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VARIOUS ASPECTS OF APPLICATION OF SILICON CARBIDE IN THE PROCESS OF CAST IRON MELTING

The article discusses benefits associated with the use of silicon carbide in the process of melting gray cast iron and ductile cast iron in induction electric furnaces. It presents the analysis of the impact of various charge materials and the addition of a variable amount of SiC and FeSi to the fixed charge when melting cast iron of grades GJS 400-15 and GJS 500-7 on mechanical properties and microstructure. Moreover, the article includes an analysis of the efficiency of carburization and the increase in the content of silicon during the application of SiC. The article also presents the results of the study of primary modification using silicon carbide at the minimum temperature of Temin eutectic and Tsol solidus. Based on analysis of the literature, conducted research, and calculations, it was found that the addition of silicon carbide has a beneficial impact on the properties of melted cast iron. The addition of SiC in the charge increases the content of C and Si without increasing the amount of contaminations. The addition of SiC at reduced pig iron presence in the charge decreases production costs, while the use of SiC as an inoculant increases both Temin and Tsol, which is beneficial from the point of view of cast iron nucleation.

Keywords: cast iron; ductile iron; silicon carbide; SiC; cast iron melting

1. Introduction

One of the aspects of improving the competitiveness of the foundry is the possibility to change the proportions of charge materials (limitation or elimination of pig iron in the charge and replacement with steel scrap). However, this creates the need to supplement the deficiency of carbon and silicon in the chemical composition of melted cast iron. Based on the analysis of the literature [1,2], we can draw the conclusion that there is a possibility to produce high-grade ductile cast iron without the use of pig iron by appropriate selection of a carburizer and the carburization method. Carburizing material was shown to have a significant impact on the properties and structure of melted cast iron, as well as on the efficiency of carburization and consequently on the use of carburizer [3]. The authors of the article developed a method for assessing carburizing materials based on the measurement of specific electrical resistance [4]. Supplementing liquid cast iron with carbon and silicon, resulting from reduction of pig iron in the charge, can be carried out by subsequent carburization and addition of silicon to FeSi, or can be carried out simultaneously by adding a metallurgical silicon carbide [5]. According to research presented in the literature, silicon

carbide has advantages over carburizers and ferrosilicon [6-8]. It contributes to the increase in solidus and liquidus temperatures. In addition, it increases the number of eutectic grains and reduces the likelihood of carbides in the casting structure at the same time. It also reduces the probability of microporosity in the casting [5,6]. The literature analysis also shows that cast iron melted on the basis of steel scrap, with appropriately selected carburizing materials and materials that introduce silicon into the metal bath, has much fewer impurities than the cast iron melted using pig iron. This cast iron also contains less sulfur and phosphorus [3].

Metallurgical silicon carbide has a bright gray color. Among the three varieties (green, black, and metallurgic), it contains the least amount of SiC (88-92%). This material may be used as an alloy additive, an inoculant, or a carburizer during the production of cast iron. It is delivered in the form of briquettes, irregular pieces, or granules of 0.2-80 mm in size. It contains impurities in the form of partially unreacted SiO₂, as well as unreacted free carbon and silicon. SiC chemical compounds are made up of 70% silicon and 30% carbon.

The metallurgical silicon carbide features a series of properties that are hugely desired from the point of view of metallurgy

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and the quality of melted cast iron. These include a very low content of harmful trace elements, which is very important in the case of its use as a carbon and silicon carrier. Because of the low amount of impurities in silicon carbide compared to traditional carburizing additives and silicon carriers, it allows the reduction of harmful elements in the chemical composition of the produced cast iron. This is very significant of the case in an increase of the amount of steel scrap in the furnace charge composition [9,10]. Another advantage is the very low sulfur, nitrogen and hydrogen content, which is shown in TABLE 1 [9,10]. According to research described in the literature, the use of silicon carbide reduces the probability of pinhole formation compared to traditional carburization methods by limiting the nitrogen and hydrogen content in cast iron, even with a constant growth of the proportion of steel scrap in the furnace charge composition [10].

TABLE 1

Sulfur, hydrogen, and nitrogen in particular carbon carriers [10]

| Carbon carrier | Content of particular elements | | | |
|-------------------------|--------------------------------|-------|---------|---------|
| | C [%] | S [%] | N [ppm] | H [ppm] |
| Graphite electrodes | 99 | 0.05 | 150 | 100 |
| Calcined petroleum coke | 98 | 1.5 | 6000 | 15000 |
| Pitch coke | 98 | 0.4 | 7000 | 2000 |
| Metallurgic SiC | 31 | 0.07 | 300 | 100 |

Furthermore, the addition of silicon carbide in an amount of approximately 2.5-5 kg per ton prevents the formation of fayalite (iron silicate Fe_2SiO_4), which is produced during the melting of cast iron as a result of the reaction between silica SiO_2 and iron oxide. Fayalite can decrease the diameter of the furnace by creating persistent growth on its walls [11]. Silicon carbide used to produce cast iron melted in an electric furnace or a cupola also works as a pre-conditioner (pre-inoculant), causing an initial cast iron inoculation effect. A very important aspect is the slow fade out of the nucleation effect caused by the addition of SiC (significantly longer uptime compared to ferrosilicon-based inoculants) [11].

Furthermore, analysis of the literature shows that silicon carbide impacts the cast iron microstructure. SiC was found to be a source of a large amount of nucleus crystallization [12-14]. The durability of those nuclei is significantly higher than that of FeSi, since silicon carbide dissolves considerably slower. This is a very important aspect, especially in the case of the melting of cast iron based on steel scrap, where nucleation is impeded.

The articles [5,12] present the course and results of studies of two series of ductile iron melts of similar chemical composition but different content of charge materials. The results of the research show a higher amount of ferrite in the structure of melted cast iron with the SiC additive compared to that of FeSi, as well as improvement of strength properties in the studied cast iron. On the basis of the research and calculations conducted, a significant increase in the number of graphite precipitations was observed in the case of ductile iron with the addition of silicon carbide.

2. The degree of dissolution of carbon and silicon with SiC through liquid metal

A meaningful indicator that characterizes the process of addition of alloy additives to obtain the intended chemical composition of the melted alloy, both from a technological and an economic perspective, is the degree of dissolution (the efficiency of use) of those additives in the melting process. The efficiency of carburization (E_C) or increase in silicon (E_{Si}) can be specified using the following relationship [2,15]:

$$E_C = M_m \cdot \frac{\Delta C}{M_C} \cdot 100\% \quad (1)$$

$$E_{\text{Si}} = M_m \cdot \frac{\Delta \text{Si}}{M_{\text{Si}}} \cdot 100\% \quad (2)$$

where: E_C , E_{Si} , the increase in carburization or silicon efficiency in relation to pure carbon or silicon introduced into SiC, M_m – the mass of the metal, ΔC , ΔSi – increase of, respectively, carbon and silicon in the alloy, and M_C , M_{Si} , the calculated mass of pure carbon or silicon introduced into the charge.

This relationship allows us to specify the efficiency of carburization and yield of the addition capabilities of silicon and, consequently, to determine the efficiency of addition of silicon carbide. The degree of efficiency also depends on the temperature of the cast iron, the type of additive and the carbon equivalent of the output cast iron, as well as the size of the SiC grains. The values achieved for this parameter will depend on the melting specificity of the melting process in a given foundry. Furthermore, it should be noted that the addition of silicon carbide alone will not ensure appropriate carbon content. Therefore, you should also introduce a carburizer to the process of melting cast iron with a lower amount of pig iron in the charge. The process of selecting the appropriate carburizers for the smelting of cast iron in induction furnaces is described in the literature [2-4].

The Department of Foundry Engineering of the Silesian University of Technology carried out research aimed at determining the degree of efficiency of carbon and silicon with SiC during its addition to a fixed charge and to the surface of liquid metal (TABLE 2). The research included melts of grades cast iron of GJL 200 and GJL 250 grades based on steel scrap (without pig iron) of various chemical compositions. In all the melts, the content of silicon was supplemented by adding silicon carbide to the fixed charge or onto the surface of liquid metal (SiC_m1_s). In the research, black SiC_cz and metallurgic silicon carbide (SiC_m1 and SiC_m2) were used. For the additions of SiC_m1 and SiC_m2, in TABLE 2 two heats (marked a and b) were presented. The expected deficiency of carbon was corrected with synthetic graphite. The melts were carried out in an induction crucible furnace of high frequency and volume of 20 kg [2].

The results of the research show that dosing into a fixed charge (the first five measurements) is significantly more efficient method of introduction of silicon carbide compared to its addition onto the surface of metal. This is shown by the degree of

TABLE 2

The efficiency of carburization and addition of silicon during the introduction of SiC to fixed charges and to the surface of liquid metal [2]

| Type SiC | M_m kg | M_{SiC} [kg] | ΔC [%] | ΔSi [%] | E_{Si} [%] | E_C [%] |
|-------------------------|-------------|-------------------|-------------------|--------------------|-----------------|--------------|
| SiC_m1_a (fixed charge) | 10.2 | 0.82 | 1.700 | 4.32 | 94.77 | 87.02 |
| SiC_m1_b (fixed charge) | 10.2 | 0.40 | 0.793 | 1.97 | 88.60 | 83.22 |
| SiC_m2_a (fixed charge) | 10.2 | 0.35 | 0.910 | 1.14 | 58.59 | 98.22 |
| SiC_m2_b (fixed charge) | 10.0 | 0.35 | 0.918 | 1.05 | 52.91 | 97.14 |
| SiC_cz (fixed charge) | 10.2 | 0.34 | 0.932 | 1.92 | 85.71 | 97.08 |
| SiC_m1_s (surface) | 9.3 | 0.32 | 0.325 | 0.80 | 41.01 | 34.98 |

assimilation obtained of carbon and silicon, as well as observation of the liquid metal, where no unreacted SiC was observed on the surface after the charge had been melted. During the addition of SiC to the surface of liquid metal, despite additional mixing of the metal bath, a significant part of the unreacted silicon carbide can be seen even after 10 minutes, which is confirmed by the two-fold lower efficiency of the use of carbon and silicon. The use of black silicon carbide causes slightly higher indicators. Having regard to its significantly higher price, we may state that the use of black SiC in the cast iron melting processes is not justified from the economic point of view.

3. Use of silicon carbide during the melting of ductile iron

The research also included melts of two grades of ductile iron – GJS 400-15 and GJS 500-7. Melts were conducted at various amounts of charge materials (pig iron, steel scrap and own scrap). The silicon deficiency was supplemented by the addition of ferrosilicon FeSi75 or metallurgic silicon carbide SiC. Carbon deficiency, resulting from a decrease in the amount of pig iron melting and replacement with steel scrap, was corrected using synthetic graphite. The melts were carried out in a network frequency induction furnace (50 Hz) with a crucible capacity that allows the melting of up to 2300 kg of liquid cast iron. In total, 31 melts were performed. The summary of charge materials for part of those melts is presented in TABLE 3.

TABLE 3

Summary of charge materials for cast iron
GJS 400-15 and GJS 500-7

| Melt no. | Grade | Charge material | | | | Additives | | | |
|----------|------------|---------------------|--------------|--------------|------------|-----------|-----------|----------|---------|
| | | Spec. pig iron [kg] | Steel 1 [kg] | Steel 2 [kg] | Scrap [kg] | Car. [kg] | FeSi [kg] | SiC [kg] | Cu [kg] |
| 1 | GJS 400-15 | 1200 | 200 | — | 700 | — | — | — | 0 |
| 2 | | 200 | — | 900 | 1100 | 40 | 8 | 10 | 0 |
| 3 | | — | — | 1200 | 1000 | 45 | — | 20 | 0 |
| 4 | GJS 500-7 | 500 | 800 | — | 900 | 40 | — | — | 5 |
| 5 | | 200 | 800 | 300 | 900 | 50 | 8 | 10 | 5 |
| 6 | | — | 800 | 500 | 900 | 50 | — | 20 | 5 |

The following were used in the melts: special pig iron of the content: 3.5–4.5% C, 0.5–1.0% Si, 0.05% Mn, 0.05% P and 0.02% S, steel scrap (Steel 1) of the following chemical composition: 0.62–0.80% C, 0.15–0.58% Si, 0.70–1.20% Mn, 0.008–0.025% S, 0.025% P, scrap deep drawing sheet (Steel 2) of the content: 0.028% C, 0.009% Si, 0.025% Mn, 0.020% S, 0.020% P. Own scrap (Scrap) consisting of ductile iron of relevant grade (GJS 400-15 or GJS 500-7). Silicon carbide used in metallurgic melts included: 85% SiC, 1.5–2.5% C, 4.58% Si, 1–2% Fe, 3–6% SiO₂, while ferrosilicon had the following chemical composition: 75.09% Si, 1.49% Al, 0.145% C, 0.026% P, 0.007% S, 0.77% Ca. Carburization was carried out using synthetic graphite of the content: C_{min} – 94%, S_{max} – 0.1%, max. ash content – 2%, max. humidity – 1%, max. volatile matter – 1%.

After the charge was melted and the required alloying elements were supplemented, the sample was cast for chemical composition tests. The metal from the furnace was then poured in portions into the treatment ladle, where magnesium treatment and inoculation were carried out. Magnesium treatment was carried out using the Sandwich method with application of the FeSiMg6Ce foundry alloy, while inoculation was carried out by adding SB5 inoculant during pouring of liquid metal from the reaction ladle to the pouring ladle after magnesium treatment.

The results of the chemical analysis of the cast iron before the spheroidization process are presented in TABLE 4 (base cast iron) and TABLE 5 (final cast iron).

TABLE 4

Results of the chemical analysis of the base cast iron
(before the spheroidization process)

| Melt no. | C [%] | Si [%] | Mn [%] | P [%] | S [%] | Cr [%] | Cu [%] |
|----------|-------|--------|--------|-------|-------|--------|--------|
| 1 | 3.85 | 1.54 | 0.26 | 0.027 | 0.020 | 0.027 | 0.05 |
| 2 | 3.84 | 1.54 | 0.28 | 0.026 | 0.018 | 0.034 | 0.12 |
| 3 | 3.90 | 1.34 | 0.18 | 0.020 | 0.018 | 0.027 | 0.03 |
| 4 | 3.89 | 1.35 | 0.41 | 0.036 | 0.018 | 0.042 | 0.28 |
| 5 | 3.78 | 1.38 | 0.45 | 0.033 | 0.026 | 0.042 | 0.32 |
| 6 | 3.83 | 1.63 | 0.48 | 0.024 | 0.023 | 0.040 | 0.39 |

TABLE 5

Results of the chemical analysis of the final cast iron
(after the spheroidization process)

| Melt no. | C | Si | Mn | P | S | Cr | Cu | Mg |
|----------|------|------|------|-------|-------|-------|------|-------|
| 1 | 3.48 | 2.53 | 0.25 | 0.028 | 0.011 | 0.031 | 0.06 | 0.052 |
| 2 | 3.68 | 2.66 | 0.28 | 0.027 | 0.012 | 0.035 | 0.12 | 0.058 |
| 3 | 3.72 | 2.55 | 0.18 | 0.020 | 0.010 | 0.028 | 0.03 | 0.058 |
| 4 | 3.66 | 2.45 | 0.40 | 0.032 | 0.014 | 0.045 | 0.28 | 0.042 |
| 5 | 3.50 | 2.47 | 0.44 | 0.028 | 0.015 | 0.042 | 0.32 | 0.046 |
| 6 | 3.64 | 2.46 | 0.48 | 0.024 | 0.016 | 0.041 | 0.39 | 0.044 |

By analyzing the composition of the ductile cast iron before and after the spheroidization process (TABLE 4 and 5), you may find that there was a drop in carbon content in the

range of 0.16-0.37% compared to the final cast iron, resulting from the oxidation of this element. During the spheroidization process, there was an increase in silicon content in the range of 0.8-1.21%, which is a consequence of a large, that is, 40-45% Si content in the magnesium foundry alloy and in the inoculant (approximately 75% Si). In all melts, the magnesium content changed in the range of 0.042-0.058%.

The research included tensile strength measurements and hardness measurements. For the purposes of the tensile strength test, samples of diameter 14 mm and length 84 mm, with threaded brackets, cut from sample ingots, separately cast in Y-shaped sand molds, were prepared. Hardness measurements were made using the Brinell method. The measurement results obtained are presented in TABLE 6. In the table, the number of graphite precipitates per 1 mm² is also presented.

Structural analysis is a very important issue in the evaluation process of ductile cast iron. This applies to both the graphite precipitates and the matrix. The amount of precipitates of graphite and their shapes, as well as various amounts of ferrite and pearlite

TABLE 6

Mechanical properties of melted ductile cast iron

| Melt no. | UTS MPa | Elongation % | YS MPa | BHN - | Number of particles of graphite, 1/mm ² |
|----------|---------|--------------|--------|-------|--|
| 1 | 474 | 23.5 | 336 | 171 | 310 |
| 2 | 470 | 23 | 329 | 170 | 331 |
| 3 | 441 | 18 | 306 | 161 | 384 |
| 4 | 542 | 16.5 | 359 | 187 | 383 |
| 5 | 509 | 8 | 365 | 191 | 380 |
| 6 | 551 | 16 | 380 | 191 | 363 |

in the microstructure, translate into specific strength properties. In addition to the chemical composition of the melted cast iron, the microstructure is determined by heat dissipation conditions, depending on the shape of the casting and the molding sand used.

Observations of fractures of samples on a scanning electron microscope were carried out for the part of melts with various SiC contents in the charge. Pictures of fractures are presented in Figs. 1 and 2.

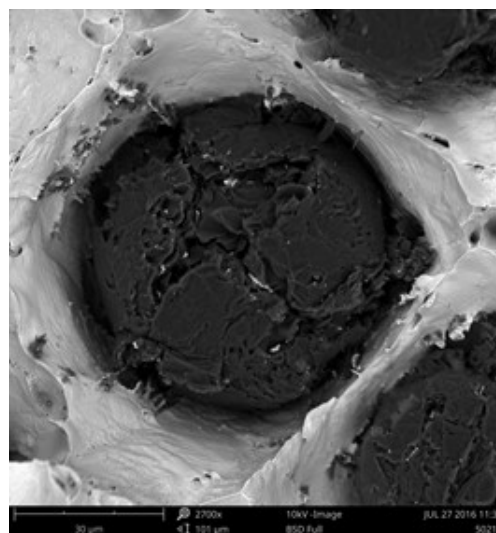
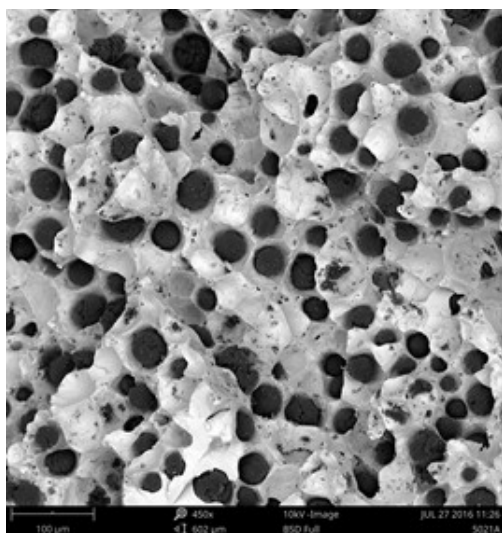


Fig. 1. Pictures of fractures of samples from melt no. 4

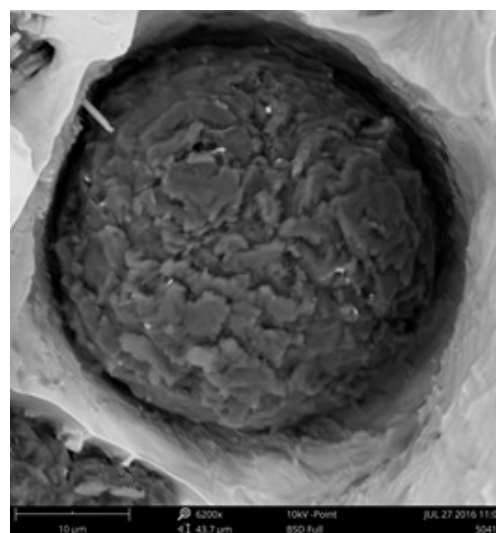
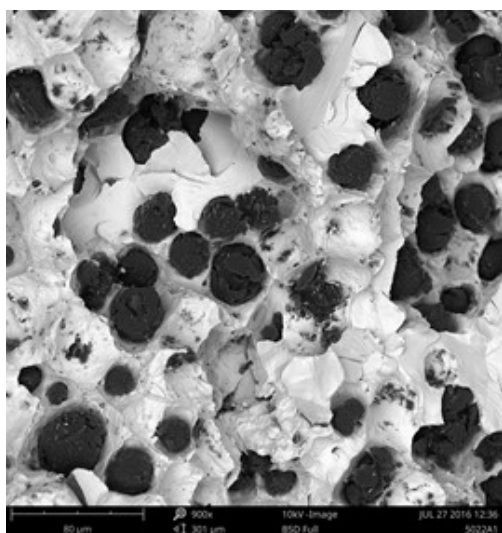


Fig. 2. Pictures of fractures of samples from melt no. 6

The analysis of the fractures of selected samples provided a series of information regarding the morphology of the surfaces of the graphite precipitates. In the case of samples analyzed in Fig. 1, related to the melting of GJS 500-7 grade cast iron (melt no. 4), we can observe similar morphological characteristics of the observed graphite precipitates. The adjacent layers are relatively large, making the observed surface of graphite 'smooth'. Also, discontinuities between layers in the form of deep cracks were observed. However, it is impossible to unequivocally state whether the observed discontinuities are an effect of the graphite crystallization process (the process of increasing the amount of separation and impeding the amount of increase by integrating elements contributing to the spheroidization into the crystallographic network) or an effect of mechanical damage to the graphite during preparation of the sample fracture. The morphology of graphite precipitates surfaces morphology for samples of GJS 500-7 cast iron (melt no. 6) is different. Small layers of crystallizing graphite are visible (Fig. 2). The adjacent layers are relatively small and create a peculiar squamous shell on the surface of the spheroidal precipitate. This microstructure could have been caused by the impact of charge materials, alloy additives, which impact precipitate growth parameters, taking into account the growth and suppression processes for the main crystallographic directions of graphite at the same time [1].

4. Primary inoculation using silicon carbide

The research also included an analysis of the primary inoculation process using SiC. Research was carried out under industrial conditions during the melting of cast iron. During the pouring of the metal from the furnace to the ladle, the inoculant in a form of SiC in the amount of 0.1% was introduced into the stream of liquid metal. As an indicator of the efficiency of the conducted inoculation, the minimum temperature of T_{emin} eutectic and T_{sol} solidus, obtained in the cooling and crystallization curve (DTA) recording process, was adopted [16]. The values obtained for those temperatures before the inoculation process (index p – yellow colors) and after the inoculation process (index k – green colors) are presented in Figs. 3 and 4.

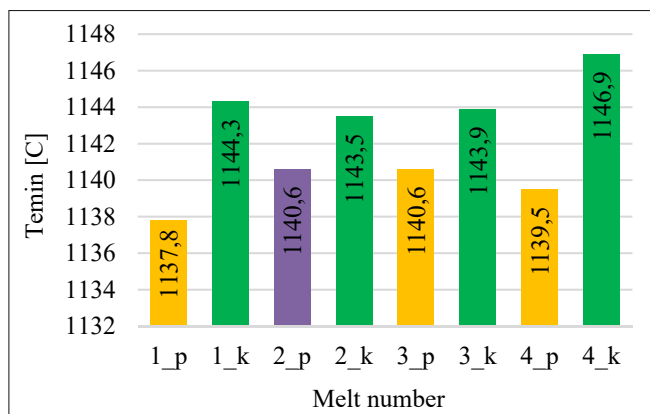


Fig. 3. Change of T_{emin} temperature after SiC inoculation

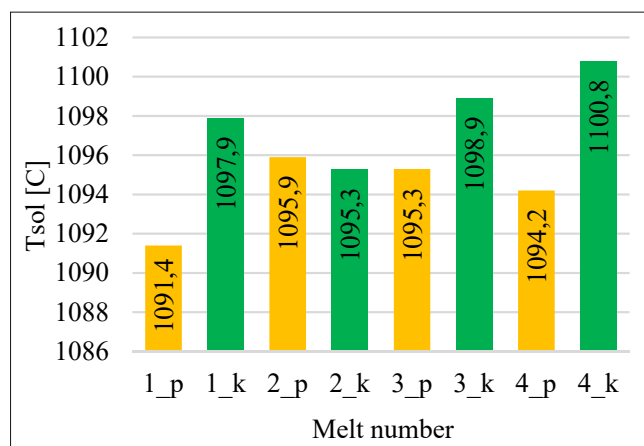


Fig. 4. Change in T_{sol} temperature after SiC inoculation

The presented research results show that silicon carbide causes an increase in both T_{emin} and T_{sol} . The increase in the minimum eutectic temperature causes an increase in the nucleation of cast iron, and consequently improves the properties of the cast iron through a decrease in the tendency for the occurrence of hard spots. It is assumed that T_{emin} should be above 1135°C. The conducted research shows that nucleation at the min. the level of 80% takes place at T_{emin} of 1142°C.

5. Summary and conclusions

The analyzed research involved the melting of GJL 200 and GJL 250 grade cast iron and ferritic cast iron (GJS 400-15) as well as ferritic-pearlitic cast iron (GJS 500-7) without the use of special pig iron in the charge or with its variable presence. The strength and microstructure properties tests show that all melts resulted in obtaining of cast iron and ductile iron that meet the assumed requirements of the standard.

The chemical composition of the melted cast iron, despite various proportions of charge components, is characterized by a very small range of variability of particular elements. A very low content of sulfur and phosphorus was obtained in all melts, which is a consequence of the low content of these elements in both pig iron and steel scrap. Analyzing the content of trace elements (B, Cr, V, Ti, As) that are not included in the tables and which may appear in the melting, e.g., as a result of the addition of SiC, no increase was observed in relation to the melting when pig iron was used.

Analysis of fractures of chosen samples under a scanning microscope shows similar morphological features of the observed graphite precipitates. Subsequent layers of growing graphite flakes are relatively large, which makes the surface of the spheroids smooth. For sample 1, the adjacent layers of graphite flakes are larger and create a 'cracked' surface on the surface of the spheroidal precipitate. Such a microstructure could have been caused by the impact of SiC, the greater participation of which may change the increase and suppression parameters for the main crystallographic directions of the graphite.

Based on the tests, calculations, and analyzes of the results obtained, the following conclusions were drawn.

1. It is possible to melt ductile ferritic and pearlitic-ferritic cast iron without pig iron in the charge while maintaining its high mechanical properties and proper microstructure.
2. The addition of SiC to the melt in the studied range (up to 0.91%) causes an increase in the content of carbon and silicon without causing an increase in the amount of impurities in the alloy.
3. Increasing the SiC addition in the charge may result in an increase in the number and size of graphite precipitates. It may also change the solidification characteristics of the alloy and the mechanism of increase of the graphite spheroids, making their surface smoother or cracked.
4. The impact of the addition of SiC and the elimination of pig iron from the charge reduces the cost of melting 1 kilogram of cast iron, while maintaining very high mechanical properties and providing constant consumption of electric energy and constant melting time.

On the basis of the complete analysis, it may be observed that silicon carbide positively impacted the alloys studied in technological and economic terms.

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