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A. A. VERTMAN and Corresponding Member of the Academy of Sciences of the USSR A. M. SAMARIN

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Abstract

Full Text

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PHYSICAL CHEMISTRY

A. A. VERTMAN and Corresponding Member of the Academy of Sciences of the USSR **A. M. SAMARIN**

ON THE STATE OF CARBON IN LIQUID CAST IRON

The question of the structure of liquid alloys of iron and carbon, despite its practical importance, is among those that have been little studied. We shall mention several works devoted to this problem.

K. P. Bunin (¹), spraying a stream of white cast iron at the surface of ice water, showed that at a cooling rate reaching several thousand degrees per second it is possible to fix in the metal a certain amount of undissolved graphite. This gave him grounds to suppose that, owing to fluctuations, in liquid cast iron there are more or less large groupings enriched with graphite.

S. T. Konobeevskii (³) found that even when a powder of iron and graphite is heated to 2000°, complete destruction of the planar layers of the graphite lattice does not occur, and the iron cations merely penetrate between the planar layers. Apparently, an analogous phenomenon also occurs in liquid iron when graphite dissolves in it, all the more so since the temperature of metallurgical processes never reaches 2000°.

D. P. Ivanov (²), studying the character of graphite crystallization during cooling of cast iron superheated to 1400°, came to the conclusion that in the liquid alloy there are separate blocks of graphite packets of various size with metallic electron bonding; regions occupied by dissolved packets in the form of planar graphite molecules with ionic bonds of interstitial solutes; and, finally, separate carbon ions introduced into the nodes of the iron lattice.

In work (⁴) the distribution of carbon in a column of liquid cast iron 2650 mm high was studied, and it was shown that a nonuniform distribution of carbon, unlike that of other impurities, is possible only in the case where some part of the carbon is present in the form of undissolved graphite.

Thus, the available data make it possible to suppose that carbon is present in liquid cast iron in the form of more or less substantial formations. The question remains unclear as to the sizes of these formations and the presence of phase

boundaries between the carbonaceous formations (colonies, micelles) and the solution.

Moreover, with the exception of the experiments of K. P. Bunin (1), the available information on the structure of liquid cast iron is indirect; it therefore seems expedient to accumulate direct experimental data on the structure of liquid cast iron. For this purpose we subjected cast iron to centrifuging. The experiments were carried out on a centrifugal machine for tests of long-term strength (5). Heating was performed in a silite furnace, which ensured the production of a sizable isothermal zone along its length. The temperature was maintained automatically within $\pm 5^\circ$ by means of a platinum-platinum-rhodium thermocouple serving as a sensor and an EPP-09 electronic potentiometer.

Centrifuging was carried out in corundum crucibles about 60 mm long and 5-7 mm in diameter. The number of revolutions was monitored with a tachometer. The crucibles were placed in special cages made of heat-resistant steel, fastened horizontally in the head of the shaft of the centrifugal machine. Owing to the presence of

the head of the shaft with the crucibles was rapidly withdrawn from the furnace by means of a telescopic lifting stand. Since the superheating above the melting point was only 30-50°, crystallization occurred practically instantaneously when the shaft was withdrawn from the furnace. The water-quenched samples were removed from the crucibles; shavings were then taken from the upper and lower ends of the sample and analyzed by ordinary methods of chemical analysis.

The results of the analysis are collected in Table 1. Despite a certain scatter in the data, it is nevertheless possible to establish clearly a tendency toward a nonuniform distribution of carbon under the action of centrifugal forces. In this case the upper end, located closer to the axis of rotation, is enriched with carbon to a greater extent than the lower one. It should be noted that the experiments were carried out in air, and therefore the open end surface of the sample was oxidized. However, despite oxidation, at rotation speeds of 1700-1900 rpm the centrifugation effect prevails over oxidation. The magnitude of the force field during centrifugation is determined by the expression

Table 1

Change in carbon content in liquid cast iron during centrifugation

Experiment no.	Carbon content C, % (top)	Carbon content C, % (bottom)	Sample length, mm	Number of revolutions, rpm	Temperature, °C	Duration of rotation, min
1	4.20	2.76	30	1700	100	1230
2	4.34	2.70	49	1700	100	1230
3	2.71	4.16	32	500	120	1250
4	4.00	2.70	33	1900	120	1275

Experiment no.	Carbon content C, % (top)	Carbon content C, % (bottom)	Sample length, mm	Number of revolutions, rpm	Temperature, °C	Duration of rotation, min
5	3.90	2.87	29	1900	120	1275
6	3.96	3.60	33	1900	120	1260
7	3.44	2.40	38	1900	120	1260
8	3.32	3.36	25	—	20	—
9	2.68	3.48	40	—	—	1250

$$L = \left(\frac{2\pi n}{60} \right)^2 \frac{l}{g}, \quad (1)$$

where n is the number of revolutions; l is the distance from the axis of rotation.

Under the conditions of our experiments, the sample at 1900 rpm was acted upon by a force exceeding the force of gravity by a factor of 320, and at 500 rpm by a factor of 20. It turned out that in the latter case the loss of carbon due to oxidation was greater than the centrifugation effect. Thus, it may be asserted that in a force field only 320 times greater than the gravitational field, separation of liquid cast iron occurs. In this respect cast iron, as a eutectic alloy, differs in no way from the low-melting eutectics studied previously^(6,7). The difference consists only in the fact that a field of considerably smaller magnitude is needed to separate cast iron, which is explained by the specific features of the graphite-iron system: the large difference in densities (2.2 and 7.8 g/cm³) and the exceptional strength of the planes of the graphite lattice.

It is possible to estimate approximately the size of the carbonaceous colonies present in cast iron. We shall restrict ourselves to considering the results of the most characteristic experiment (no. 4), since the change in carbon content in this experiment is close to the average. The number of particles in a colony is determined by the expression⁽⁷⁾:

$$\nu = \frac{kT}{C_2^0 \delta} \ln \frac{C_1(x_2)}{C_1(x_1)},$$

where

$$\delta = \frac{\omega^2 M_1 M_2 \Delta d (x_2^2 - x_1^2) C_2^0}{2N_a g [M_1 C_1^0 d_2 + M_2 C_2^0 d_1]},$$

ω is the angular velocity; M_1, M_2 are the molecular weights of the 1st and 2nd components, respectively; Δd is the difference in densities; x is the distance from the axis of rotation; C_1^0, C_2^0 are the initial concentrations of the 1st and

2nd components, respectively, in atomic fractions; $C(x)$ is the concentration of the component at a distance x from the axis of rotation; T is the temperature (in °K).

It is easy to see that in our case $\delta = 3.36 \cdot 10^{-21}$. Hence the number of carbon particles in liquid cast iron is $\nu = 2.5 \cdot 10^7$. From the number of particles in a colony one can

determine the volume and dimensions of the colony. According to ⁽⁸⁾, a graphite lattice consisting of 12 atoms has the parameters: $a = b\sqrt{3} = 4.252 \pm 0.003 \text{ \AA}$; $b = 2.455 \pm 0.002 \text{ \AA}$; $c = 6.69 \pm 0.010 \text{ \AA}$. The volume of such a lattice is $23.2 \cdot 10^{-24} \text{ cm}^3$.

Thus, the volume of the colonies is

$$V = \frac{\nu}{12} 23.2 \cdot 10^{-24} \text{ cm}^3 \simeq 50 \cdot 10^{-18} \text{ cm}^3,$$

i.e., the particle diameter is of the order of 10^{-6} cm . Such a particle size is characteristic of colloid-dispersed systems, which are distinguished by high stability (their particles, in particular, do not settle under the action of gravity).

Thus, there are grounds to believe that cast iron is a nonequilibrium microheterogeneous system consisting of a dispersion medium, which is a saturated solution of carbon in iron, and colonies or micelles enriched with carbon, with particle diameters of the order of 10^{-6} cm . In the present communication we do not touch upon questions of the structure of the micelles and their connection with the dispersion medium. It should only be emphasized that the experimentally established fact of the separation of liquid cast iron during centrifugation may be interpreted as one of the proofs of the colloidal state of carbon in liquid iron.

Institute of Metallurgy named after A. A. Baikov
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.

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