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A comparison of the oxygen, nitrogen and hydrogen content in ductile iron castings and their effect on microstructure and mechanical properties

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Abstract

Two different spheroidization methods were compared in terms of the effect they may have on gas content (oxygen, nitrogen and hydrogen) in ductile iron castings and process efficiency.

Two methods of cast iron treatment were investigated, i.e. spheroidization in the foundry mould using a reaction chamber (reactor) developed by the Foundry Research Institute and, as a reference, the method currently used by foundry shops, i.e. spheroidization in the foundry ladle.

The effect of spheroidization process was evaluated on test castings. The results of metallographic examinations and mechanical tests as well as the results of measurements of the oxygen, nitrogen and hydrogen content in cast iron after spheroidizing treatment were presented.

Keywords: *ductile iron, oxygen/nitrogen/hydrogen content, methods of spheroidizing treatment, reaction chamber (reactor)*

1. Introduction

It is generally known that cast iron remains the leading casting material used for the manufacture of items serving various purposes, and made in various sizes and weight ranges from several kilograms up to several hundred tonnes. The term "ductile iron" denotes a casting material for numerous and varied applications. This is mainly due to the beneficial mechanical properties of this material, depending on the number and size of the spheroidal graphite precipitates and also on the type of matrix. Due to its very good performance, ductile iron is considered one of the leading casting Fe-C alloys and as such is primarily used for cast components operating in the automotive industry, agricultural machinery, fittings and many other items [1–5].

When the required chemical composition of base cast iron for the spheroidizing treatment has been provided, another very important element in the manufacture of high quality material is the introduction of a proper amount of spheroidizer into the metal melt. Magnesium-based ferroalloys for the secondary treatment of molten cast iron are among the most expensive ferroalloys used in foundries worldwide, while being at the same time the most commonly used semi-products for the manufacture of spheroidal graphite cast iron [6].

Over the years of using magnesium as a spheroidizer, different methods have been developed for its introduction into molten cast iron [7–8]. Currently, the spheroidization process is carried out in the casting ladle, most often using the method of flexible PE wire [1].

An in-mould spheroidization technique is also widely known, wherein the essence of cast iron treatment consists in placing the spheroidizer and inoculant in the mould cavity in a reaction chamber reproduced by the moulding sand [9]. Various technological solutions are available to increase the efficiency of this process [10–13], but none of them uses a reactor made outside the mould cavity.

The in-mould spheroidization process using the reaction chamber developed at the Foundry Research Institute is a world-wide innovative technique of cast iron treatment [14,15]. The innovative character of this method consists in the use of a properly designed and constructed reactor placed in the mould cavity.

The properly designed reactor in which the metallurgical process takes place is made outside the casting mould and then placed in this mould before its final assembly in a way resembling the installation of a typical foundry core. The reactor incorporates a casing composed of two split halves. In the interior of the reactor, the spheroidizer, the inoculant and a filter for metal filtration are placed. During pouring of mould with molten cast iron of the required chemical composition, the reactions of spheroidization, inoculation and filtration are all effected simultaneously in the reaction chamber on cast iron flowing through a gating system into the mould cavity. The reactor casing is made of appropriately selected binder-bonded sand, self-hardening after the casing has been moulded in a special die. The material used for the casing is totally water-free, and owing to this fact, during the process of spheroidization or vermicularization and subsequent inoculation of molten cast iron in the reactor, the effect of water decomposition and the risk of penetration of the gaseous products of this decomposition into molten cast iron are practically totally eliminated.

When the reactor is poured with molten cast iron, as a result of the process of pyrolysis of the organic material (reactor casing) taking place under the effect of high temperature, the process of gasification of this material occurs and a reducing atmosphere is created. The construction of the reactor and the presence of the reducing atmosphere allow avoiding the risk of magnesium oxidation with oxygen present in the air, as well as the glare effects and the evolution of a large amount of harmful gases emitted into the atmosphere.

The new method of making castings from the spheroidal graphite cast iron has been developed for use in the two basic technological variants of making foundry moulds and castings, i.e. with either horizontal or vertical mould parting plane. For this purpose, the reactor of a suitable shape and structure has been designed [16].

As it is generally known, the effect of spheroidization tends to fade with time, and therefore in the methods used currently it is so important to control the time between spheroidization and mould pouring. This also involves the need to completely empty the ladle into casting moulds. The use of reaction chamber for the cast iron treatment effectively eliminates all these problems.

2. Research methodology

As indicated by the results of preliminary laboratory tests, the assimilation rate of magnesium is much lower in the conventional method than in the in-mould spheroidization process using the reaction chamber.

Test melts were made at the Foundry Research Institute to examine how the method of spheroidization can affect the gas content (oxygen, nitrogen and hydrogen) in cast iron and the efficiency of spheroidizing treatment. Two methods of cast iron treatment were investigated, i.e. the method of in-mould spheroidization using the reaction chamber developed within the project and, for comparison, the method currently used by industrial plants comprising the spheroidization in a foundry ladle. To make the comparison it was necessary to use the same amount of spheroidizer and inoculant (assuming that the post-spheroidization percent magnesium content in cast iron is at a level of 0.05%), the same base cast iron composition and the same pattern set. The goal was to obtain the GJS-450-10 ductile iron grade. Numerous microstructural examinations and mechanical tests were performed to evaluate the effectiveness of the spheroidizing treatment.

Melts were prepared in a laboratory of the Foundry Research Institute. A 50 kW medium frequency induction furnace and a crucible of 100 kg capacity were used as a melting unit. A 50 kg batch of cast iron was prepared for the spheroidization process; the cast iron composition is given in Table 1. The mould with the reaction chamber placed in its cavity was the first one to be poured.

To make a reference casting by the commonly applied industrial spheroidization technique, the remaining batch of cast iron was re-heated to obtain the same starting conditions and then spheroidization was performed in a ladle and the second mould was poured. In both cases, the spheroidizer was ferrosilicon containing about 9% Mg. It was added in an amount of 0.9% relative to the mould capacity (13 kg), while the inoculant was added in an amount of 0.2% relative to the mould capacity.

Test castings for both spheroidization methods (Fig. 1) had the same shape and weight and were poured in foundry moulds made from the conventional bentonite-bonded sands.

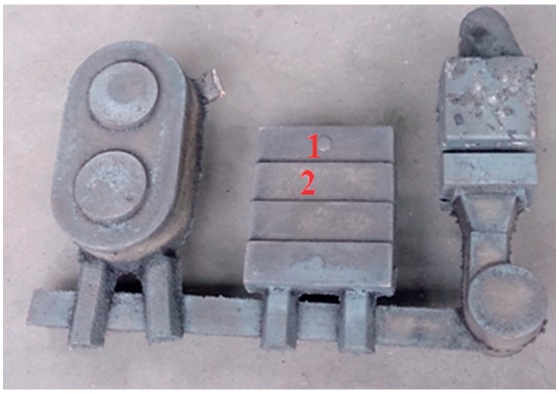


Fig. 1. Ready test castings with the gating system and reaction chamber

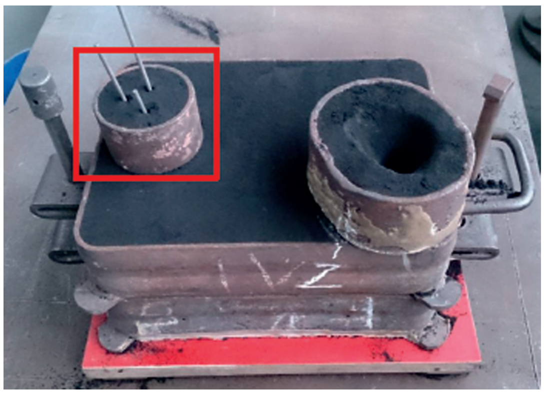


Fig. 2. Casting mould showing marked place where samples were taken for the determination of gas content

Test castings were made and samples for the determination of oxygen, nitrogen and hydrogen content were taken from the specially cast overflows (Fig. 2). The samples had a cylindrical shape with the diameter and length of 6 mm and 13 mm, respectively. The collected samples were placed in a container with liquid nitrogen. The time lapse between the end of pouring and placing samples in nitrogen did not exceed 2 minutes.

Metallographic studies, which included the evaluation of graphite precipitates and metal matrix, were carried out on samples cut out from the casting with a wall thickness of 13 mm (number 1 in Fig. 1). An Axio Observer Z1m metallographic microscope was used for this purpose. Strength parameters were tested on standard specimens taken from the 16 mm thick casting and prepared for tests by turning (number 2 in Fig. 1). Tests were carried out on a programmable machine operated by hydropulse system.

3. Results and discussion

In both methods of spheroidization, the same amount of spheroidizer and inoculant was added relative to the effective mould capacity.

The chemical composition of cast iron before and after the spheroidization treatment is compared in Table 1. Samples for the spectral analysis of chemical composition after the spheroidization process were poured as an integral part of casting, using specially designed chills placed in the mould cavity. The chemical composition obtained by each spheroidization method showed that, compared to the conventional method, the rate of magnesium assimilation was over two times higher in the in-mould spheroidization process using the reactor.

Table 1. Chemical composition of cast iron before and after spheroidization

	Chemical composition, wt. %					
	C	Si	Mn	P	S	Mg
Base cast iron	3.98	2.12	0.27	0.035	0.018	–
Ductile iron – sferoidization in reaction chamber	3.31	2.38	0.27	0.029	0.019	0.060
Ductile iron – sferoidization by conventional method	3.71	2.60	0.27	0.035	0.011	0.024

Table 2 shows the results of gas content measurements in cast iron samples taken during melting.

The gas content in castings was measured with a LECO Corporation TCH600 analyzer, suitable for parallel measurements of the oxygen, nitrogen and hydrogen content in steel, cast iron, non-ferrous metal alloys, and solid non-metallic materials. For measurement, the sample was placed in a graphite crucible in an electrode furnace and melted in a helium jet, determining next, through absorption of the infrared radiation, the amount of the developed carbon dioxide and water formed on a CuO catalyst; the nitrogen content was determined by measuring the thermal conductivity of a mixture of gaseous helium and nitrogen [17].

The results of measurements of the content of oxygen, nitrogen and hydrogen in cast iron samples are presented in Table 2. The permissible oxygen content in cast iron is 4−100 × 10^{-4}%, while for nitrogen it amounts to 15−140 × 10^{-4}%. Total hydrogen content in the cast iron under discussion was below 11 ppm.

The results clearly show that, compared to the conventional method, the use of the in-mould spheroidization process with reaction chamber reduces the gas content in cast iron nearly two times.

Table 2. Oxygen, hydrogen and nitrogen content in cast iron, %

Sample designation	N	O	H total
Mould 1 spheroidization in mould	77 × 10^{-4}	220 × 10^{-4}	7 × 10^{-4}
Mould 2 spheroidization in ladle	197 × 10^{-4}	393 × 10^{-4}	11 × 10^{-4}

Mechanical tests carried out on standard 7 mm diameter specimens have proved that only the spheroidizing treatment using the reaction chamber can yield the values conformant to the EN-ISO standard and thus produce the EN-GJS-450-10 grade of cast iron (see Table 3).

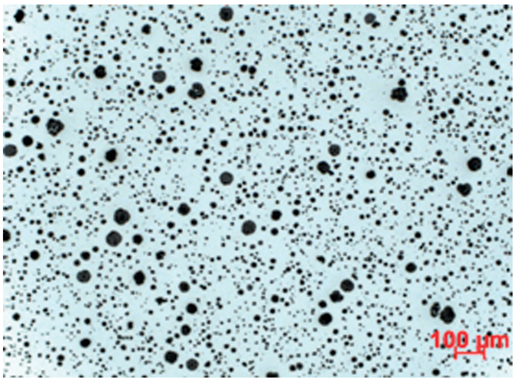
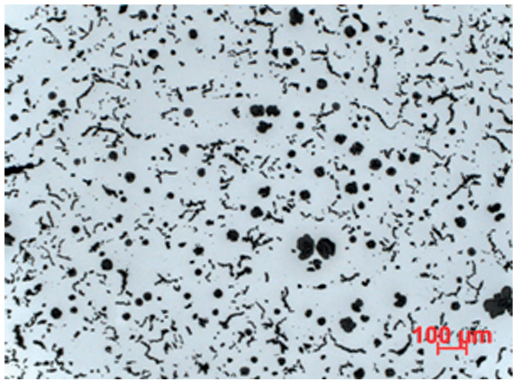
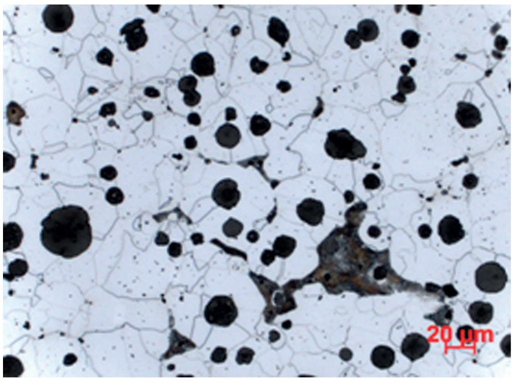
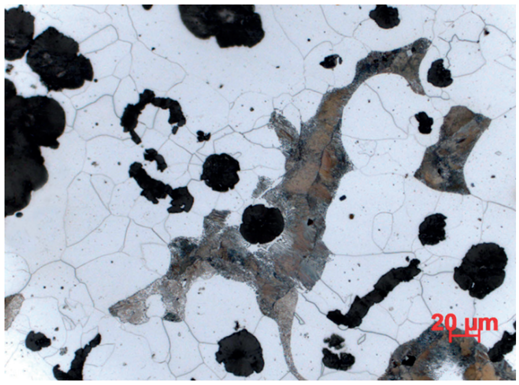
Table 3. Mechanical properties of the tested ductile iron

Parameters	Results obtained	
	Spheroidization in reaction chamber	Conventional spheroidization
Tensile strength R_m, MPa	466	353
Yield strength $R_{p0.2}$, MPa	341	298
Unit elongation A_5, %	11.6	3.9

Information on the microstructure of graphite precipitates and metal matrix is provided in Table 4.

The evaluation of graphite microstructure according to PN-EN ISO 945-1 is a benchmark-based method. The standard defines that measurement uncertainty is within the two neighbouring reference patterns. The result of the measurement is an average of the three randomly selected fields of view. The above ISO standard does not take into account the measurement of the nodule count per unit area.

Table 4. Microstructure of the examined ductile iron

	Results obtained	
	Spheroidization in reaction chamber	**Conventional spheroidization**
Microstructure of graphite according to PN-EN ISO 945-1	90% VI 7 + 10%V 5 VI – spheroidal graphite V – irregular spheroidal graphite	90% III 5 + 10% VI 6 VI – spheroidal graphite III – vermicular (compacted) graphite
Microstructure of metal matrix according to PN 75/H-04661	P0	Pf1-P6-Pd1,0
Unetched sections		
Sections etched with Mi1Fe		

The evaluation has shown that in the samples of ductile iron made with the use of reaction chamber, 100% of graphite precipitates were spheroids (VI and V) and only 10% of these spheroids had an irregular shape (V). On the other hand, spheroidization by conventional method produced only 10% of spheroidal graphite (VI) with the remaining 90% assuming a vermicular (compacted) form (III). This is clearly visible in the unetched metallographic sections. Metallographic sections after etching show in both cases the prevalence of a ferritic matrix (Table 4).

4. Conclusions

Based on the obtained preliminary results it can be concluded that, compared to the conventional method, the in-mould spheroidization process carried out in reaction chamber reduces the gas content in cast iron nearly two times.

The results also show that, compared to the conventional method, the new method of in-mould spheroidization using the reactor has doubled the content of residual magnesium in post-spheroidized castings. Under industrial conditions, this is expected to significantly reduce the cost of ductile iron production by reducing the consumption of spheroidizer, as confirmed by the test results using the reactor. The indicated economic effect is one of many positive aspects of the new spheroidization process.

Compared to the in-mould process, higher gas content and significantly lower magnesium content obtained in the cast iron produced by conventional method affect the microstructure (several times lower spheroidal graphite content) and deteriorate the mechanical properties, making this cast iron incompatible with the GJS-10 requirements.

Summing up the results obtained, it can be concluded that the use of reactor in spheroidization process allows making high quality castings. Additionally, it should be emphasized that with the properly selected technological process conditions, industrial castings can be made by this new method from high quality iron.

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References

1. Guzik E. 1998. "Struktura i właściwości żeliwa sferoidalnego otrzymanego techniką PE". *Solidification of Metals and Alloys* 36 : 57−62.

2. Tabor A., J.S. Rączka. 2005. "Optymalizacja składu chemicznego i technologii wytwarzania austenitycznego żeliwa sferoidalnego". *Archiwum Odlewnictwa* 5 (17) : 333−340.

3. Kinal G. 2011. "The effects of laser treatment on the abrasive wear resistance of selected iron machine parts – assessment". *Journal of Research and Applications in Agricultural Engineering* 56 (2) : 72−77.

4. Stawarz M. 2004. "Kompleksowa ocena jakości żeliwa sferoidalnego". *Eksploatacja i Niezawodność* 22 (2) : 55−58.

5. Souza T., R. Nogueira, F. Franco, M. Aguilar, P. Cetlin. 2014. "Mechanical and microstructural characterization of nodular cast iron (NCI) with niobium additions". *Material Research* 17 (5) : 1167−1172.

6. Myszka D., T. Babul. 2010. "Wytwarzanie żeliwa sferoidalnego ausferrytycznego w piecu próżniowym z chłodzeniem gazowym". *Archiwum Technologii Maszyn i Automatyzacji* 30 (3) : 35−42.

7. Kostrzewski Ł., R. Kołodziej, J. Szajnar. 2013. "Metoda oceny skuteczności sferoidyzacji żeliwa za pomocą uproszczonego wzoru na uzysk magnezu". *Archives of Foundry Engineering* 13 (3) : 79−82.

8. Guzik E. 2001. *Procesy uszlachetniania żeliwa. Wybrane zagadnienia*. Monografia nr 1. Katowice: Wyd. Archives of Foundry. Komisja Odlewnictwa PAN.

9. Warchala T. 1995. *Metalurgia i odlewnictwo*. Wydawnictwo Politechniki Częstochowskiej.

10. Smalley O. 1975. "Treatment of nodular-graphite iron by the inmould process". *Foundry Trade Journal* 139 (3068) : 423−430.

11. Ohide T. 2000. "Hybrid control of graphite cast iron structure by partial melt treatment process". *International Journal of Cast Metals Research* 12 (5) : 277−282.

12. Ohide T., M. Kishida, T. Kimura, Y. Takemoto. 1997. "Formation of alteration morphology of graphite structure by modified inmould process and observation of fluid flow by water model". *Journal of Japan Foundry Engineering Society* 16 (1) : 27−34.

13. Juretzko F.R., J. Hitchings, D.M. Stefanescu. 2006. "A new modified in-mould treatment for ductile iron production using a direct-pour container technique". *Transactions of the American Foundry Society* 115 : 7−46.

14. *Reaktor do wytwarzania żeliwa wysokojakościowego, zwłaszcza sferoidalnego lub wermikularnego.* Stefański Zbigniew, Andrzej Pytel, Polska, 2015, Patent, PL 220357 B1.

15. Stefański Z., J. Kamińska, M. Angrecki, E. Pamuła, A. Palma. 2017. "Nowa, ekologiczna metoda uszlachetniania żeliwa w formie odlewniczej". *Odlewnictwo Współczesne – Polska i Świat* 10 (1) : 5−11.

16. http://photos.labwrench.com/equipmentManuals/1541-4182.pdf.

17. Kuder M. 2012. "Zastosowanie nowatorskiej metody pomiaru aktywności tlenu w kontroli procesu wytwarzania żeliwa sferoidalnego". *Prace Instytutu Odlewnictwa* 52 (3) : 31−44.