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The Problem of Assessing the Graphitizing Abilities of Near-eutectic Cast Iron - Basic Cast Iron for Modification

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Abstract

Cast iron destined for spheroidization is usually characterized by a near-eutectic chemical composition, which is a result of the necessity of maintaining its high graphitizing ability. This graphitizing ability depends mainly on the chemical composition but also on the so-called physical-chemical state. This, in turn, depends on the melting process history and the charge structure. It happens quite often, that at very similar chemical compositions cast irons are characterized by different graphitizing abilities. The hereby work concerns searching for the best method of assessing the graphitizing abilities of near-eutectic cast iron. The assessment of the graphitizing ability was performed for cast iron obtained from the metal charge consisting of 100% of special pig iron and for synthetic cast iron obtained from the charge containing 50% of pig iron + 50% of steel. This assessment was carried out by a few methods: wedge tests, thermal analysis, microstructure tests as well as by the new ultrasonic method. The last method is the most sensitive and accurate. On the basis of the distribution of the wave velocity, determined in the rod which one end was cast on the metal plate, it is possible to determine the graphitizing ability of cast iron. The more uniform structure in the rod, in which directional solidification was forced and which had graphite precipitates on the whole length, the higher graphitizing ability of cast iron. The homogeneity of the structure is determined by the indirect ultrasonic method, by measurements of the wave velocity. This new ultrasonic method of assessing the graphitizing ability of cast iron of a high S_c (degree of eutectiveness) and CE (carbon equivalent) content, can be counted among fast technological methods, allowing to assess the cast iron quality during the melting process.

Keywords: Near-eutectic cast iron, Graphitizing abilities, Ultrasonic method

1. Introduction

The cast iron ability of nucleation is one of its basic physical-chemical features, describing its quality in a liquid state. Striving to achieve the high ability of nucleation, regardless of graphite precipitates shapes, concerns all grades of grey cast iron. Cast irons of a high nucleation ability are solidifying with higher amounts of eutectic nuclei, which causes a higher number of eutectic cells. In effect, the fine-grained structure is formed, which always causes that cast iron has better mechanical properties. Such structure provides higher strength, yield point, and higher plasticity, especially when the graphite is in a compact form.

The ability of nucleation, which in the case of cast iron should be related to graphitizing (eutectic cells are built with a graphite fraction), depends on several factors, such as chemical composition, cooling rate, inherited features of alloy transferred by metal charges. In the case of high-quality cast iron, which is produced with the participation of metal secondary metallurgy in a liquid state (balling, inoculation, combination of both treatments), the ability to nucleation is stimulated by heterogenic nuclei, which sources are inoculants. Regardless of the additional stimulators, such as modifiers based mainly on ferrosilicon inoculants (with Al, Ca, Sr, Ba, Ti, graphite, etc.), the crucial factor constitutes the physical-chemical state of initial cast iron.

The highest nucleation ability has these grades of cast iron, which melts are based on high-quality pig irons containing a lot of carbon. Carbon, which is mainly in a graphite form, undergoes dissolving in a liquid solution during melting. However, its part remains in a form of graphite clusters, which - during solidifying - are becoming very good natural nuclei of eutectic grain crystallization. The knowledge of the favorable influence of foundry pig irons on cast iron quality is widely known. However, on account of pig iron prices, less and less often the cast iron production is only based on pig iron. This concerns also the production of grades in which carbon and silicon content should be maintained on a high level. More and more often synthetic cast iron, in which steel scrap is used as the basic component of a charge, is produced. The carbon content is increased in the carburizing process by means of the so-called ‘carburizers’. These are natural or synthetic graphite, coal dust, anthracite, coke, and others. There are several carburizing techniques [1,2], such as adding graphite into a charge at the beginning of the melting process, introducing it on a surface of liquid metal, or blowing it in a stream of compressed gas [1,2]. Contemporary carburizing techniques allow obtaining - in a short time - the expected carbon content, reaching even more than 4.0% of carbon.

During melting and carburizing the assumed chemical composition is reached, including the declared carbon content. However, the question remains, whether synthetic cast iron constitutes an equivalent initial material suitable for the secondary metallurgy treatments (modification, spheroidization, vermicularization), such as the one, which is obtainable from foundry pig iron. There is a justified opinion that, from the point of view of graphitizing ability, these are significantly different materials. Several technological properties of cast iron (especially spheroidal) depend on this ability including the ability to self-feeding and to limit defects of a shrinkage origin. The high graphitizing ability is a necessary condition for producing large castings in the technology without a rider head [3,4,5,6].

Investigations, which results are given below, were directed towards looking for the method assessing the graphitizing ability of cast iron grades having near-eutectic chemical composition. Since the graphitizing ability of these cast iron grades is very high, its estimation by traditional methods is difficult. This concerns, first of all, ferritic cast iron grades of an increased impact strength: EN GJS 380-22LT, EN GJS 400 -18LT; EN GJS 400-15. In order to obtain the ferritic structure, the initial cast iron must be characterized by the highest graphitizing ability. Within carried out investigations, a few methods were used for assessing this ability. All this allowed performing the comparative analysis, which aim was to find the most efficient method of assessing cast iron produced on the foundry pig iron base as well as the synthetic cast iron of high eutectic saturation.

In the case of cast iron grades having a low ability of nucleation (graphitizing), even a small increase of a cooling rate leads to the formation of partially white or totally white structures. A low ability of nucleation can be observed in the analysis of pathways of thermal analysis curves, where the under-cooling value - within the range of eutectic solidification - constitutes a good indicator. Investigations of the hereby work are focused on assessing the nucleation ability by means of the thermal analysis as well as on testing the sensitivity for cooling rates.

Methods of assessing the graphitizing ability of cast iron. One of the important criteria of the assessment of the graphitizing ability or inclination to whitening (forming structures with cementite precipitates) is the time of the test [7,8]. In general, the less the metal is held in the furnace, the better. On the basis of the assessment the chemical composition of metals being in the furnace is corrected. Therefore, the assessment result is needed as fast as possible. This condition is satisfied by a group of technological tests in which test samples are solidifying fast and their shapes allow to obtain diversified cooling rates (fig.1, fig.2) [9]. In effect, the whole spectrum of structures is obtained on their fractures: from white cast iron (cementite) via partial and up to grey cast iron. For ductile cast-iron, the ring test shown in fig.3 is usually used to evaluate the structure.

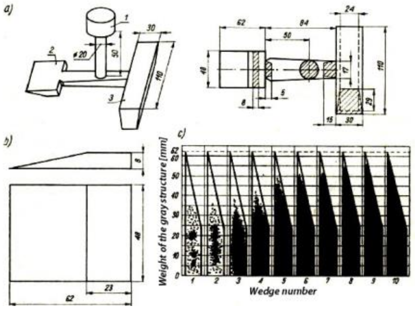
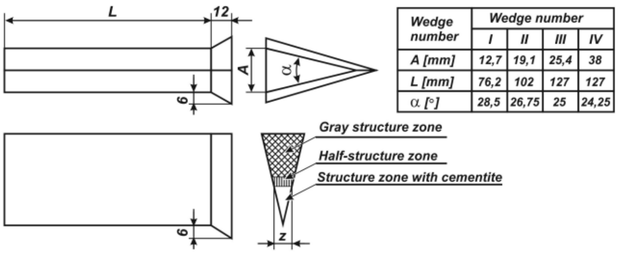


Fig. 1. Methods of assessing whitening tendency PN – 61/H-04675



Wedge number	Wedge number			
	I	II	III	IV
A [mm]	12,7	19,1	25,4	38
L [mm]	76,2	102	127	127
α [°]	28,5	26,75	25	24,25

Fig. 2. Meehanite test for inoculating cast iron (Sc<1.0) and CE <4.26 [9]

Solidification rates of cast iron in test samples are also relatively slow, appropriately to the thermal conductivity of sand moulds. In the second group of methods, assessing the cast iron inclination to whitening (indirectly to graphitizing ability), samples are cast with utilising metal coolers. They are cast in such a way that one wall of the sample adheres to the cooler. Fast carrying away of heat causes forming the whitening structure layer, which thickness depends on the graphitizing ability of cast iron. This group of tests is shown in figures 4 – 6 [10,11,12].

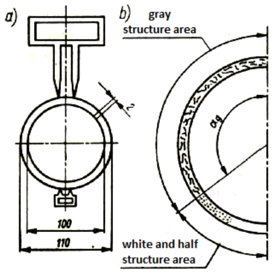


Fig. 3. Ring test for cast iron with S_c >1.0 [9]

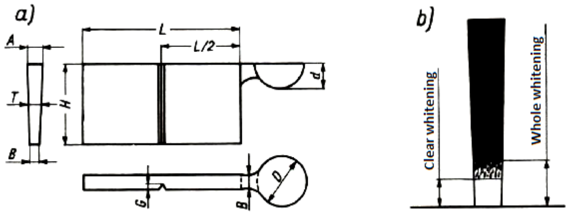


Fig. 4. Casting of samples in the metal moulds - research on breakthroughs acc. to ASTM A367 [10]

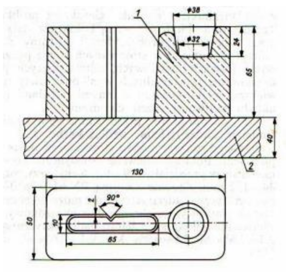


Fig. 5. Casting of samples in the metal moulds [12]

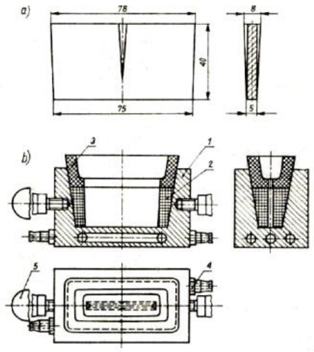


Fig. 6. Casting of samples in a water-cooled metal mould [11]

In all samples in which the casting (sample) solidifies with various rates in individual fractures, the segment with whitened structure occurs (fig. 7) [11]. At a wide range of the chemical composition variability, these tests are good indicators of the cast iron ability to graphitize. However, as it is marked in figures 1 and 7, when the graphitizing ability of cast iron is not much diversified, these tests can be of low sensitivity.

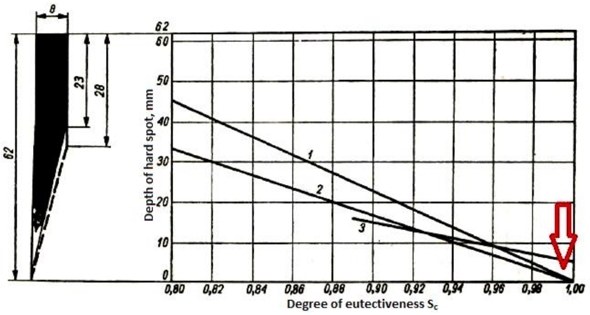


Fig. 7. Effect of the degree of eutectiveness (S_C) on whitening. Lines 1, 2 and 3 refer to similar research carried out at AGH and in other research institutions [11]

2. Investigation methodology

Experimental melts were performed in the Experimental Casting House in the Faculty of Foundry Engineering, AGH. The induction crucible furnace of an average frequency and the crucible volume of 15 kg was applied for melting cast iron.

Metal charges in the subsequent melts contained special pig irons of a composition: C = 4.20%; Si = 0.97%, Mn = 0.05% P = 0.03%; S = 0.013% and steel scrap in a form of rods 15x15mm of chemical composition: C = 0.32÷0.39%, Si < 0.4%, Mn = 0.5÷0.8%, P < 0.045%, S < 0.045. Synthetic granulated graphite of granules size ~ 5.0 mm was used for carburizing. A silicon content in cast iron was supplemented by ferrosilicon FeSi75.

Each time after metal melting, correcting its composition by carburizing and supplementing other components by means of ferroalloys, specimens were cast:

- for tests of the chemical composition (roller cast in the copper gravity die),
- for thermal analysis - pouring sampler with cold water for recording the cooling pathway,
- for assessing inclinations for graphitizing (wedge samples as in fig. 2 and Meehanite tests as in fig. 3),
- for the tests shown in Fig. 4 and 5, the shape of the test casting has been changed, in order to facilitate the subsequent measurements, to the shape of a rod and a hexagon (easy ultrasonic measurement thanks to parallel walls). One end of the cast bar sample was placed against the cooler wall. There is no significant difference in the cooling rate and structure between the rod and the hexagon.

3. Results of own investigations

As part of the research, many test melts were carried out. For the comparative analysis, samples from two exemplary trials were used. These melts had substantially different structures of the metal charge: melt W-1 was totally based on the special pig iron of the given above composition, while melt W-2 was based on the following charge: 50% pig iron + 50% low-carbon steel + synthetic graphite. The obtained chemical compositions are shown in Table 1.

Table 1.
Chemical composition of cast iron

Melt Number	C	Si	Mn	P	S	Sc
	%	%	%	%	%	
W-1	3.88	2.22	0.019	0.067	0.0160	1.093
W-2	3.58	2.11	0.289	0.035	0.0039	1.004

In both cases, hyper-eutectic cast iron Sc > 1.0, of high graphitizing ability, occurs. The series of test specimens, presented in figure 8, were cast from each melt. Samples were cast at a temperature: T =1420°C.

Fig. 8. A set of cast test specimens

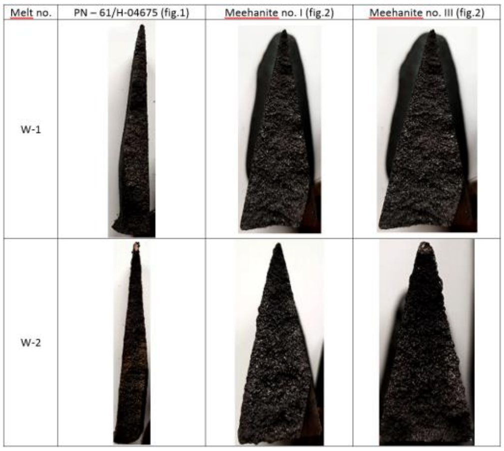


Fig. 9. Fractures from edge tests

Results of edge tests - assessments of the inclination for whitening - are presented in Fig.9 (photographs of fractures). Edge specimens were produced as shown in Fig. 2 and 3. Fractures of edges from two melts, being compared, indicate that in both cases cast iron retained a very high graphitizing ability. The whole surfaces of both fractures are grey. Thus, it is not possible to state - on their bases - which cast iron has a higher ability of graphitizing.

It was indicated in paper [11] that the sensitivity to the cooling rate and - indirectly - the graphitizing ability, can be controlled by the ultrasonic technique. The test was developed for assessing the efficiency of the inoculation process of grey cast iron. The test sample is of a module build of rollers of various thicknesses, in which metal solidifies with various rates. The measurement of wave velocity is performed in each module. The wave velocity results obtained in specimens from melts W-1 and W-2, are presented in Fig.10.

More graphite (better nucleation) is present in cast iron melted from pig iron than in synthetic cast iron. In ultrasonic tests, distinctly lower values of the wave velocity are observed in the same segments of the sample (Fig.10). In addition, cast iron from the pig iron melt is less sensitive to the cooling rate, which reveals itself, in the ultrasonic method, as a smaller diversification of velocities in individual segments of the sample. The ultrasonic test of the cooling rate sensitivity provides better bases for the cast iron (from two melts) assessment than the normal edge test.

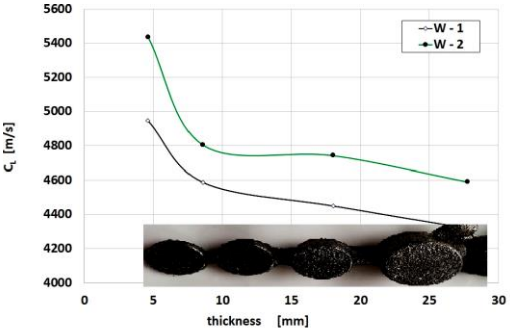


Fig. 10. Sensitivity tests of the cooling rate - ultrasonic tests

Casting of the specimen for the ultrasonic method in a form of the rod with one end placed on the cooler is a certain modification of the method. Higher cooling rates in zones adjusted to the cooler should allow to reveal differences in the graphitizing ability of near-eutectic cast iron. Rods of circular and hexagonal fractures were cast.

Several thermocouples were installed in the sand mould for recording cooling rates in individual layers, being at various distances from the cooler (see Fig.11). The recorded cooling curves are shown in figure 12, while pathways of the cooling rates changes in figure 13. As the result of a high diversification of rates, a very diversified structure along the cast test bars is obtained.

Fig. 11. A cast sample for the analysis of the cooling rate as a function of the distance from the surface of the cooling plate, with the view of the positioning of the thermocouples

Next, after cooling of the casting, measurements of the ultrasonic wave, of a frequency 2.0 MHz, were performed in successive cross-sections of the specimen. The results are shown in figures 14 and 15.

When analyzing pathways of the wave velocity changes in specimens obtained from melts W-1 and W-2, it is possible to single out - on their length - two segments. In the first segment, near the cooler, large changes of the wave velocity occur, while in the second one these changes are significantly smaller. Cast iron of high graphitizing ability is characterized by low sensitivity to cooling rates, which means that the length of the segment with the changed structure as well as the scale of rate changes will be smaller.

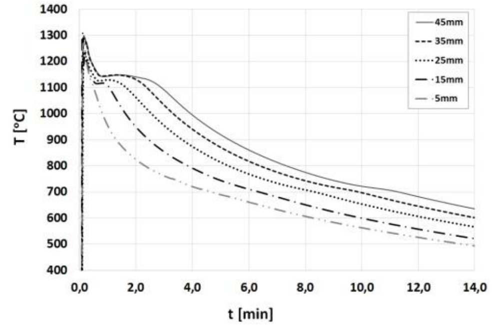


Fig. 12. Cooling down of the sample W-2 - selected points – hexagonal sample

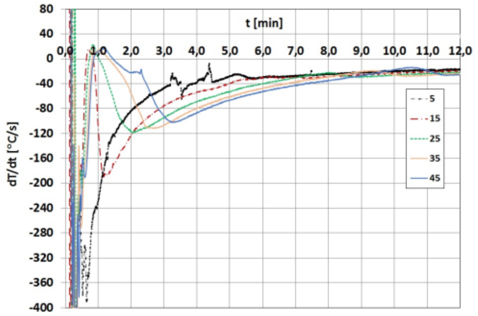


Fig. 13. Cooling rates in sample W-2 at points distant from the cooling plate by 5,15,25,35,45 mm – hexagonal sample

Cast iron obtained from pig iron only (melt 1) is characterized by a more uniform structure than synthetic cast iron obtained from pig iron (50%) and steel scrap (50%) (melt 2). The wave velocity in cast iron depends on the form and amount of graphite and also partially on a metal matrix. The more graphite and the larger its precipitates the lower wave velocity [12]. In the sample made from melt W-1 the wave velocity is much lower (Fig. 14) and less diversified along the sample (Fig 15).

This means that, in this cast iron structure, more graphite precipitates occur. These precipitates are less diversified along the sample than in the case of synthetic cast iron. The assessment of the graphitizing ability, in which the structural homogeneity of rod specimens cast ‘on the cooler’ is determined by means of the ultrasonic technique, is sensitive, and can be utilized in assessing this feature in near-eutectic cast iron grades.

Assessment of the nucleation ability by means of the thermal analysis (TA). Assessments of the effects of carbonization, from the point of view of retaining the cast iron high ability of nucleation, were also carried out by means of the thermal analysis. It is used for the determination of the eutectic saturation degree as well as the ability of cast iron nucleation. Pathways of cooling curves of cast iron obtained from the melt with pig iron charge (W-1) and from the melt with pig iron + steel scrap + carbonizer (W-2), are shown in figure 16.

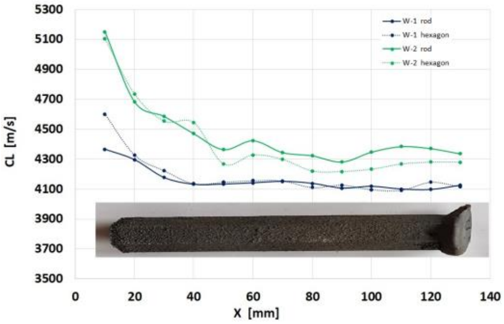


Fig. 14. Wave velocity changes along the length of the sample (distance from the metal plate)

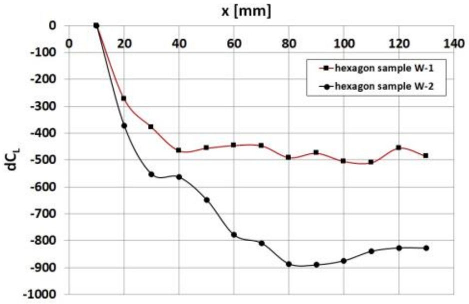


Fig. 15. Wave velocity variations along the sample

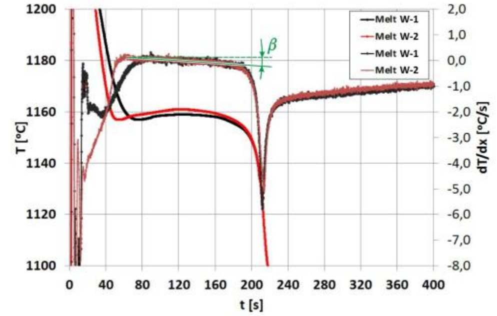


Fig. 16. TA and DTA image - cast irons W-1 and W-2

The indicators of the cast iron ability of nucleation, obtained by means of DTA (differential thermal analysis), are values of the angle of inclination ß (line marked in red in figure 16) and the recalescence measured in degrees (ΔT_{eut}). Both parameters should have small values, recalescence below 4-5°C, while the angle of inclination (ß) – not more than a dozen or so degrees.

In the melts performed with the application of carburizer (by synthetic graphite) in synthetic cast iron the high graphitizing ability was obtained. Both the recalescence and ß angle had low values, the example of which are results shown in figure 16. This was the melt, in which 50% of steel and 50% of foundry pig iron were used in the charge. Differences in the carbon content were supplemented in the carbonizing process. The ß angle, as well as the recalescence value, are very low, which allows inferring that the high ability to nucleation was retained. However, on the basis of the recorded cooling pathways, it is difficult to state which cast iron has a higher graphitizing ability.

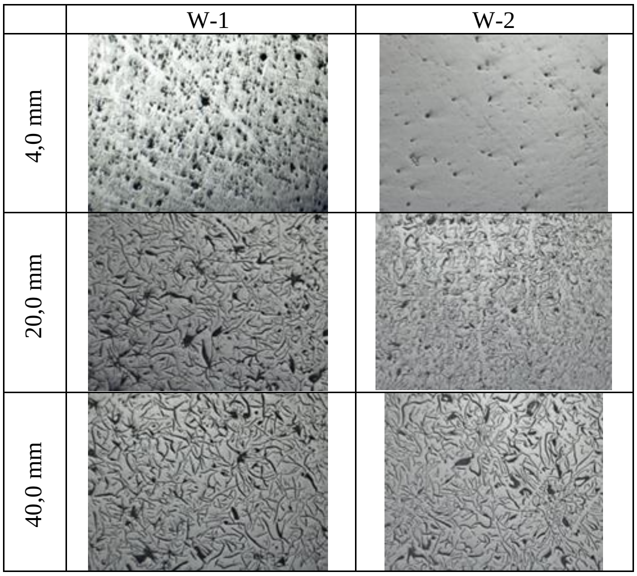


Fig. 17. Comparison of microstructures of cast iron obtained from W-1 and W-2, magnification 100x

Photographs of microstructures of cast irons obtained from melts W-1 and W-2 are listed in Fig.17. Unetched metallographic microsections were made from rod specimens cast on the metal cooler. Microstructures of specimens fractures, being at a distance of 4, 20, and 40mm from the cooler, are shown. Cast iron W-1 of a high graphitizing ability already at the distance of 4 mm has graphite in its structure, which means that it is at most partial. At the same distance of 4 mm in cast iron W-2 graphite does not occur. As the distance from the cooler is increasing and the cooling rate decreases, both cast iron structures are becoming similar.

Summary

Performed investigations confirmed that indicating the diversified graphitizing ability of cast iron grades of a near-eutectic composition is difficult. Technological methods applied for hypoeutectic cast iron are not suitable. Also, a simple thermal analysis does not provide an explicit assessment. Investigations indicate that ultrasonic tests of rod specimens, cast on coolers, provide such possibility. At very high cooling rates the diversity of the graphitizing ability is revealed, even when the tested and compared cast iron has a very high graphitizing ability.

4. Conclusions

The performed investigations allow several conclusions to be drawn.

- The assessment of the graphitizing ability of cast iron of high eutectic saturation is difficult and traditional assessment methods are not very suitable.
- Cooling rates of technological samples in sand moulds are too small to allow assessing the graphitizing ability of near-eutectic cast iron in edge tests. In general, it is high enough to remain outside the sensitivity range of such tests.
- Tests of casting rods with the face surface cooled by the metal plate (cooler) allow obtaining high enough cooling rates, that even in cast iron of a very high graphitizing ability the gradient structure - with various amounts and forms of graphite - is obtained.
- The ultrasonic technique allows the fast assessment of the graphitizing ability of near-eutectic cast iron. The assessment is carried out on samples with strongly directed cooling (with using the cooler).

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