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Influence of the hardener type on the sulfur diffusion from moulding sand to the casting surface

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Abstract
The article is discussing authors examinations concerning the influence of the sulphur diffusion from moulding sand on reduction the efficiency of modifier elements in the process of making the nodular cast iron. In case of magnesium decrease of its content is observe, as a result of forming the magnesium sulphide. In consequence the participation of magnesium is falling below the concentration essential to create a spheroid graphite. The source of sulphur in no-bake sand with resin modified by furfuryl alcohol is a hardener, on the basis of sulphonic acids and sulphuric acid. Described examinations relate to no-bake sands made on the warp of fresh quartz sand.

Key words: Moulding sands; Sulpur; Nodular cast iron

1. Introduction

Making nodular iron castings in moulds drawn up in no-bake sand with resin modified by furfuryl alcohol (in so-called furan sand), it is possible sometimes to observe the degradation of spheroid graphite and passing him into the lamellar form on outside surfaces of casting. Changes of this type are being attributed to the diffusion of sulphur of moulding sand to the surface of the solidifying casting or/and the oxidation of nodular element in the layer of the casting cuticle. The flake graphite by the surface in a nodular iron casting is an one of anomalies of spheroid graphite that affects for lowering its mechanical properties. Reducing a limit of the material fatigue is being watched of about 15 % whether it causes stresses which can sometimes appearance of the crack. Moreover small petals of graphite in surface layer are supporting oxidizing and the sensitivity to decarburising of the subjected casting for heat treatment [1-8].

An analysis of the effect of the sulphur diffusion of moulding sand for lowering the efficiency of the modifier element, in this case of magnesium, by reducing its content as a result of magnesium sulphide being formed, below the concentration necessary for creating spheroid graphite is the subject of the research of authors. The source of sulphur in no-bake sand with resin modified by furfuryl alcohol is a hardener, on the basis of sulphonic acids and sulphuric acid. This occurrence is intensifying particularly in no-bake moulds on the base of reclamation sand. Under the impact of the high temperature the disintegration of the hardener proceed, product of which are sulphur compounds, mainly sulphur dioxide and hydrogen sulphide, diffusing to molten metal and intensifying in used moulding sand and get from it mechanic reclamation sand.

Influence of the quality of the reclamation sand to the structure of the cuticle of an nodular iron casting was described in detail in the separate publication [9], where was demonstrated the distinct reaction of reclamation sand, with different content of sulphur, applied as the warp of sand, for creating flake graphite zone of an iron casting with spheroid graphite. This study is dedicated however for discussing the influence of the type of the applied hardener on the diffusion of sulphur from furan sand, drawn up on the warp of fresh quartz sand, to the surface of molten metal.

2. Own investigations

2.1. Examination methodology

Own examinations included experimental castings made of the nodular cast iron, EN-GJS 500 – 7 type, with the application of no-bake sand with four hardeners differing in the content of sulphur. The shape and the construction of these experimental castings as well as the place of the sampling for examinations were selected as a result of the literature data analysis [5]. The scheme of this casting was placed in Figure 1.

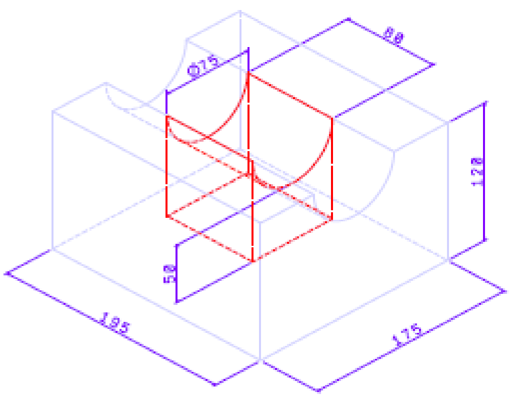

Fig. 1. Scheme of the experimental casting with marked the sampling place for examinations

For making moulding sands Grudzeń Las quartz sand was applied (the granulation 0.20 / 0.32 / 0.40; d 50 = 0.31 mm; pH= 7) and fenol- formaldehyde Kaltharz resin, about the low content of the free formaldehyde (0.1 - 0.2 %), nitrogen (0.35 - 0.5 %) and furfuryl alcohol ~ 50 %. Four different hardeners were applied, of which composition was placed in Table 1.

Table 1
Composition of individual hardeners

Type of the hardener	PTS %	Sulphuric acid, %	Phosphoric acid, %
Aktivator 1	50-65	<5 + 10% (solution 69%)	-
Aktivator 2	40-50	<1,5	20-25
Aktivator 3	65	<0,5	-
Aktivator 4	30-40	<0,23	-

Individual moulding sands was being carried out, about the following composition:

quarz sand	100 parts by weight
Kaltharz resin	1,1 part by weight
hardener	0,55 part by weight

SAND 1 – Aktivator 1
SAND 2 – Aktivator 2
SAND 3 – Aktivator 3
SAND 4 – Aktivator 4

Samples of sand this way prepared were taken for indication the sulphur content with thermal method with Leco CS 444 apparatus. These examinations were conducted at the Foundry Research Institute in Kracow – Table 2.

Table 2
Content of sulphur in individual moulding sands

Sand no	Content of sulphur in moulding sand, %
SAND 1	**0,080** ± 0,006
SAND 2	**0,070** ± 0,008
SAND 3	**0,072** ± 0,006
SAND 4	**0,045** ± 0,007

The other research stage consisted in cutting samples from experimental castings with a view to carrying out metallography investigations. The research was conducted on samples cut out sheer to the surface, in the place of the greatest concentration of gasses, from every experimental casting. Their surfaces were subjected to examinations of the chemical composition and the microstructure by means of the method of dispersion of roentgen rays EDS and analysis of optical images and scanning. These examinations were performed in Department of Materials Science and Analysis of the Faculty of Metal Engineering and Industrial Computer Science AGH. Samples were sinked in conducting bakelite, they were grinding and polishing. After polishing, samples were being etched 3% nitalem with a view to revealing differences of the structure among the outer surface and the interior area. Examinations of the microstructure were being conducted with using the light microscope Zeiss and electron scanning Hitachi 3500 N. Moreover behind the help of the EDS microanalyser of the Noran company, examinations of the content and elements arranging in chosen areas and current phases in outer layer were executed.

2.2. Examination results

Figure 2 shows the scanning image of the outer layer of the sample of the experimental casting made in SAND 4 about the content of sulphur 0.045 % with two areas marked, in which the chemical composition analysis was performed (Fig. 3).

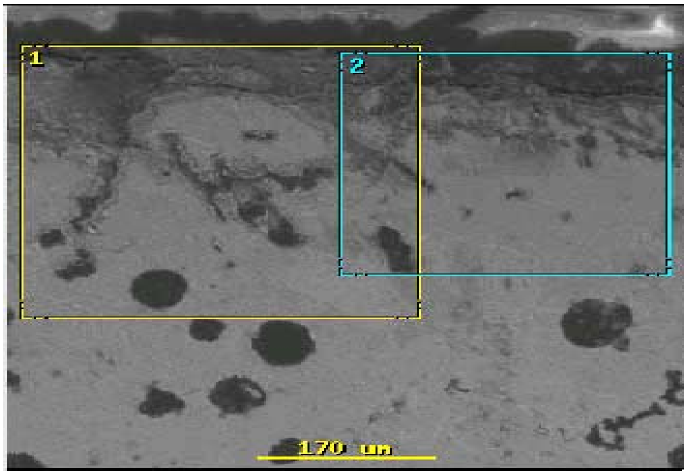

Fig. 2. Scanning image of the outer layer of the sample made in SAND 4 with two areas marked

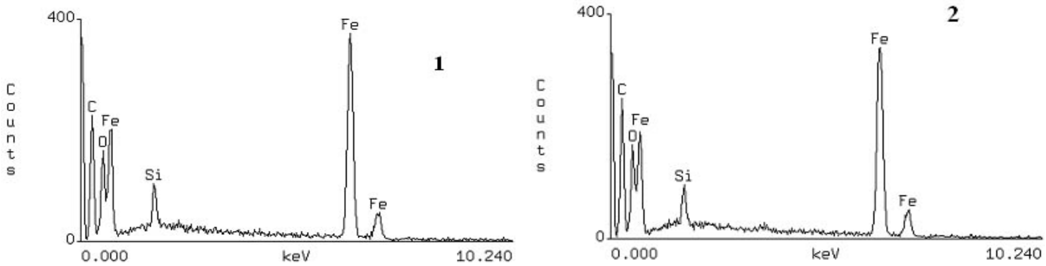

Fig. 3. EDS spectrograms for area 1 and 2 of Fig. 2.

Above only an example is placed among many of such analyses performed in various places of the outer layer of the sample made out in SAND 4. Apart from content of main elements, iron, coal, silicon and oxygen, none of analyses showed the presence of sulphur in the chemical composition of the casting cuticle. Similarly in case of experimental castings made in SAND 1 and SAND 2, where the content of sulphur in the external layer wasn't stated. EDS analysis showed little tracks of this element for the sample of the casting made in SAND 3 about the content of sulphur 0.072 %. Below a chosen scanning image was placed for this sample of the experimental casting with four areas marked, in which chemical composition analysis was performed (Fig. 5).

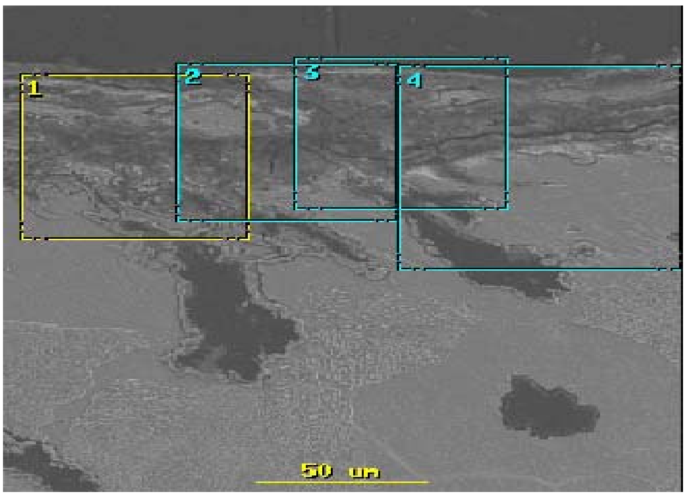

Fig. 4. Scanning image of the outer layer of the sample made in SAND 3 with four areas marked

In areas 2 and 4 a presence of sulphur was confirmed in the chemical composition of outer layer. EDS analyses in other places of the sample also showed trace amounts of this element.

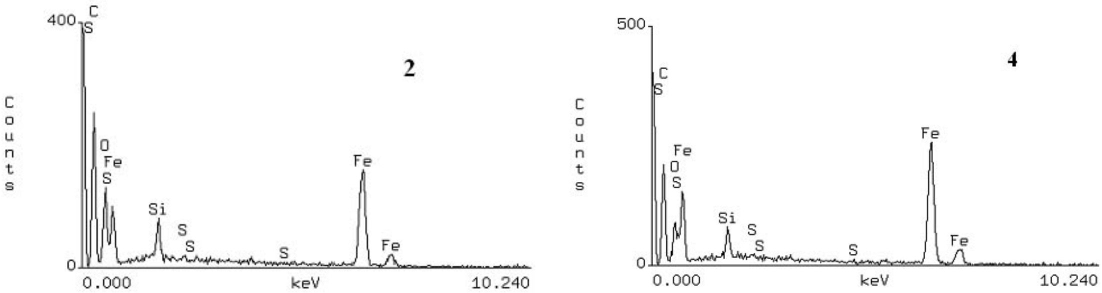

Fig. 5. EDS spectrograms for area 2 and 4 of Fig.4.

Through the application of the high definition method images of the distribution for Fe, Si and S were made out (Fig. 6), where the form of sulphur emission is evident. However Figure 7 even more precisely shows these spot clusters of sulphur on the surface of the experimental casting.

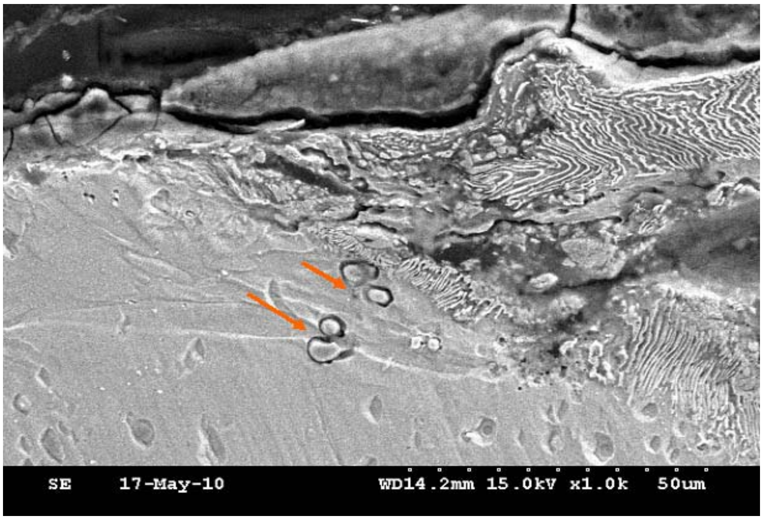

Fig. 7. Scanning image of the outer layer of the sample made in SAND 3 with marked spot clusters of sulphur

Next step was the analysis of the structure of the external layer of experimental castings. In spite of the appearance of trace amounts of sulphur in the chemical composition of the casting made in SAND 3, in the cuticle structure emission of flake graphite weren't observed (Fig. 8). Similarly in case of remaining castings made in SAND 1, SAND 2 and SAND 4. External layer had the appropriate structure of the cast iron with spheroid graphite.

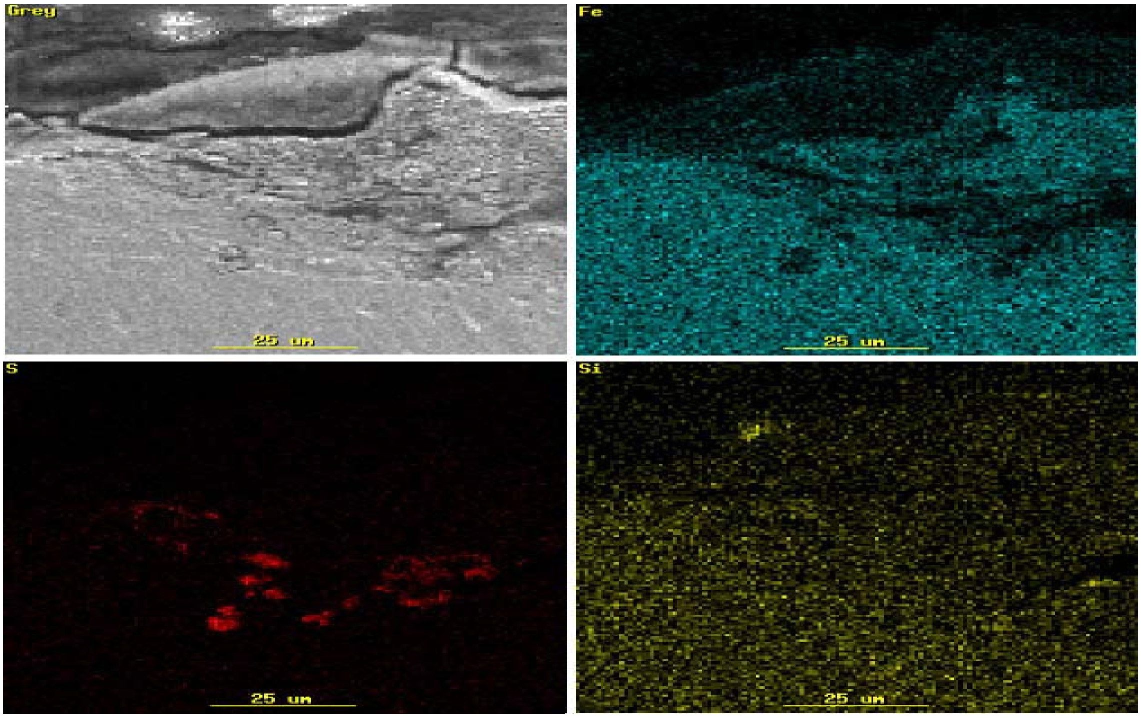

Fig.6. SEM image of the topography of the area and images of the distribution for Fe, S, Si

3. Conclusions

Conducted examinations showed that the content of sulphur in sand to 0,080 % do not cause appearing of the defect of spheroid graphite deformation in the external layer of the casting. This application is consistent with some literature data, that this effect can appear only after crossing the content of sulphur in sand according to 0.15 %. Even relatively high content of sulphur in hardeners, when preparing sand based on fresh quartz sand, isn't threatening with negative consequences in forming degenerate graphite.

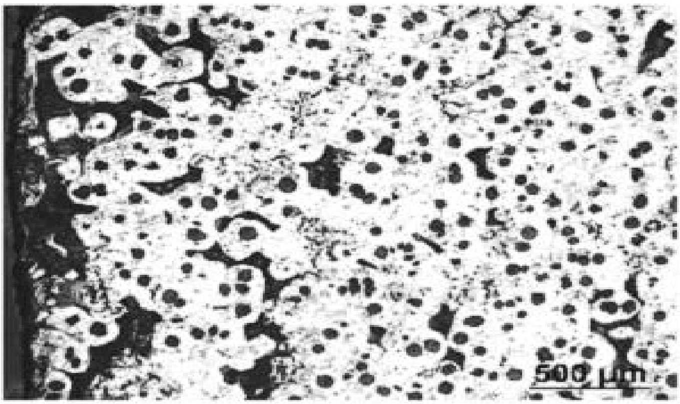

Fig.8. Light microphotograph presenting the structure of the sample in SAND 3

Acknowledgments

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