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Effect of Alloying Elements on the Wetting of Graphitized Carbon with Copper Alloys

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Abstract—The influence of various alloying elements on the wetting of graphitized carbon with copper-based alloys is considered. The effect of alloying titanium, manganese, vanadium, molybdenum, cobalt, tungsten, nickel, chromium, niobium, and phosphorus on the surface activity and the contact angle of wetting a carbon substrate with the copper melt is described.

Keywords: composite material, impregnation, graphitized carbon frame, copper alloys, alloying

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INTRODUCTION

The main purpose of modern materials science is the development of novel materials with a wide range of physicomechanical properties. Ordinary homogeneous systems not always meet the high requirements imposed on modern materials; hence, sufficient attention is paid by researchers to designing and development of various composite materials. This can be exemplified by graphitized carbon materials impregnated with antimony or copper alloys [1] characterized by high chemical resistance, superior antifriction, electrotechnical (in the case of copper matrix), and mechanical properties. This determined their successful application in the petrochemical industry and railway electric transport. However, the development of such composites is sometimes accompanied by certain difficulties. The main concern is that, under natural conditions, the graphite surface is actually not wetted with the copper melt, since molten copper is characterized by selective chemical activity and does not react with carbon even at high temperatures. As was demonstrated in [2], the contact angle of graphitized carbon surface with molten copper at 1100°C is 140°, which prevents the penetration of the melt into open pores in graphitized carbon. Thus, graphitized carbon workpieces are impregnated with copper melts at high temperatures (>1200°C) and a high excess pressure (10–100 MPa), which needs complicated autoclave facilities and leads to significant difficulties and high costs. Hence, the necessity to develop special copper alloys is obvious, aiming at active wetting of the graphite surface with melts that can penetrate into fine pores of graphitized carbon without a significant excess pressure.

Generally, the wetting of the graphitized carbon surface with a molten metal occurs when the latter sufficiently intensely reacts with carbon, nontransition metals (including copper) are chemically inert with regard to carbon, and the contact angle of the metal droplets contacting with the graphite surface are obtuse ($\theta > 90°$).

This problem can be solved for copper by its modification with proper surface active alloying elements. The alloys thus formed should be characterized by low shrinkage, an increased mechanical strength, and a high electrical conductivity. At the same time, the mutual solubility of a matrix alloy and the carbon base should be minimal and prevent deterioration of the operation characteristics of the composite material. Recently, the wetting of graphitized carbon with copper alloys with addition of certain surface active alloying elements has been studied [3].

In this work, the influence of addition of titanium, manganese, vanadium, molybdenum, cobalt, and tungsten on the wetting of graphitized carbon with copper alloys is experimentally studied, and the role of such alloying elements as nickel, chromium, niobium, and phosphorus is refined.

Table 1. Physicomechanical properties of experimental graphitized carbon materials

Property	GE	AG1500	CG365 (Slovakia)
Density ρ, kg/m^3	1600 (1520)*	1780 (1700–1800)	1630 (1600–1650)
Ultimate compressive strength $\sigma_{u.comp}$, MPa	24–26	80–85 (80–100)	50–55 (60)
Ultimate bending strength σ_{bend}, MPa	6–8	35–37 (40–50)	18–20 (30)
Porosity, %	30 (24)	22 (14)	18 (15)
Open porosity, %	24 (18)	18 (10)	14 (12)
Pore radius R_{eff}, μm	4.33	0.84	0.91 (0.8–1.1)

* Reference data are given in brackets.

EXPERIMENTAL

The experiments were carried out using M00 copper of high purity (Russian standard GOST 859–2001). The graphitized substrate was made of graphitized carbon materials: GE, AG1500, and CG365 (Slovakia). Their properties are summarized in Table 1. The experimental copper alloys were produced using an Indutherm VC-400 vacuum casting machine, and its design and operation were described elsewhere [3]. This equipment makes it possible to melt a metal, to cast the melt in inert environment under excess pressure, and to form cast copper samples with various content of alloying elements. Wetting at the carbon/copper alloy interface was studied on laboratory experimental facility by the sessile drop method [4]. After melting, a drop was held for 10–15 min. Its images were processed on a PC and the contact angle was calculated using the Darcy theoretical approaches [5], which enable the contact angle, the surface tension, and the work of adhesion to be determined from a drop contour.

RESULTS AND DISCUSSION

While selecting alloying elements, the substances would be preferable that provide the wetting of graphite substrate with the copper melt without preliminary application of special coatings.

At the first stage of the studies, the influence of titanium on the interphase interaction between the copper melt and graphitized carbon was analyzed. Titanium is well soluble in copper and acts as a strong surfactant in the melt. Addition of titanium in amount from 0.1 to 1 at % to the melt improved wetting of graphitized carbon and decreased the contact angle from 130°–140° for pure metal to 50°–10°. This is confirmed by the fact that the surface tension increases with the titanium content in the melt [6].

Addition of manganese to copper significantly affects the wetting of graphitized carbon only at its high content (about several tens of an atomic percent); however, the alloy production becomes more complicated.

Analysis of adhesion activity of copper melt with vanadium additives revealed its low level. This can be attributed to the low solubility of vanadium in copper. Thus, additional ~10 wt % nickel was added to the melt; then the adhesion activity of the melt slightly increased and the melting point of the copper alloy increased.

Copper alloying by cobalt did not improve its adhesion activity, though, in pure form, cobalt wets graphite sufficiently. In addition, this alloying element initiates recrystallization in graphitized carbon, decreasing its strength [6].

The use of molybdenum and tungsten as surfactants is possible only in Cu–Ni, Cu–Co, and Cu–Ni–Sn alloys. However, the experiments demonstrated low wetting quality of the graphitized carbon surface by the mentioned alloys. Herewith, a significant increase in the melting points of these alloys was detected (up to 1174–1289°C).

Alloying of copper alloys by chromium, nickel, niobium, and phosphorus as the most efficient alloying surfactants should be considered separately. The influence of chromium on the adhesion activity of copper at the interface with graphitized carbon was studied on Cu–Cr and Cu–Ni–Cr alloys. Kh99 chromium was used in this study (Russian standard GOST 5905–2004). It is known [7, 8] that, depending on the melt temperature, chromium dissolves completely in molten copper at its content of 1–10 at %. The experiments detected noticeable influence of chromium on the alloy activity at the interface. At a chromium content of 1 at % the contact angel decreased from 140° to 40° as in the case of titanium addition. Upon nickel addition to a copper–chromium alloy, its surface activity increases even higher. It should be mentioned that, in comparison with chromium, alloying of copper alloys by titanium is more efficient. Thus, at 1150°C and 12 at % chromium in copper, the contact angle decreased to 23°, whereas about the same titanium content (10.2 at %) resulted in complete spreading of copper–titanium alloy over the graphite surface. However, in practice, copper–chromium alloys are more preferable, since they are processed better in comparison with copper–titanium alloys. In addition, with increase in the chromium content in copper, the

Table 2. Influence of alloying elements on the wetting of the carbon surface with copper and its alloys and the characteristics of the developed alloys

Alloy	T_S, K	θ, deg	α, J/m^2	σ, MS/m	λ, W/(m K)	*HB*	$\sigma_{u.comp}$, MPa
Cu	1356	140	1.81	57.0	401	35	62
Cu + 1 at % Cr	1350	40	0.48	37.0	260	52	66
Cu + 5 wt % Ni	1383	132	1.70	28.0	197	120	80
Cu + 10 wt % Ni + 2 at % Nb	1368	6	0.04	21.0	148	179	98

T_S is the solidus temperature; θ, contact angle; α, surface tension; σ, electrical conductivity; λ, heat conductivity; and *HB*, Brinell hardness.

mechanical properties of the alloy are improved as well as its corrosion resistance.

The influence of niobium on the surface tension of copper alloy was also studied in this work. A drawback of this alloying element is its poor solubility in molten copper. To increase the niobium solubility in copper and to improve its adhesion activity, 10 wt % of nickel was added to the melt. In the presence of nickel, the influence of niobium is more significant. For instance, the contact angle varied from 150° in the presence of 0.68 at % niobium to 5° at 2.07 at % niobium. Table 2 summarizes the influence of some elements (Cr, Ni, and Nb) on the activity of copper alloy upon wetting the carbon surface.

The influence of phosphorus on wetting was experimentally estimated in this work using MF9 phosphorus copper (Russian standard GOST 4515–93). In the case of alloying of copper by phosphorus, the most efficient decrease in the contact angle (<90°) and the surface tension is observed at 6.5–7 wt % phosphorus (Fig. 1). Further increase in phosphorus content (to 9 wt %) decreases the contact angle even stronger. In comparison with pure copper, the use of a copper–phosphorus alloy made it possible to decrease the contact angle at 870°C to 84° (Fig. 2). At the same time, the melting point of the alloy and, hence, the impregnation temperature of the graphitized carbon frame also decrease. Thus, at phosphorus content up to 8.4 wt % in copper, the melting point decreases to 714°C.

Therefore, alloying of copper with phosphorus decreases the impregnation temperature, decreases the contact angle to 84°, increases the rate of infiltration of porous graphitized carbon base of the composite material, and improves its mechanical properties. However, when phosphorus content reaches 9 wt %, the electrical conductivity of the material decreases in addition to a further decrease in the contact angle. Table 3 demonstrates the influence of the phosphorus content on the properties of the copper alloy. The influence of niobium, nickel, chromium, and phosphorus on microstructure of copper alloys is illustrated in Fig. 3. It can be seen that niobium leads to the

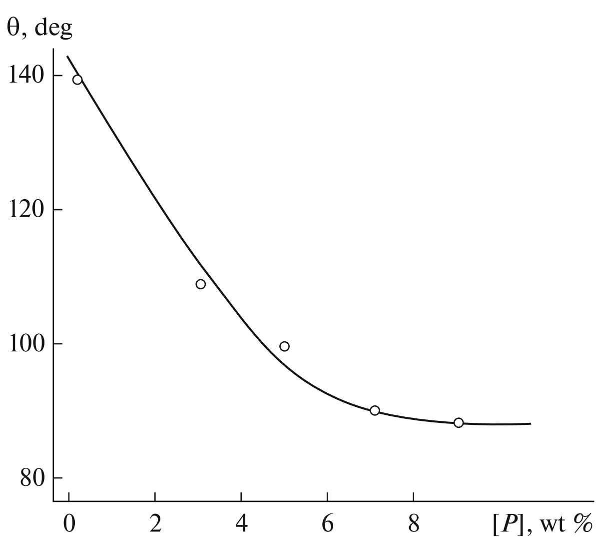

Fig. 1. Influence of the phosphorus content in a copper alloy on the angle of wetting of a graphite substrate with the alloy.

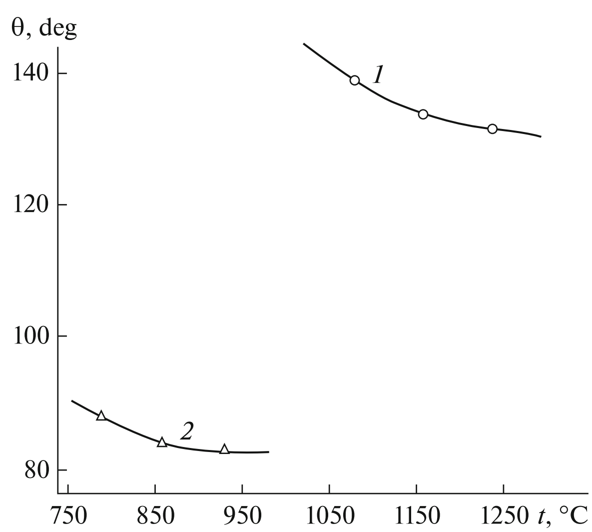

Fig. 2. Contact angle of graphitized carbon substrate with a copper alloy as a function of the heating temperature: (*1*) pure copper and (*2*) copper–phosphorus alloy (9 wt % [P]).

Table 3. Influence of phosphorus additives on the characteristics of copper and phosphorus alloys

Alloy	T_S, K	θ, deg	α, J/m^2	σ, MS/m	λ, W/(m K)	*HB*	$\sigma_{u.comp}$, MPa
Cu	1356	140	1.81	57.0	401	35	62
Cu + 3 wt % P	1263	121	1.63	9.8	69	90	81
Cu + 5 wt % P	1183	105	1.52	8.7	61	132	95
Cu + 7 wt % P	1113	89	1.25	8.2	58	171	106
Cu + 9 wt % P	1043	84	1.01	6.9	49	210	117

See the notes to Table 2.

formation of active centers of crystallization, promoting fragmentation of the alloy structure.

It is established that AG1500 and CG365 (Slovakia) graphitized carbon materials are most suitable for impregnation with copper alloys. Application of these materials provides good adhesion of copper alloys to the graphite surface and, hence, promotes achievement of the maximum infiltration of the melt into the open porosity of the graphitized carbon frame.

Therefore, the used alloying elements differently affect the ability of copper to wet the graphitized carbon surface. Herewith, the alloys in comparison with pure metals acquire new practically valuable properties (increased mechanical strength, corrosion resistance, heat resistance, arc resistance, and so on). It is important to select the alloying surfactants that provide good wetting of graphitized carbon and its high-quality impregnation by an alloy without special-purpose coatings on the graphite surface and the achievement of radically new engineering and operational properties of metal–graphite composite materials.

CONCLUSIONS

(1) The most efficient wetting of the graphitized carbon surface with a copper alloy is achieved upon its alloying with titanium. Combined application of chromium and nickel or nickel and niobium as additives either addition of phosphorus is less efficient with

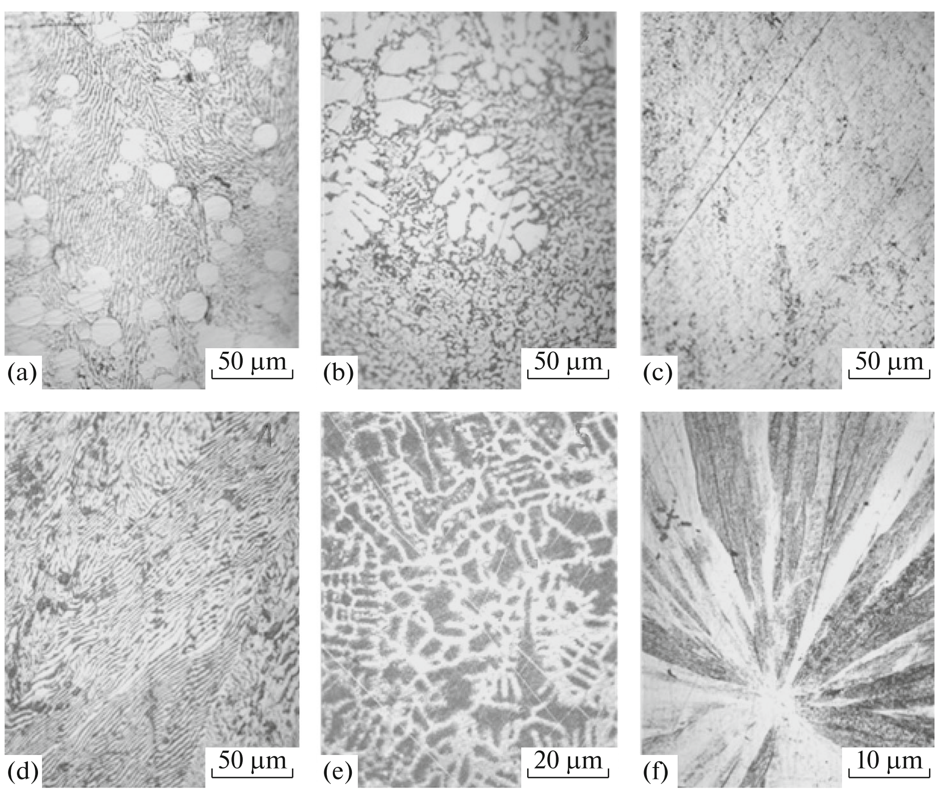

Fig. 3. Microstructures of copper alloys with addition of (a) niobium, (b) nickel, (c) chromium, and (d–f) phosphorus.

regard to the wetting of graphitized carbon with the copper melt.

(2) Concerning a decrease in the impregnation temperature, the most efficient additives to copper melt are phosphorus, tin, zinc, and manganese.

(3) The most suitable for impregnation with copper alloys are AG1500 and CG365 (Slovakia) graphitized carbon materials.

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