Carbon-graphite preparation for impregnation with aluminum alloy

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Abstract. The possibility of increasing the efficiency of gasostat-free impregnation of porous carbon-graphite materials with aluminum alloys by applying thin high-purity metal alloying coatings by galvanic method to the surface of the pores of a carbon-graphite specimen is studied. It is shown that the preliminary application of such coatings by an electroplating method allows obtaining the effect of alloying with highly pure elements, increases the filling of pores with matrix melt and decreases the impregnation temperature (750°C). This technology makes it possible to obtain high-quality composite materials using simple technological equipment.

1. Introduction
Modern industry and manufacturing shows great interest in functional composite materials based on porous carbon materials impregnated with various metal alloys such as copper, antimony, aluminum. Metal-impregnated carbon composite materials occupy a significant share of the product range of top manufacturing companies of antifriction materials such as Ringsdorf (Germany), Schunk (Germany), Morgan (Great Britain), Mersen (France), Toyo (Japan) [1-4]. Interest in these composites is caused by characteristics that combine the advantages of a carbon material (high antifriction characteristics, self-lubrication, chemical resistance, ability to work successfully at high temperatures) with the properties of metals (high hardness, strength, electrical conductivity and thermal conductivity) [5, 6]. Composite materials with a copper matrix are most successfully used for the runners of the current collectors on electrified railway and urban transport under conditions of high currents. However, the disadvantage of a copper matrix is instability in some chemically active environments. Composite materials based on antimony matrix have high performance at high speeds and loads under dry friction conditions. In addition, these composites have high corrosion resistance, but they have low electrical conductivity, which limits their use [7, 8].

The aluminum matrix improves the strength characteristics of the composite material, such composite materials have high performance compared to materials based on copper and antimony. In addition, the aluminum matrix has high corrosion resistance in many corrosive environments [9, 10]. The combination of these properties makes aluminum alloys very promising as matrix alloys for obtaining composite materials. The difficulty of synthesizing such composites by liquid-state methods consists in the formation of an oxide film on the surface of aluminum, which prevents the chemical interaction of molten aluminum and the surface of carbon-graphite, impregnation is possible under conditions of very high temperatures (1200°C) [11]. Another way is to use high temperatures in combination with high pressure. However, there is a need to use complex and expensive autoclave...
equipment. An alternative solution is alloying the matrix alloy with surface active elements, which are elements with a low surface tension or metals with a low melting point. At the Department of Machines and Technology of Foundry of Volgograd State Technical University developed an experimental method for autoclave-free impregnation, and inexpensive standard furnace equipment and relatively simple technological equipment were used to implement this method [12]. The method consists of utilizing the pressure in a hermetic container made of a material with a low value of thermal expansion during heating and a metal (alloy) inside a device with a higher value of the coefficient of thermal expansion, for example, an aluminum matrix alloy and a device for impregnation made of a titanium alloy. As a result, the pressure inside the impregnating device is up to 5 MPa. However, the specified pressure is insufficient for the required filling of the pores of the carbon-graphite. To increase the filling of the pores, this method was improved by applying thin coatings of alloying high-purity metals on the inner surface of open pores and the perimeter of carbon frame by galvanic method.

The aim of this work was to improve the method of gasostat-free impregnation of porous carbon frame with aluminum alloys and to increase the quality and efficiency of impregnation.

2. Materials and methods
To increase the quality of impregnated carbon-graphite, the gas-free technology was divided into separate stages. At the first stage, preliminary preparation of carbon-graphite was carried out, during which galvanic coatings were applied to the walls of open pores. From a technological point of view, copper and nickel plating are acceptable. They can simply applied to carbon-graphite, differ in acceptable room requirements, available chemical reagents, do not require a powerful current source and are easy to prepare electrolyte. The disadvantage of these metal coatings is their recrystallization temperature, which for both metals is at the level of the melting point of aluminum. Moreover, the application of another alloying metal, such as zinc or chromium, without one of these coatings is already difficult or impossible. For example, to apply a zinc coating on carbon-graphite, it is necessary to use high current strength (20-40 A). And for those already covered with copper or nickel, these indicators decrease to 0.5-2 A. The initial solution was to apply the thinnest coatings, 5-10 µm thick, so that they did not affect the impregnation parameters, but reduced the contact angle and intensified the process.

Zinc was chosen as the main alloying element. Zinc has a high coefficient of thermal expansion, maximum fluidity and low melting point (419.5°C). Nevertheless, in the presence of oxygen and high temperature, zinc is rapidly oxidized, which leads to a significant decrease in the assimilation of the alloying element and environmental safety. This can be solved by applying an additional thin "protective" coating over the zinc, such as a layer of copper. In the impregnation process, zinc, having a low melting point, melts under the copper layer, increasing the initial infiltration of the matrix alloy into the pores. The copper coating will temporarily limit contact of the matrix alloy with zinc until oxygen is removed from the device.

Before coating, the carbon-graphite frame was degassed in a zinc electrolyte, and then a zinc coating was applied. This made it possible to fill open pores with zinc electrolyte and, upon further galvanization, to obtain a metal layer on the surface of the pores and to alloy the interface between the carbon-graphite and the matrix alloy with pure elements [13]. After applying a zinc layer, a copper coating was applied to the sample. After the completion of the formation of the copper coating, the sample was washed in water and dried. Then the carbon-graphite frame with galvanic coatings was placed in a small crucible with a volume of 100 ml, filled with an aluminum matrix alloy at a temperature (750°C), fixed the carbon-graphite with a special device from floating up and installed on a vibrating table. After that, it was covered with a vacuum hood, then the unit was connected to a vacuum pump, and the carbon-graphite frame was degassed in the matrix alloy, together with vibration treatment for 180 s at a temperature of 700°C. This treatment allows to dissolve a thin copper and zinc coating, and partially fill the pores of the carbon-graphite framework. After this treatment, the contents
of the crucible were removed, fixed with a device that excludes the floating of carbon-graphite, and placed in a gasostat-free impregnation device, which was pre-filled by 2/3 with a crystallized matrix aluminum alloy. This makes it possible to achieve an additional increase in the volume of aluminum by 6% due to the fact that the transition of the metal to the liquid state is accompanied by an increase in volume and a decrease in density.

Then the impregnation device was covered with a lid heated to 800°C and the required amount of aluminum matrix alloy was added through the filling hole, and then hermetased with a plug heated to 900°C. At the next stage, the stopper was fixed with a cold wedge and the device for impregnation was placed in an oven heated to 750°C with isothermal holding for 20 minutes.

At each of these stages, the change in the weight of the carbon-graphite sample was recorded, which is shown in table 1.

Table 1. Change in the weight of carbon-graphite at the stages of its production.

| Initial weight, g | After degassing in electrolyte, g | After drying, g | After impregnation, g |
|-------------------|----------------------------------|----------------|----------------------|
| 4.4               | 4.7                              | 4.45           | 5.7                  |

The final stage of fabricating composite material was its additional compaction with a lead alloy in a pressure form mold at a temperature of 500°C for 60 s [14]. Such thermomechanical treatment allows to compact the aluminum alloy in the pores of carbon-graphite, and modify the surface of the matrix alloy with lead, which has a positive effect on the antifriction characteristics of the composite material.

A sample for impregnation was made of AG-1500 carbon-graphite (open porosity of 15%) in the form of a cube with a side size of 30 mm. The sample volume was 900 mm³ and the pore volume in it was 135 mm³. The microstructure and chemical composition of the matrix metal in the composite material were investigated using a Versa 3D double beam electron scanning microscope in case of increase from 7000 to 22000 x, and acceleration voltage 15 kV.

3. Results and discussion
Figure 1 shows the microstructure of carbon-graphite after impregnation and compaction.
Studies of the chemical composition of the matrix alloy in the filled pore (figure 2) show that the matrix alloy in the initial state consisted of an alloy of aluminum and silicon, which is part of the A04130 alloy, and additionally the alloy was alloyed with magnesium (5 wt.%). Zinc and copper were applied to the walls of open pores of carbon-graphite in the form of thin galvanic coatings and their minimum amount confirms the effectiveness of their interaction with the matrix aluminum alloy, when they are completely dissolved.

![Figure 2. Studies of the chemical composition of the matrix alloy in the filled pore.](image)

The presence of lead no more than 5% indicates (table 2) that in a short time (60 s) under the simultaneous action of temperature (500°C) and pressure, the lead alloy interacts with the surface of the matrix alloy, modifying it, which increases the antifriction characteristics of the composite material. It is worth noting the presence of titanium in the impregnated sample, titanium “came from the tooling material” into the alloy composition in the pore, since it was not introduced into the initial alloy for impregnation.

| Point | C     | Al    | Pb    | Zn  | Si   | Cu   | Mg   | Ti   |
|-------|-------|-------|-------|-----|------|------|------|------|
| 1     | 10.23 | 84.17 | 1.13  | 0.98| 0.12 | 0.65 | 1.78 | 0.94 |
| 2     | 8.96  | 83.72 | 2.45  | 0.16| 0.26 | 0.31 | 2.56 | 1.58 |
| 3     | 9.16  | 76.96 | 4.55  | 0.13| 0.51 | 0.25 | 2.75 | 5.69 |
| 4     | 4.64  | 85.74 | 1.83  | 0.62| 1.68 | 0.54 | 2.14 | 2.81 |

This is consistent with the presence of magnesium in the alloy, which, according to the electronegativity of Pauling's elements (figure 3), is located to the left of the other elements and has a higher selectivity with respect to carbon in the selected aluminum-based impregnation alloy.
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Molten aluminum is a very active material and its interaction with carbon should be further studied in conjunction with such not less active elements as titanium and magnesium.

4. Conclusion
Improving quality of impregnated graphite-carbon consists in the preparation and application of high-purity alloying metals (zinc, copper) to the inner surface of the pores by galvanic method. The combination of simultaneous exposure to temperature and pressure made it possible to obtain composite materials carbon-graphite aluminum alloy, economically using surface active elements in the form of galvanized layers (zinc, copper), reducing the impregnation temperature. Additional thermomechanical treatment of the aluminum alloy in the composition allows for the technological operation of compaction with the simultaneous modification of the surface of the matrix alloy with lead.

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