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CONDITIONS FOR PRODUCING THE LIQUID PHASE OF CARBON

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Consideration is given to the results for carbon melting under the conditions of electric-arc heating. An experimental scheme is realized, where a graphite specimen, which is one of the electrodes, is heated from below. It is shown that the equilibrium pressure of carbon vapor, which provides a reliable melting of the graphite specimen under steady conditions, is not higher than 0.2 MPa.

Thermophysical properties of graphite have been studied for more than a hundred years [1], but its active investigation after the 40s was prompted, first, by the need for carbon in nuclear (for example, a neutron moderator in the first reactors) and rocket (for example, nose cones and nozzles) engineering [2] and, of course, by the possibility of producing synthetic diamond. Exactly at that time a phase diagram of carbon in the diamond–graphite–liquid equilibrium region was first proposed [3].

For a long time graphite was produced mainly by high-temperature methods of powder metallurgy. Recrystallized graphites produced by thermomechanical (TMT) and thermomechanochemical (TMCT) treatments should be noted specially. Their properties approach those of a graphite single crystal [4]. However, requirements for materials possessing high thermal stability, mechanical strength, erosion resistance, etc. cannot be fully met without setting up new methods of treatment and production of special structural graphites.

According to a new version of the carbon phase diagram, in the vicinity of a graphite–liquid–vapor triple point, put forward in [5] (see Fig. 1), the parameters of this point must be as follows: pressure 0.1 MPa and temperature 4000 K. The latter is indicative of the possibility of graphite melting at practically atmospheric pressure, which opens up new prospects in the applied area because it can be used in devising relatively simple (in comparison with high-pressure methods) methods of producing structural graphite in single- and polycrystalline form via melting of pure starting material.

The current study aims at practically realizing the conditions and producing the liquid phase of carbon in the range of predicted parameters of the graphite–liquid–vapor triple point. The electric arc is used as the heating source.

The electric arc provides the heating of any material up to a melting temperature [6]. With its use as early as in 1914 it was first noticed [7] that, in short-duration arcing, a liquid phase of carbon is formed, in the author's opinion, on the surface of a graphite electrode in the anode spot (the spot brightness increases) at atmospheric pressure. After the experiment, no changes or melt on the surface of the graphite electrode were detected.

Figure 2 illustrates an experimental scheme based on electric-arc heating. In working water-cooled chamber 1, filled with argon, there are two, one above the other, graphite electrodes made of MPG-6 graphite of 99.9% purity (and also of MPG-6 graphite doped with molybdenum of 3–5 wt.%) 2 and 3, one of which is specimen 2. The arc is ignited via short-time contact of phase electrode 3 with zero electrode 2 with the aid of electrode holder 4. An ACD-200 ac power transformer and an AOMH-40 regulating autotransformer are used as the power source.

The graphite-electrode specimen has a larger surface than the second specimen. Since direct measurement of the pressure of carbon vapor is not feasible, the pressure of the buffer gas is usually measured, which

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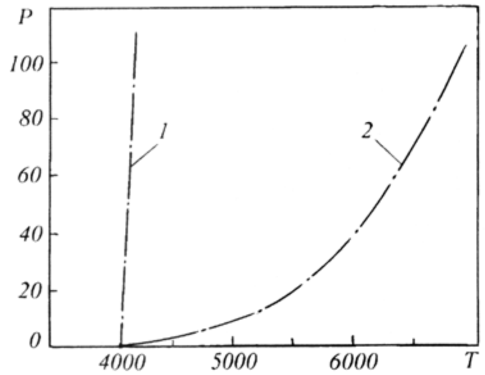

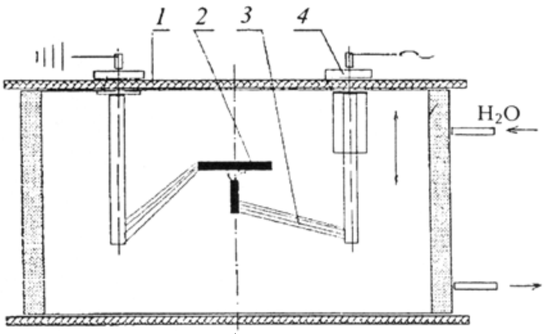

Fig. 1. *P–T* diagram of carbon in the vicinity of a graphite–liquid–vapor triple point: 1) melting; 2) boiling. *P*, MPa; *T*, K.

Fig. 2. Basic diagram of a working chamber with electric-arc heating.

under certain assumptions is correlated with the pressure of carbon vapor. With a steady heating of the surface of the graphite specimen from the external source, when the heating spot is above the specimen, the partial pressure of carbon vapor above the heating surface will be lower than the equilibrium pressure corresponding to a given temperature because carbon vapor is continually carried away by convective flows. To avoid this, it is more rational to perform the heating from the bottom surface of the specimen. In this case, a stagnation zone is formed near the heating surface, and the partial pressure of carbon vapor can reach an equilibrium value.

The experiment was conducted in the following sequence: the working chamber was pumped out to a vacuum of 0.66 Pa and filled with argon up to 0.2 MPa. During the experiment (1 min), the pressure rose to 0.3 MPa. The voltage and arc-current ranges were 30–40 V and 120–140 A.

After the electric-arc treatment, the surface of the graphite-electrode specimens was studied on a Hitachi S 405A electron-scan (ES) microscope by a standard procedure, by the method of x-ray diffractometry (XD), and also by Raman scattering laser microspectrometry (RSLM).

The ES method demonstrated that, in the region of the arc action, the specimens had droplike formations with dimensions of up to 3 mm, whose surface was covered with a black carbon deposit, with a very weak adhesion. On removal of the black carbon deposit, the droplike formation had a firm, smooth surface with metallic luster and differed dramatically from the rough surface of the initial specimen (see Fig. 3a, 1). The droplike formation could result from the transfer of liquid material or a mixture of liquid and solid materials to the front surface of the specimen during the experiment. Yet another possible mechanism of its origination could be the impregnation of the surface layer of the specimen with a small amount of the melt. On the lateral surface of the specimen, contiguous to the droplike formation, there was a microstructure made up by spherical particles 3–20 μm in diameter (Fig. 3a, 2). It seems that the spherical particles, which create a multilayer coating, could emerge from spraying of the liquid that partially solidified during the migration. It is not ruled out that the source of these materials could be a responsive electrode. Investigations of the droplike formation by the RSLM in the spectral range of Raman shifts from 1250 to 1700 cm^{-1} indicated the presence of two broad spectral lines of 1350 and 1580 cm^{-1}, which are typical of nanocrystalline amorphous carbon [8].

Consideration was also given to the graphite-electrode specimens doped with molybdenum. In this case, the specimen surface in the zone of the arc action was covered with a layer of material that differed from the remaining part of the specimen by a pronounced luster, which resembled that of polished metal (see Fig. 3b, 1). According to the XD data, graphite, which is a constituent of the lustrous material, is represented by two components that differ by the degree of three-dimensional order of the crystal lattice. The component with a fairly high degree of three-dimensional order $d = 3.3559$ Å and $p = 0.851$ is prevalent, with crystallographic planes 001 of the crystals of this phase oriented mainly in parallel to the specimen surface. The second graphite component is distinguished by a low degree of three-dimensional order of the crystal lattice $d = 3.4269$ Å and $p = 0.079$. Material of the initial specimen is hexagonal graphite with interlayer spacing $d = 3.3775$ Å and

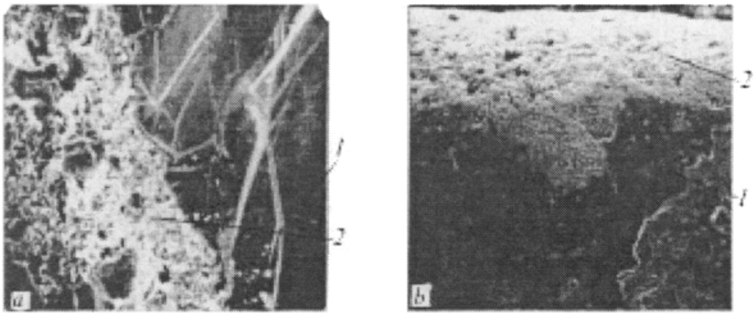

Fig. 3. Microstructure of the surface of a conventional graphite electrode specimen (a) and a specimen doped with molybdenum (b) after electric-arc treatment: a: 1) firm, smooth surface of a droplike formation with metallic luster; 2) microstructure made up by multilayer spherical particles; b: 1) region with a high degree of three-dimensional order (plane [001] is oriented mainly in parallel to the specimen surface); 2) region with a low degree of three-dimensional order of the crystal lattice.

parameter of three-dimensional order of the crystal lattice $p = 0.477$. It can be assumed that graphite with a fairly perfect structure, recorded by XD in the lustrous material, was crystallized from a solution in the melt, and graphite with an imperfect crystalline structure (Fig. 3b, 2) is a product of vapor-phase crystallization.

The graphite doping with molybdenum leads to a decrease in both the melting temperature and the pressure of carbon vapor. However, because the atomic weight of Mo is rather large, 96, its mole fraction for the indicated weight concentration is small and, correspondingly, the deviation from the melting parameters of pure graphite is in this case insignificant. Indeed, the decrease in the melting temperature ΔT_m is determined by the cryoscopic constant of graphite θ and by the mole fraction of the dissolved material r [9]

$$\Delta T_m = \theta r \, .$$

With a mass concentration of molybdenum equal to 3–5%, its mole fraction is $r = 0.5–1\%$. The cryoscopic constant can be evaluated proceeding from data on the graphite temperature T_m and heat L_m

$$\theta = (RT_m^2)/L_m \, .$$

According to [10], $T_m = 4000$ K and $L_m = 105–120$ kJ/mole. From the data of [11], $T_m = 5000$ K and $L_m = 150$ kJ/mole. Hence, $\theta \sim 1000–15000$ K and $\Delta T_m \sim 10–15$ K.

The pressure of carbon vapor in the case in question also decreases very slightly in comparison with the vapor pressure above the melt of pure graphite. In conformity with Raoult's law [12] for diluted solutions, the vapor pressure above the molten solution decreases relative to the vapor pressure above the melt of a pure solvent P_0 by

$$\Delta P = P_0 r \, .$$

Thus, the vapor pressure above the molten solution (at the liquidus point) is lower than the vapor pressure above the melt of pure graphite by as little as 0.5–1%. Graphite doped with heavy metals, among which is molybdenum, is a convenient object for studying the melting parameters. In this case, the melting effect manifests itself fairly clearly, whereas the melting parameters deviate insignificantly from those of pure graphite.

Conclusions. The melting of MPG-6 graphite has been recorded during steady electric-arc heating. A pressure of the buffer gas (argon) equal to 0.2 MPa is sufficient for producing the liquid phase of carbon, which is supported by the pressure parameters for the graphite–liquid–vapor triple point predicted previously.

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