %Zn; 0.12…0.25 wt %Si; 0.30…0.50 wt % Mn; 0.60…0.90 wt %Te; S≤0.03 wt %; Fe≤0.10 wt %; Ni≤0.20 wt %; Cu – res.) with hardness 130…170HB and Aeterna VL22 (Zn≤0.5 wt %; Si≤2.0 wt %; Al≤1.4 wt %; Pb≤0.7 wt %; Cu≤58 wt %) with hardness 160…190HB [7]. However, due to the limited heat resistance of these materials, their use in more advanced boosted engines becomes impossible. This is explained by the fact that at high temperatures the finely dispersed hardening phases contained in the copper matrix of such alloys are dissolved in it.

It is also impossible to use for these purposes and gaining popularity sintered powder materials based on aluminum. In particular, in the source [8, 9] it is proposed to use Al-SiC<sub>p</sub> composites as an alternative material for engine valve guides. But the softening temperature of these composites is much lower than the heating temperature of the valve bushing of the forced engine.

In contrast to dispersion-hardening alloys, dispersion-strengthened materials contain such finely dispersed refractory particles (dispersoids) as phase-hardeners that do not dissolve in the copper matrix and do not interact with it up to its melting temperature [10-12]. This determines the best strength characteristics of materials of this class at high temperatures. Moreover, the smaller the size
of the dispersoids, the recrystallization temperature of the material is higher [8]. In copper dispersion-strengthened materials containing nanoscale dispersoids (less than 100 nm), the coefficient of hardening (the ratio of the strengths of hardened and non-strengthened copper) with an increase in temperature up to 0.9...0.95 the melting temperature of copper continuously increases [11-13]. In addition, the structure of such materials corresponds to the well-known rule of Georges Charpy, according to which the antifriction materials must have a ductile base and uniformly distributed therein solids.

Based on the above, it seems reasonable to use copper nanocomposite material with a dispersion-strengthened structure as a promising material for the valve guide bushings of high-forced engines. The present work is devoted to the development of such copper-base material of the Cu-Al-C-O system and its production technology. At the same time, the developed material must have a high recrystallization temperature (more than 800°C), satisfactory thermal conductivity (not less than 15% of the thermal conductivity of copper), low coefficient of linear thermal expansion (not more 17·10^{-6} 1/°C at 20...100°C and 23.0·10^{-6} 1/°C at 700...800°C), high hardness and strength at these temperatures. The material should have better tribotechnical characteristics than standard materials for similar applications. It should also not contain any toxic elements or compounds.

2. Experimental materials and methods

To determine the most optimal composition of the powder material of the Cu-Al-C-O system, initial mixtures were prepared from electrolytic copper powder PMS-1 (38 µm), aluminum powder PP-1 (75 µm) and powder of pencil graphite GK-3 (40 µm). The carbon content of the mixture was changed depending on the amount of aluminum powder contained in it from the following calculation: 1 mass fraction of aluminum should be 0.1; 0.2; 0.3; 0.4 and 0.5 mass fraction of carbon, and the aluminum content ranged from 2 wt% to 4 wt%.

To obtain a nanocomposite material from this mixture, the method of reactionary mechanical alloying in the attritor and the technology of powder and granular metallurgy were used. The reaction process of mechanical alloying was carried out in the air of the working chamber of attritor are considered with a capacity of 15 litres constructions of the Chuvash State University for 60 min at a rotor speed of the attritor are considered 600min⁻¹. At the same time, 2 kg of a powder mixture of each chemical composition was subjected to treatment.

The granules obtained as a result of mechanical reactionary alloying were pressed in a cold state at a pressure of 600 MP into briquettes with a diameter of 54 mm. Then the briquettes were heated in technological steel capsules with wood carburizer at a temperature of 850 °C for 50 minutes, after which the capsules were alternately directed from this temperature to a hydraulic press container heated to 450 °C, the heated briquette was removed from each capsule and placed into a press container and extruded into a bar diameter of 13 mm through a conical matrix with a cone angle of 120°.

The obtained bars were used to produce samples for testing according to the relevant standard methods to determine the physical and mechanical properties of the materials obtained. The microstructure was studied using a microscope with a magnification of 1200 times. The fine structure of the materials was investigated using X-ray diffraction analysis and transmission electron microscopy (thin foils were made of this material and carbon extraction replicas taken from its thin sections). The parameters of fine structure components (dispersoids, grains) of the materials were determined according to the method described in [14].

Tribotechnical tests were carried out on the friction machine according to the «pad - roller» scheme. At the same time, the pads were made of the standard materials studied and compared with it, and the rollers were made of chromium steel with 0.4 wt. % carbon, hardened to a hardness of 52...53HRC. The standard material CuNi2Si F65 DIN 17666 with a hardness of 180...220 HB and a tensile strength of 640 MPa was used as a comparative material, which found application in valve guides of powerful and forced engines of engine-building companies. Tests for wear-resistance and score-resistance of the studied samples were carried out under constant load and continuously
increasing load, respectively. In case of continuously increasing load, the loading rate of the samples was 35 kg/h. The maximum load (300 kg) attributable to the samples under study was achieved in 8.5 hours. The rotational frequency of the roller was 500 min\(^{-1}\).

The coefficient of wear-resistance for the material of the guide sleeve \(K_1\) and the pair of « pad (valve guide) - roller (valve)» \(K_{1-2}\) was calculated respectively by the formulas:

\[
K_1 = \frac{J_1^R}{J_1} \quad \text{and} \quad K_{1-2} = K_1 \times \frac{J_2^R}{J_2},
\]  

(1)

where \(J_1^R\) is the specific wear of the pad (guide) when the pad is made of standard material (reference);  
\(J_1\) - specific wear of the pad (guide) when the pad is made of the material under study;  
\(J_2^R\) - specific wear of the roller (valve) operating in conjunction with the pad (guide) of the standard material (reference);  
\(J_2\) - specific wear of the roller (valve) operating in conjunction with the pad (guide) of the material under study.

The coefficient of score-resistance to the material of the valve guide \(K_3\) was determined by the formula:

\[
K_3 = \frac{P_{Cr} \times p}{P_{Cr}^R \times p^R},
\]  

(2)

where \(P_{Cr}^R, p^R\) is, respectively, the critical load and the specific load of specific load of seizing for pairing the pad with the roller (valve with the valve guide) when the pad is made of standard material (reference);  
\(P_{Cr}, p\) - respectively, the critical load and the specific load of specific load of seizing for pairing the pad with the roller (valve with the valve guide), when the pad is made of the material under study.

The coefficient of durability \(K_D\) for the material of the valve guide assuming the same effect of wear-resistance and score-resistance on durability was determined by the following formula:

\[
K_D = \sqrt{K_1 \times K_3}.
\]  

(3)

3. Test results and discussion

Table 1 shows the test results of standard samples made of hot-extruded bars of materials of the Cu-Al-C-O system.

From Table 1 it follows that for each specific aluminum content, there is an optimal amount of carbon at which the material has the greatest thermal conductivity or hardness.

In particular, the maximum thermal conductivity of the material occurs when the carbon content in the amount of 0.1 mass fractions per 1 mass fraction of aluminum, and the maximum hardness - at 0.4 mass fractions of carbon per 1 mass fraction of aluminum.

Analysis of the properties given in Table 1, also shows that the best combination of characteristics such as hardness, elongation (characterizes the technological properties of the material – its ductility) and thermal conductivity have the materials shown in Table 2.

The importance of plastic properties of the material for the guide bushings is caused by the fact that in the manufacture of these parts from hot-extruded tubes need to refine their hole to the required size and surface cleanliness using machining methods. In this case, the resulting axial cutting forces with a large longitudinal feed of the cutting tool can lead to cracks or even to the destruction of the valve guide.
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                                          |
| 2.0                                         | 0.2                                       | 756                   | 3.9                    | 216              | 28.5                                          |
| 2.0                                         | 0.4                                       | 767                   | 3.1                    | 225              | 25.3                                          |
| 2.0                                         | 0.6                                       | 772                   | 1.1                    | 235              | 23.4                                          |
| 2.0                                         | 0.8                                       | 838                   | 1.7                    | 243              | 19.6                                          |
| 2.0                                         | 1.0                                       | 814                   | 1.4                    | 237              | 19.5                                          |

| 3.0                                         | 0.0                                       | 790                   | 5.9                    | 219              | 18.0                                          |
| 3.0                                         | 0.3                                       | 816                   | 3.5                    | 230              | 22.9                                          |
| 3.0                                         | 0.6                                       | 830                   | 2.6                    | 224              | 18.7                                          |
| 3.0                                         | 0.9                                       | 836                   | 2.5                    | 238              | 17.4                                          |
| 4.0                                         | 1.2                                       | –                     | –                      | 254              | 15.6                                          |
| 4.0                                         | 1.5                                       | –                     | –                      | 244              | 15.4                                          |

| 4.0                                         | 1.2                                       | –                     | –                      | 260              | 13.2                                          |
| 4.0                                         | 1.6                                       | –                     | –                      | 244              | 13.1                                          |
| 4.0                                         | 2.0                                       | –                     | –                      | 260              | 15.2                                          |

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

Table 2. Properties of materials of Cu-Al-C-O system with the most optimal chemical composition.

| Material symbol | Initial content in the powder mixture, wt.% | Tensile strength, MPa | Relative elongation, % | Hardness HB5/250 | Thermal conductivity, % of the thermal conductivity of copper |
|-----------------|---------------------------------------------|-----------------------|------------------------|------------------|-------------------------------------------------------------|
| AL2/C08         | 2.0                                         | 838                   | 1.7                    | 243              | 19.6                                                        |
| AL3/C09         | 3.0                                         | 836                   | 2.5                    | 238              | 17.4                                                        |
| AL4/C08         | 4.0                                         | 850                   | 2.0                    | 260              | 15.2                                                        |

In connection with the above, from the presented in Table 2 material preference should be given to the material with the symbol AL3/C09. Therefore, all further tests and studies were carried out on this material.

The developed copper powder material has a recrystallization temperature equal to 1000°C and has high hardness values at high temperatures, which allows it to be classified as heat-resistant and heat-resistant materials. At the same time, it has a fairly good thermal conductivity, which in the direction of hot extrusion of the material is 65.0 W/m·°C at 25 °C and 36.4 W/m·°C at 700 °C. The material also has a low coefficient of linear thermal expansion: 17.0·10⁻⁶ 1/°C at 20...100°C and 22.6·10⁻⁶ 1/°C at 700...800°C.

The photo of the microstructure of the material AL3/C09 (Fig. 2, a) clearly shows the boundaries of the granules of which it consists. High recrystallization temperature, heat-resistance and the high-temperature strength of the material due primarily pronounced it subgrain structure and it is
dynamically stable particles of aluminum oxide $\gamma$-Al$_2$O$_3$ (Fig. 2, b), formed as a result of mechanochemical synthesis (solid-phase reaction between aluminum and oxygen of the air in attritor working chamber) when carrying out the operation of reactionary mechanical alloying [12,13,15].

![Figure 2. Structure of copper nanocomposite material AL3/C09: a) x 400; b) x20000 (TEM, replica).](image)

Stereological analysis of the replicas showed that the average particle size of the hardening phase for the material AL3/C09 is 39±7 nm, and therefore this material can be attributed to nanocomposite materials.

The above-described features of the structure of the material, as well as the presence of finely dispersed free carbon in an amount of 0.69...0.73 wt % in conjunction with these physical and mechanical properties, were to provide the material with the same good performance properties. This assumption was confirmed by Table 3 results of the comparative tribotechnical tests.

From table 3 it follows that the developed nanocomposite material AL3/C09 by its tribotechnical characteristics significantly exceeds the bronze CuNi2Si F65. In particular, the wear-resistance coefficient for the guide bushing made of this material is 17 times higher than for the bushing made of standard bronze. In this case, the coefficient of score-resistance of the bushing of the new material is 2.54 times higher than the same index for the bushing of bronze. Moreover, it also provides the least wear not only of the guide bushing but also of the valve, i.e. of the entire coupling as a whole.

**Table 3.** Tribotechnical characteristics of various tested materials.

| Characteristic                          | Designation | Developed material | Standard material |
|----------------------------------------|-------------|--------------------|-------------------|
| Hardness, MPa                          | HB$_{5/250}$| 238                | 225               |
| Specific wear:                         |             |                    |                   |
| -pad (valve guide), mm$^3$/km          | $J_1$       | 0.024              | 0.403             |
| -roller (valve), mg/km                | $J_2$       | 0.028              | 0.036             |
| The coefficient of wear resistance:    |             |                    |                   |
| -pad (valve guide)                     | $K_1$       | 17                 | 1                 |
| -interfaces                           | $K_{1/2}$   | 21                 | 1                 |
| Critical load, kg                      | $P_{cr}$    | 145                | 88                |
| The specific load of seizing, MPa      | $p$         | 66.3               | 16.9              |
| The coefficient of score-resistance    | $K_Z$       | 2.54               | 1.00              |
| The coefficient of durability          | $K_D$       | 7.3                | 1.0               |
4. Conclusions
A new nanocomposite material based on copper powder of the Cu-Al-C-O system has been developed, which, thanks to the optimally selected chemical composition and dispersion-strengthened structure with the $\gamma$-Al$_2$O$_3$ hardening phase of the nano-dispersed range, has a combination of physicomechanical and operational characteristics that greatly exceed similar characteristics of standard bronze CuNi2Si F65 DIN 17666, used by a number of engine-building companies for valve guides of powerful and high-efficiency internal combustion engines. In this regard, this material can be recommended for use in the specified details of perspective high-forced engines.

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