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The diffusion of sulphur from moulding sand to cast and methods of its elimination

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Abstract

The care of high quality castings requires taking into account the possible negative influence of decomposition products of moulding and core sands on the structure of castings produced. Such products are emitted both from the sands of I generation, meaning sands bound by bentonite, especially those containing carbon forming additives, as well as from the sands of II generation, meaning the sands with the binding materials or even the sands without any binders, such as the forms produced by using the LOST FOAM technology. The literature often refers to the negative effects of nitrogen emitted from the sands with the urea resins on the tendency to create surface defects. That is why the aim of this study was to assess the degree of sulphur diffusion to the ferroalloy castings and the proposal of its limitation.

Key words: Moulding sands; Sulphur

1. Introduction

The issue of a diffusion of the components of the moulding sand to the surface cast structure has been an object of many studies (1-4). While producing the cast-iron castings with spheroidal graphite in the forms of self-hardenered moulding sands with furfuryl resins (so called furan sands) we can occasionally observe the spheroidal graphite degradation on the external surfaces of the castings and its transition into a flake form. This type of change is attributed to the diffusion of sulphur from the moulding sand to the surface of the solidifying casting. This can result in a reduction in the efficiency of the modifier - magnesium in the form of MgS, by reducing its content below the concentration needed for the creation of spheroidal graphite. Self-hardenable loose sands are hardened with acid hardeners, on the basis of sulphide acids, sulphuric or phosphoric acid. Increasing the concentration of sulphur on the surface of the form causes that often more than 90% of reclaimed sands has excessive amount of sulphur.

This process is the result of the formation of SO_2 as a product of decomposition of a hardener, for example, sulphide acid:

$$C_7H_7SO_3H \rightarrow C_7H_7OH + SO_2 \quad (1)$$

During pouring into the mould there appears its shift to the casting surface, inquiring of SO2 into casting alloy and reaction of SO2 with a metallic Mg:

$$SO_2 + Mg \rightarrow MgS + O_2 \quad (2)$$

Reduction of concentration of Mg in the casting surface area, leads to the formation of flake (degraded) graphite. This form of graphite may, among other negative effects, especially when dynamically loaded castings, change its position and initiate the formation of fractures. Except for the extraction of degraded graphite, additional emission of sulphides will intensify this tendency. Therefore, to the forms and cores made of sands with acid hardeners, we may use special protective coatings (so-called: absorbing), containing calcium carbonate. After a thermal decomposition CaO is created

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$

which fixes SO_2

$$CaO + SO_2 \rightarrow CaSO_3 \quad (4)$$

Releasing CO2 may create blisters, that is why the coatings based on silicates are used. Currently, many companies produce such protective coatings.

2. Own researches

2.1 Assessment of sulphur diffusion to the casting surface

The first task was to determine the degree of the diffusion of sulphur to the surface of the cast iron alloy. Sulphur saturation of the castings' surface zones, made in the forms of self-hardenered moulding sands with furfuryl resins, can also be observed in cast-steel castings. These diffusion changes are stimulated by solidity of castings, wall thickness and solidification time.
This process was analyzed - by the authors of the work in one of the Czech foundries - on the experimental casting measuring 0.6 x 0.6 x 0.6 m, pourred from the bottom with the cast-steel ČSN 422712, with a mass of raw casting 1.65 Mg. The form was made of self-hardenable loose sand of the following composition:

- chromite sand - 100 part of weight.,
- furfuryl resin TDE20 - 1,2 part of weight.,
- hardener 500-T1 - 0,5 part of weight.

After pouring, there was cut a sample of the size of 80 x 80mm and 50mm of thickness, from the surface of the casting. Changes in the chemical composition (content of S) were marked on the surfaces of mm distances from the surface of the casting. The measurements were carried out to a depth of 10mm, using the EDS technique – of microanalyser LINK AN 10/85S coupled with the electron microscope JSM 840. At the same time on milled surfaces at a distance of 1 mm from the casting surface, the carbon and sulphur contents were marked by using the Leco spectrometer. The results of this analysis are given in Table 1

Table 1
Changes of concentration of carbon and sulphur in different distances from the casting surface.

Distance from the casting surface [mm]	content of [%] * sulphur	Content of [%] ** sulphur	Content of [%] ** carbon
0	0,442	-	-
1	0,342	0,153	0,059
2	0,055	0,014	0,110
3	-	0,0097	0,153
4	0,050	0,0098	0,183
5	-	0,0097	0,202
6	0,020	0,0096	0,210
7	-	0,0094	0,212
8	-	0,0099	0,214
9	-	0,0098	0,217
10	0,021	0,0096	0,219

* microanalyser, average from 6 markings
** spectrometer LECO (S, C)

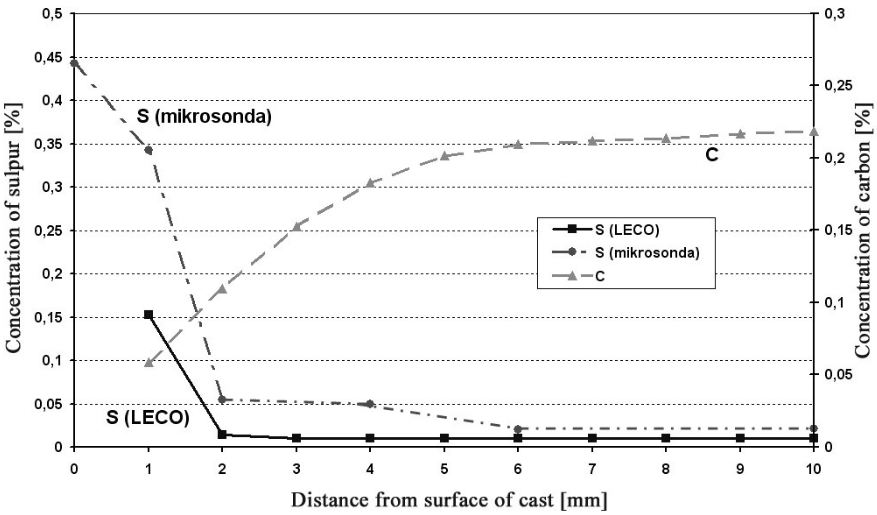

Fig. 1. Change of the chemical content of the cast-iron (content of C and S) in reference to the distance from the casting surface

As you can see from the research, there is a high probability, conditioned on the size of casting, of the diffusion of sulphur coming from the decomposition of hardeners to the surface structure of the casting. This phenomenon is particularly dangerous in the production of cast-iron castings with spheroidal graphite. That is why the aim of this paper is to present new hardeners with reduced emission of sulphur, produced by Hüttenes-Albertus Poland.

2.2. Studies of new hardeners with a reduced sulphur content

In order to look accurately at the new hardeners with reduced sulphur content, the series of tests were made on the prepared moulding masses whose matrix was a quartz sand Grudzeń Las (1K-0, 20 / 0.32 / 0.16). As a binder there was used the liquid phenol-furfuryl resin Kaltharz 2 - with a low content of free formaldehyde and the reduced nitrogen content, in combination with four different hardeners. Hardeners used in the tests are made on the basis of a mixture of organic and inorganic acids, but they differ among each other by the content of sulphur-derivative acids. For comparative purposes there was used the standard hardener - Aktivator 1, which contains up to 70% sulphur-derivative acids. Other hardeners are characterized by a reduced content of sulphur-derivative acids, and so Aktivator 2 contains approximately 50%, Aktivator 3 and Aktivator 4 - about 40%.
The research was conducted - in accordance with appropriate procedures for the following sand composition:

- quartz sand -100 part of weight.,
- resin Kaltharz 2 - 1,1 part of weight.
- hardener:

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

Research was carried out for various hardener contents within the limits: 40, 50, 55 and 60% in relation to the quantity of resin. Mechanical properties were measured as a function of hardening time: 2, 6 and 24h. The final results are presented in fig 2-5.

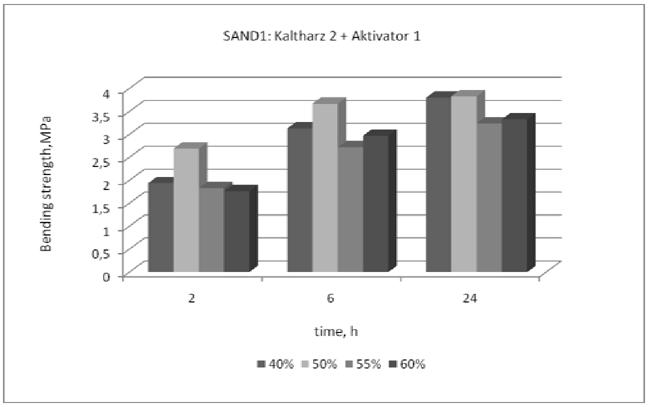

Fig. 2. Bending strength as a function of hardening time, with different contents of hardener, for SAND 1

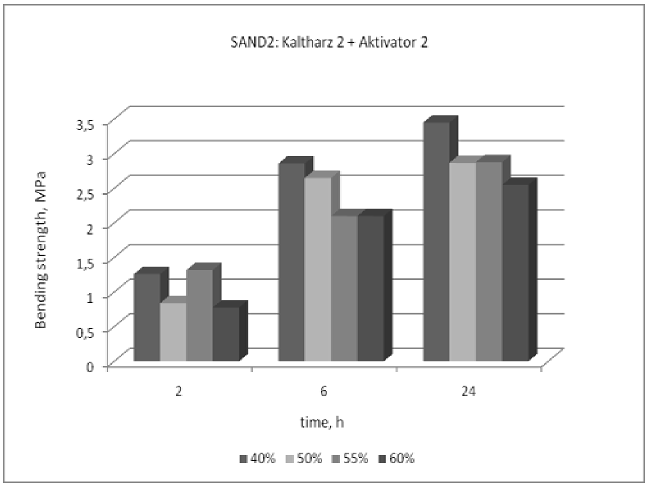

Fig. 3. Bending strength as a function of hardening time, with different contents of hardener, for SAND 2

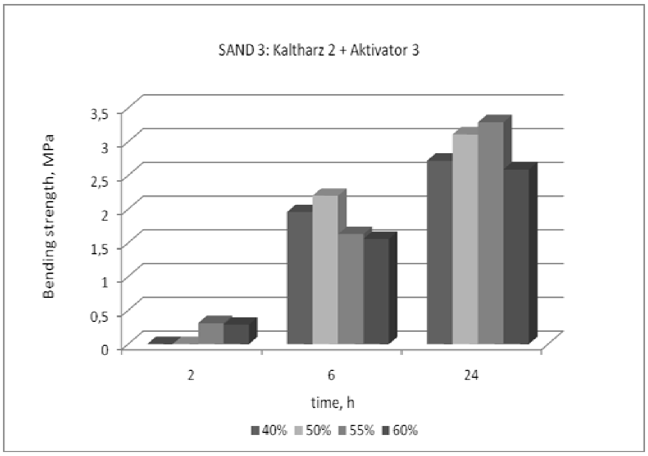

Fig. 4. Bending strength as a function of hardening time, with different contents of hardener, for SAND 3

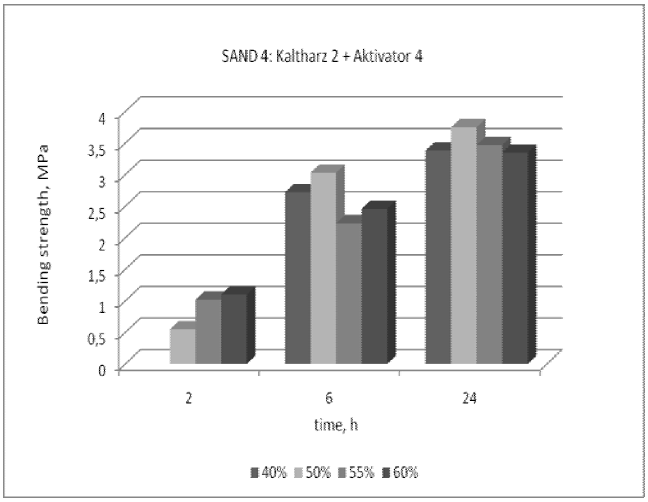

Fig. 5. Bending strength as a function of hardening time, with different contents of hardener, for SAND 4

As you can see the optimal content of hardener for all tested moulding sands is 50%. Only for the sand 2 the highest strength was achieved at 40% of hardener. Furthermore, it was found that all used hardeners give similar binding kinetics.

2.3. Determination of sulphur content in the moulding sands tested

The next stage of the study was to determine the content of sulphur in the moulding sands. The contents shall be labelled using the thermal method with the apparatus Leco CS444. The results were as follows:

SAND 1 – Aktivator 1 – 0,077% S
SAND 2 – Aktivator 2 – 0,053% S
SAND 3 – Aktivator 3 – 0,045% S
SAND 4 – Aktivator 4 – 0,052% S

As you can see the use of hardeners with reduced content of sulphur-derivative acids resulted in a significant reduction in the sulphur content in the sands tested. Classical hardener for such kind of resins (Aktivator 1), containing about 70% of sulphur-derivative acids, caused the sulphur content at the level of 0.077%. Aktivator 2 containing about 50% of sulphur-derivative acids, decreased the content of this harmful element by more than 30%. Hardeners with sulphur-derivative acids content of about 40% (Aktivator 3 and 4) decreased the sulphur content in the sands of 41.5% and 32.5%.

3. Conclusions

The analysis of the source data and own research confirmed the possibility of diffusion of sulphur, coming from the decomposition of the hardeners to the surface structure of castings. Depending on the type of casting alloy, the interaction can cause changes in the casting structure, both in the form of phase deformation and in the fracture initiation. Hence the undertaking to do a research aiming to develop new types of hardeners with reduced emission of sulphur is fully justified. The new types of hardeners which decreased the emission of sulphur were proposed. These studies are continued in order to develop the best compositions conforming the needs of foundry practice.

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