

# THE TIME FACTOR IN THE SPHEROIDIZING AND GRAPHITIZING MODIFICATION AND CAST IRON CRYSTALLIZATION

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**ABSTRACT:** This work was carried out studies on the effect of different ways of modifying the microstructure and mechanical properties of cast ductile irons identical to the final chemical composition. For comparative studies have chosen three ways of modifying the molten iron, characterized the time interval between the introduction of additives into the melt and crystallization of iron – autoclave method, processing method in an open ladle ( "Sandwich process") and a method of in-mold melt processing ("Inmold-process").

It is found that the process mold inoculation molten iron a more effective compared to other methods studied, by reducing the time interval between entering modifier in liquid iron and the onset of crystallization. This in turn enables the production of castings of several grades of ductile iron in the total process stream without additional alloying and heat treatment.

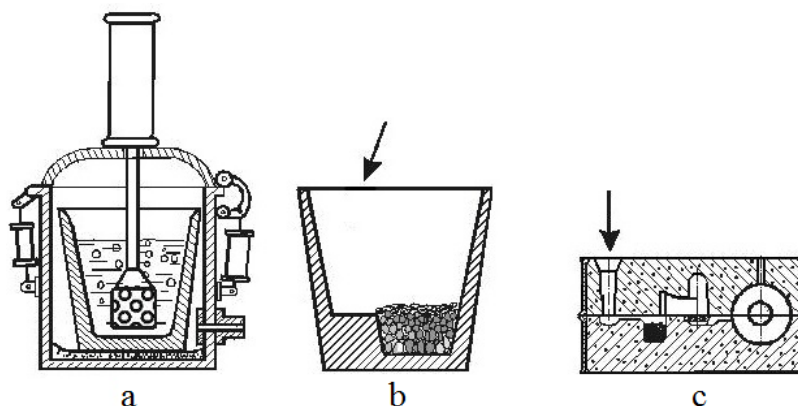
Results of research testify in favor of the fluctuation hypothesis about straight line graphitization of cast iron during primary crystallization.

**KEYWORDS:** HIGH-STRENGTH CAST IRON, MODIFIER, METHOD OF MODIFYING, MICROSTRUCTURE, STRENGTH, HARDNESS, INMOLD- PROCESS, SANDWICH-PROCESS, AUTOCLAVE METHOD.

Structure and mechanical properties of ductile iron with nodular graphite in cast condition defined by four technological factors and may be substantially changed by heat treatment of castings. Influence of chemical composition of the base alloy, amount and absorption degree of spheroidizing magnesium and graphitizing silicon introduced into the liquid iron, as well as the cooling rate of the metal in the mold for the modification results in a sufficiently studied full [1-5]. Fourth factor influencing these results – the time interval between the input modifiers in liquid melt and the beginning of crystallization – most researchers pay negligible importance. Meanwhile it is well known that in contrast to the alloying efficiency of modification during isothermal exposure worsens: increased cast iron tendency to metastable

system crystallization "Fe-Fe<sub>3</sub>C" and reduced the degree of graphite nodularity [1,2].

In the process of sequential replacement on four industrial enterprises autoclave method of ductile iron production (fig. 1, a) first by ladle (fig. 1, b), and then in-mold (fig. 1, c) accumulated extensive statistical material on the technical and economical efficiency of these methods of modification. Analysis of the results proved conclusively advantage of in-mold method of input magnesium and silicon in liquid iron, as compared with previous methods, and that was the main reason for its implementation in the production of complex thin-walled castings of hydraulic equipment weighing up to 180 kg of ferritic spheroidal graphite cast iron.



**Fig. 1.** Methods of complex spheroidizing and graphitizing modifying of cast iron in a sealed autoclave (a), in open ladle by "sandwich" process (b) and directly in the casting mold by "in-mold" process (c).

From the data array of plant laboratories accumulated during great enough time for analysis selected only the results of meltings, in which iron chemical composition meets the conditions listed in tab. 1. All three methods of modification provided a high (96...98%) degree of nodularity in metal castings suitable.

The microstructure of cast iron was determined on the templates made of the middle part of cylindrical samples of 140 mm and a diameter of 6 to 40 mm, as well as standard samples for mechanical testing, made from the casting samples of 10...12 kg of the working part having a thickness of 25 mm. Values of the mechanical characteristics of the cast irons set by standard methods.

**Table 1.** Chemical composition of initial and modified cast-irons and amount of the silicon and magnesium entered in initial cast-iron

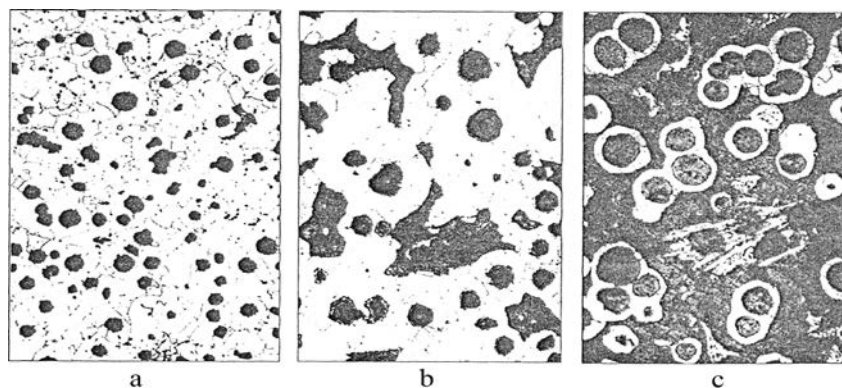
Object of analysis		Chemical composition, % (weight percentage)					
		C	Si	Mn	S	P	Mg
Initial cast iron		3,70 ±0,08	2,15 ±0,07	0,32 ±0,02	0,029 ±0,002	0,070 ±0,002	–
Modifier, introduced	into the mold reaction chamber	–	1,01 ±0,07	–	–	–	0,23 ±0,07
	into the open ladle	–	1,14 ±0,04	–	–	–	0,19 ±0,01
	into the ladle in the autoclave	–	0,95 ±0,05	–	–	–	0,23 ±0,01
Iron, modified	into the mold	3,64 ±0,06	3,06 ±0,05	0,32 ±0,02	0,018 ±0,002	0,070 ±0,002	0,058 ±0,008
	into the ladle	3,58 ±0,04	3,18 ±0,07	0,32 ±0,02	0,012 ±0,002	0,070 ±0,002	0,042 ±0,004
	into the autoclave	3,62 ±0,08	2,92 ±0,07	0,32 ±0,02	0,008 ±0,002	0,070 ±0,002	0,062 ±0,008

According to the results of dispersion analysis comparing the experimental and tabulated values of Fisher's exact test with a coefficient of 95% found that the amount of silicon and magnesium, which is added to the molten metal, as well as the chemical composition of the studied cast irons modified by various methods did not significantly affect the microstructure and mechanical properties of the alloy. At the same time, these characteristics in the cast state essentially depend on the method of modification.

Mean values and the dispersion of mechanical characteristics of the cast iron modified into the reaction chamber of the mold by "in-mold"-process, into the ladle bottom lining open by "sandwich"-process and into the ladle placed in the autoclave mark "KM-2" are shown in tab. 2. Typical

microstructure of cast iron in the relevant standard samples is illustrated in fig. 2.

Found that in the cast iron in-mold modified, the amount of graphite spheroids in 1 mm<sup>2</sup> area microsection 40% more than in the iron modified in the ladle, and 60% more than in the iron modified in an autoclave. With the same carbon content, average diameter of the spheroids is respectively 50, 65 and 85 μm. In cast iron, modified in an autoclave, there are separate sections ledeburitic eutectic, which are absent in cast irons, modified in-mold or in the ladle. Percentage of ferrite in cast iron in-mold modified is 85...95% and a metal matrix of cast iron, modified in the autoclave, preferably pearlitic with a fine ferrite rim around the graphite spheroids.

**Fig. 2.** The microstructure of the cast iron casting in-mold modified (a), in an open ladle (b), in an autoclave (c). × 100.**Table 2.** The mechanical properties of cast iron in-mold modified, in a ladle or in the autoclave in the cast state

Name of the mechanical characteristics	Arithmetic mean and the dispersion of the mechanical characteristics of cast iron		
	modifying		
	into the mold	into the ladle	into the autoclave
Tensile strength $\sigma_{t,s}$ , MPa	513 ± 23	553 ± 24	603 ± 28
Yield strength $\sigma_{y,s}$ , MPa	342 ± 20	348 ± 28	394 ± 18
Relative elongation $\delta$ , %	13,5 ± 1,8	7,0 ± 1,2	2,4 ± 0,8
Impact elasticity KC, kJ/m <sup>2</sup>	750 ± 210	350 ± 90	120 ± 60
Hardness HB	156...170	197...207	302...321

Microstructures difference (fig. 2) makes a significant difference of the mechanical properties of cast irons, modified by various technological options. Found by dispersion analysis that the process of in-mold modification provides production of casts with high plastic properties without bleaching in thin sections of the walls in the cast state more reliably than the process of modifying in an open ladle or in an autoclave. At the same time,

due to the increased dispersion of graphite and eutectic grains of metal matrix, the strength characteristics of ferritic iron in-mold modified, to stabilize at a high level. From tab. 2 shows that by modification in the form of as-cast iron is obtained with a tensile strength  $\sigma_{t,s}$  of more than 500 MPa and elongation  $\delta$  more than 12%. This corresponds to the iron requirements of ДСТУ 3925-99 (standart) for industrial marks БЧ 420-12, БЧ 450-10, БЧ 450-5,

BЧ 500-7, BЧ 500-2. Mechanical characteristics of cast iron, modified in an autoclave in the cast state do not meet the requirements of ДСТУ 3925-99 to mark BЧ 600-3 ductility, and to mark HF 700-2 strength. Therefore, to achieve the desired combination of strength and ductility of autoclave casts, depending on the desired mark, factories generally subjected to further ferrite annealing or perlite normalizing.

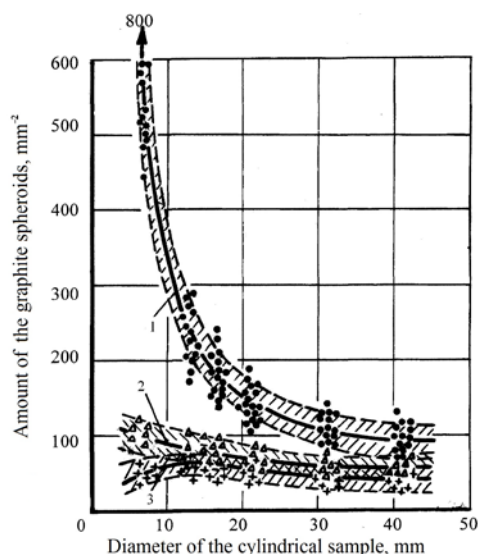
Thus, by method of in-mold modifying under certain conditions can stably produce castings from nodular iron several brands in the general process flow without additional alloying and heat treatment.

It confirms metallographic analysis of the microstructure of cast irons in the cylindrical samples of different diameters. In the in-mold modified cast irons, in the samples of 6 mm diameter graphite spheroids number reaches 500...800 units per 1 mm<sup>2</sup> area microsection (fig. 3, curve 1) at their size 15...20 μm (fig. 4, curve 1). With the increase in the diameter of the sample, i.e. with reduced cooling rate, the amount of graphite spheroids rapidly decreases with a corresponding increase of their size in samples of 40 mm diameter to 45...55 μm. In cast iron, in an open ladle is modified or modified in the autoclave, the samples of 6 mm diameter graphite inclusions sizes are 20...25 μm, i.e. only slightly exceed the graphite dimensions of similar samples of cast iron, in-mold modified. However, the low degree of graphitization their amount does not exceed of 125 units per 1 mm<sup>2</sup> area microsection (fig. 3 and 4, curves 2 and 3). In cast iron samples with a diameter of 6 mm, in-mold modified, a eutectic cementite is absent (fig. 5, a), whereas in the cast iron in the ladle or in the autoclave modified, main part of carbon in samples connected to the needle cementite of ledeburitic eutectic (fig. 5, b, c). In the ladle modified cast iron, the eutectic cementite disappears only in the samples of 20 mm diameter (fig. 5, e). In the autoclave modified cast iron, individual inclusions of

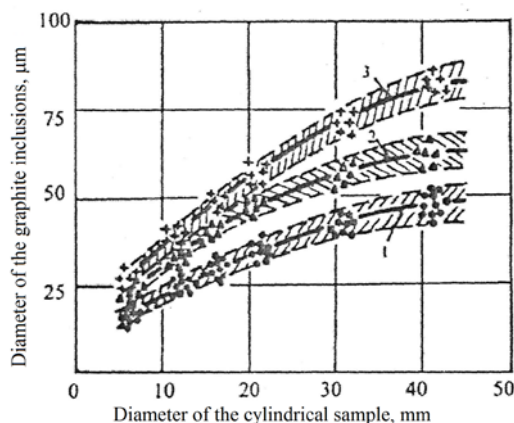
ledeburitic eutectic observed even in samples of 40 mm diameter (fig. 5, f). At the same diameter of cylindrical samples microsection area occupied by ferrite in cast iron, in-mold modified (fig. 6, curve 1), significantly more than in the ladle modified cast iron (fig. 6, curve 2). Cast iron metal matrix structure modified in the autoclave, in all the samples mostly pearlitic with fine ferrite rim around the graphite spheroids (fig. 6, curve 3).

Ceteris paribus, the main technological difference between the three methods of modification lies in the different time interval between introduction of modifier elements into the molten metal and the beginning of crystallization in the mold. To reduce the pressure in the autoclave to atmospheric, opening the autoclave and removed from him the ladle, slag removal, transportation and casting modified cast iron in form in a manufacturing conditions is spent 8...12 minutes. If the total time for these operations is more than 14...16 minutes, the propensity of cast iron to graphitization and degree of graphite nodularity in the modified cast iron begins to decrease rapidly. The removal of slag, transportation and metal pouring spent 4...6 minutes after modifying in the open ladle. Gist of the in-mold modifying cast iron method reduces that interval up to several tens of seconds, regardless of which form the first poured and which latter.

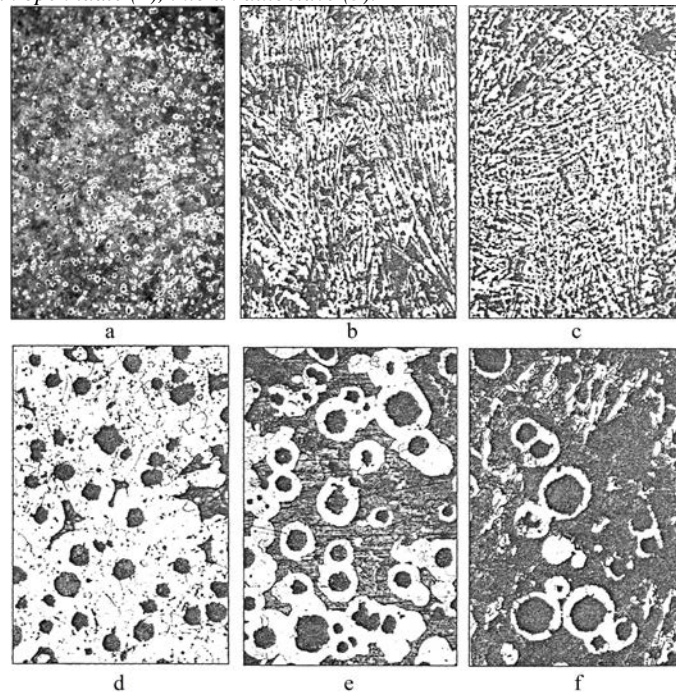
Thus, in the cast state with the same chemical composition and the same cooling rate inclination to graphitization during eutectic and eutectoid transformation, the amount of graphite inclusions, graphite spheroids dispersity, eutectic grain dispersion in the cast iron in-mold modified higher than in the cast iron, modified in ladle, and significantly higher than in the cast iron modified in the autoclave. The difference of these indicators is particularly evident at high cooling rate (fig. 3...6).



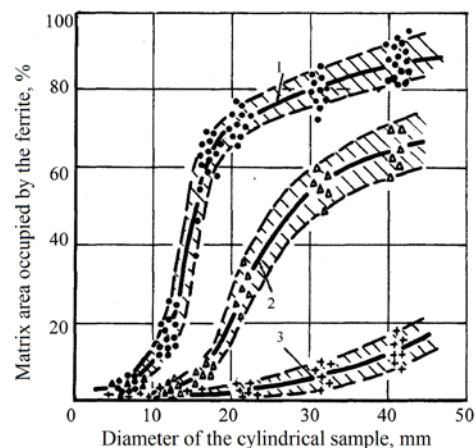
**Fig. 3.** The cooling rate influence (diameter of the cylindrical sample) by the amount of graphite spheroids in 1 mm<sup>2</sup> area of cast iron microsection modified into the mold (1), into an open ladle (2), into an autoclave (3).



**Fig. 4.** The cooling rate influence (diameter of the cylindrical sample) by the diameter of the graphite spheroids in the cast iron modified into the mold (1), into an open ladle (2), into an autoclave (3).



**Fig. 5.** The microstructure in cast iron specimens of 6 mm (a, b, c) and 40 mm diameter (d, e, f) modified: a, d – into the mold; b, e – into an open ladle; c, f – into an autoclave.  $\times 100$



**Fig. 6.** The cooling rate influence (diameter of the cylindrical sample) by the relative microsection area occupied by ferrite in the cast iron modified into the mold (1), into an open ladle (2), into an autoclave (3).

Tendency to crystallize on a metastable system "iron-cementite" mainly explaining by the fact that when the cast iron temperature drops to eutectic mean, probability of phase fluctuations with carbon concentration, approximate to the 6,67%, significantly higher than the probability of micro volumes with carbon concentration, approximate to 100%. But, from the point of view of thermodynamics, the minimum value of the free energy corresponds more stable equilibrium of "iron-graphite" system. Therefore, the propensity to structure formation by stable, metastable or mixed system primarily depends on the length of cast iron stay in the solid-liquid state at the eutectic solidification, which determined by the rate of heat transfer between the micro-volume of the alloy in the wall section of the casting and the mold. The smaller section of the wall of the casting, the greater the rate of its cooling, the shorter the duration of the isothermal eutectic crystallization, the less the probability of increasing carbon concentration from 6,67 to 100% in its fluctuation groupings in the residual liquid and the greater the probability of formation unstable cementite in ledeburitic eutectic.

Results of the study are in good agreement with the fluctuation hypothesis and contradict to the inoculation hypothesis about the mechanism and kinetics of graphitizing modification and structure formation of cast iron in the primary crystallization.

According to the inoculation hypothesis additional nucleant of crystallization of solid graphite phase during eutectic crystallization of cast iron are refractory silicon carbides, iron silicides or complex iron-carbon-silicon chemical compounds which forming in the melt by modifying by the ferrosilicon or ferrosilicon-magnesium. According to this hypothesis is difficult to explain the effect of time factor on structure formation between the introduction of additives in the alloy and the beginning of the eutectic crystallization. The more uncertain the mechanism and kinetics of deactivation refractory inoculators that leads to gradual demodification of molten cast iron.

Fluctuation hypothesis assumes that the microparticles of graphitizing modifier containing 45...75% of the silicon during the dissolution time replacing part of the carbon in alloy from the surrounding them microvolume of equilibrium solution of carbon and silicon in the liquid iron. Depleted carbon and enriched silicon fluctuation microvolumes of liquid become additional potential nucleuses of primary austenite grains. Liquid in microvolumes distant from ferrosilicon particles overloading repressed carbon, fluctuation groups which are close to 100% concentration and become additional potential nucleuses of graphite phase in crystallizes eutectic. During the relatively long exposure in ladle concentration fluctuations of carbon and silicon gradually uniformly distributing in the volume of liquid cast iron

and efficiency of graphitizing modification respectively reduced to zero. During cast iron modification directly into the mold such exposure does not exceed ten seconds. Therefore, the graphitizing efficiency of adding even small amounts of silicon in molten cast iron is shown at the maximum level.

The results of experiment are not quite consistent with the hypothesis mediated cast iron graphitization. According to this hypothesis, the eutectic crystallization of cast iron always takes place at a metastable system, followed by dissociation of the formed solid ledeburite cementite to austenite and graphite by "self-annealing" by the heat of the casting, cooling in the mold, similar to high temperature annealing white cast iron at malleable. In samples with a diameter of 6 mm made of cast iron in-mold modified cooling which occurs with the high speed inclusions of cementite or it "self-annealing" remains isn't observed (fig. 4, a). Probably, under certain conditions graphite separation directly from the residual liquid without forming an intermediate cementite during eutectic crystallization takes place. However, at higher cooling rate, a low content of carbon and silicon, the presence of chromium or other carbide stabilizing elements, absence the operation of modification or long exposure of the modified alloy to it beginning of crystallization conditions are taking shape for full or partial crystallization by a metastable system. Thus, the hypothesis of a direct graphitization from liquid phase has the same right to exist as the hypothesis of iron mediated graphitization.

## CONCLUSIONS

Technological process of spheroidizing and graphitizing modification directly into the mold provides a tendency of cast iron to graphitization at the eutectic and eutectoid transformation, the refinement of austenite grains and graphite spheroids, increased ductility with high strength cast iron more efficiently and reliably than the process of modification in the ladle or in an autoclave.

The researching shows the benefit of the fluctuation hypothesis of graphitizing modification and hypothesis about the possibility of a direct cast iron graphitization from liquid phase at the primary crystallization.

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