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# The Use of Phosphate Binder for Ablation Casting of AlSi7Mg Modified TiB Alloy

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## Abstract

The possibilities of using an inorganic phosphate binder for the ablation casting technology are discussed in this paper. This kind of binder was selected-for the process due to its inorganic character and water-solubility. Test castings were made in the sand mixture containing this binder. Each time during the pouring liquid alloy into the molds and solidification process of castings, the temperature in the mold was examined. Then the properties of the obtained castings were compared to the properties of the castings solidifying at ambient temperature in similar sand and metal molds. Post-process materials were also examined - quartz matrix and water. It has been demonstrated that ablation casting technology promotes refining of the microstructure, and thus upgrades the mechanical properties of castings ($R_m$ was raised about approx. 20%). Properties of these castings are comparable to the castings poured in metal moulds. However, the post-process water does not meet the requirements of ecology, which significantly reduces the possibility of its cheap disposal.

**Keywords:** Ablation casting technology, Alumina, Phosphate binder, Self-hardening sands, Inorganic binder

## 1. Introduction

Ablation casting is a relatively new technology not used so far by the industry in Poland. The essence of the process consists in pouring metal into sand moulds, which are intensively cooled with water during casting solidification until they completely disintegrate. This process is applicable to both aluminium and magnesium alloys cast into single-use moulds. Sand moulds with water-soluble binders are used in this process [2].

Numerous authors have confirmed that the microstructure of castings made by this technology is much more refined than in the case of the conventional aluminium alloy casting technology [3-5]. By increasing the cooling rate, both the secondary dendrite arm spacing (SDAS) and the size of the eutectic phases are reduced [6-8]. Thus, the ablation casting technology is a cost-effective process, which enables producing high-quality castings with the fine structure of dendrites and other secondary phases, characterized by an even distribution. This, in turn, improves the mechanical properties of the finished castings [9-15]. The ablation casting process produces very rigid castings capable of operation in the zones of cold work or functioning as large aluminium structural nodes. Then aluminium profiles are inserted into the sockets of the ablation cast nodes, and the nodes act as holders to keep the components of a spatial frame in the right position during welding [16-18]. An additional advantage of the ablation process is the possibility of recovery of the sand grains without the need to carry out the process of mechanical reclamation. When the mould disintegrates, the binder dissolves in water and is washed off from the sand grains, while the sand thus recovered has after drying the properties similar to fresh sand.

When assessing the methods of making moulds and cores, environmental protection, type of technology and cost-effectiveness are primarily taken into account. In the scope of environmental protection, the following factors are considered: the composition of the materials used, the emission of harmful substances during the production of moulds and cores, the emission of such substances during mould pouring and during casting cooling and knocking out, the storage of waste sand and the possibility of its re-use [19]. Chemical hardening of moulding sands is an economically viable process. It also allows obtaining the optimal strength properties with a low content of the binder in the sand mixture. The way in which the hardening takes place produces castings with high surface quality and the process is widely used in industry. Phosphate binders are characterized by good solubility in water. They are non-toxic, non-harmful to the environment, and do not require organic compounds for their hardening. The sands with these binders are characterized by good knocking-out properties and reliability. Phosphates, mainly aluminium orthophosphate, are the basic binding component. The most commonly used hardener is powdered magnesium oxide MgO [20].

## 2. Materials and Methods

**Molding sand used in the tests**

A phosphate binder was used in the research. Its datasheet is presented in the table:

Table 1.
Datasheet for phosphate binder (Glifos) [Sulfochem. 2015. Karta charakterystyki spoiwa Glifos CE. Sulfochem. (In Polish)]

| Binder | Phosphate Binder (Glifos) |
|---|---|
| Form | mixture |
| Physical state | liquid |
| colour | green |
| pH (20°C) | 3 |
| Density (20°C), g/cm$^3$ | 1.6 |
| Viscosity (25°C), MPa·s | 6-8 |

On the basis of our previous research [1] wybrano skład masy formierskiej wykonanej na bazie spoiwa fosforanowego, utwardzonej tlenkiem magnezu, był on następujący:

- medium quartz sand: 100 parts by weight;
- phosphate binder: 2.5 parts by weight;
- MgO—5% relative to the binder quantity.

**Mould wettability testing**

To produce high-quality castings, the moulding material should not enter into reaction with molten alloy, as it may result in the formation of unfavourable phases in the skin of the casting. To obtain a high quality of the casting surface, it is necessary to provide an optimal contact angle between the liquid metal and the mould material, which is 90-180°. This allows the mould to be filled without infiltrating its porosity. Additionally, the liquid metal should not react with the mould material or, if it does, the reaction products should remain on the mould side. To determine the interaction between selected grades of aluminium alloys and casting mould, high-temperature tests of the thermophysical properties of molten metals were carried out, including also the phenomena of wettability, reactivity and infiltration in contact with ceramic materials.

The phenomena of wettability and reactivity between liquid aluminium alloy and moulding material were studied by the sessile drop method and a non-contact heating procedure combined with capillary purification (CP). The substrate (a 17 mm diameter specimen with a thickness of 5 mm) made of moulding material and placed on a movable table was quickly transferred from the cold part of the chamber to the hot part of the chamber when the temperature of 720°C was reached in the latter one. Subsequently, the tested molten aluminium alloy was squeezed out of a graphite capillary located directly above the substrate. To increase the cooling rate, in the tests simulating the ablation casting process, the formed droplet/substrate couple was immediately drawn back into the cold part of the chamber, which allowed for relatively high cooling rates (although probably still significantly lower than in the case of real process conditions).

**Test casting and thermal analysis**

To compare the impact of ablation casting technology on the casting solidification process, a metal mould (die) was designed. This allowed for the comparison of three casting technologies, i.e. traditional casting and cooling in a sand mould, casting and cooling in a metal mould, and casting in a sand mould with ablation breakdown of the mould and casting cooling. The shape of the casting is shown in Figure 1.

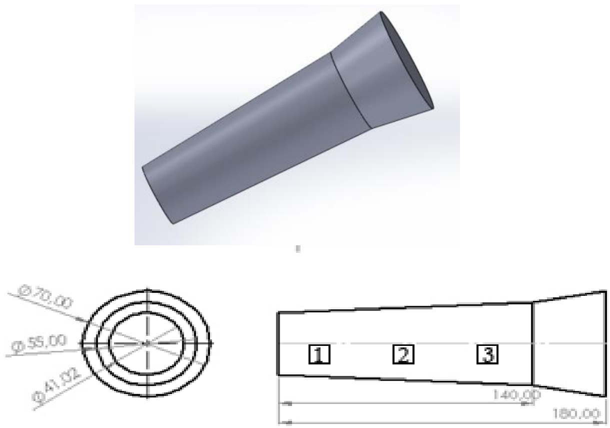


Fig. 1 Schematic representation of the test casting

Test castings were made of aluminium-silicon alloy (AK7). The alloy was modified with a "TIBAL" master alloy (5% Ti, 1% B). Melting was carried out simultaneously for the casting process in a conventional sand mould, metal mould and ablation sand mould, i.e. the sand mould intensively cooled with water. In each mould, the thermocouples were attached at three different levels to measure at three different points the temperature of the casting during the entire process (the upper, central and lower part of the casting).

The thermal analysis was carried out using two measuring devices, i.e. a multichannel MrAC-15 recorder for traditional casting and a portable TES 1384 recorder for ablation casting. Owing to this solution, it was possible to record the course of casting solidification and cooling over time. In the case of ablation casting technology, the time of 1 minute elapsing from the moment of pouring the mould with liquid alloy was considered to be the safe time after which cooling of the mould with water could be started. Shorter time might not be sufficient for the casting to keep its proper shape, while a long time did not guarantee the required changes in casting structure.

**Examination of casting microstructure**

The aim of the conducted research was to show differences in the microstructure of castings at three different levels in a way similar to the thermal analysis, i.e. in the upper, central and lower part of each casting (respectively: 3, 2 and 1 in figure 1). The differences resulted from changes in the crystallization path, caused by the use of three different casting technologies ensuring different heat dissipation rates from castings, and from the shape of the casting the upper part of which, by being directly connected to the gating system, was much wider than the lower part. To carry out the examinations allowing for the assessment of differences in microstructure at the three different points in casting, samples were cut out from each part of the casting. They were polished on a Struers grinding polisher, following the program established for soft materials (using 220, 500 and 1000 papers with 9, 3, 1 and ¼ micron diamond pastes). The samples were then etched with a 1% HF solution in distilled water. The examinations were made using a Zeiss light optical microscope and an AxioObserver Zm10 program. Secondary dendrite arm spacing (SDAS) was examined by the 10 oriented secant method on the etched samples at 50x magnification.

**Testing the strength properties of castings**

The static tensile test at ambient temperature was performed in accordance with PN-EN ISO 6892-1: 2016-09, Method B "Metallic materials. Tensile testing. Part 1: Method of test at room temperature”. The EU-20 testing machine with a maximum range of 200 kN was used for the tests. The stress velocity increase was 15.9 MPa/s. Standard samples according to PN-EN ISO 6892-1: 2010 (Metallic materials - Tensile Testing) were used in the tests.

**Testing the post-ablation process water and moulding sand**

The aim of the tests was to check whether the applied binder had a negative effect on the ablation medium (water) after the process. For the safe disposal of the wastewater, it must meet the requirements concerning the concentration of pollutants (Table 1).

Table 2.
The allowable concentration of pollutants specified in Council Directive 91/271/EEC, Regulation of the Minister of the Environment, Journal of Laws No. 27 of 19 February 2009, item 169, and in the Contractual Warranties

| Parameter | Average concentration of pollutants (mg/l) |
|---|---|
| $BOD_5$ | 15 |
| COD | 125 |
| Suspension | 90 |
| Total nitrogen | 10 |
| Total phosphorus | 1.0 |

The results of the post-process water tests were compared with the results obtained on fresh water taken from the water supply network and used for the ablation casting process.

Another important advantage of the ablation casting technology is the possibility of re-using the waste sand without the need to subject it to mechanical reclamation. For this purpose, it was decided to examine the content of organic compounds in the waste sand mixture, and the sand was re-examined by scanning electron microscopy combined with EDS analysis.

## 3. Results

**Wettability test**

Figure 2 shows the course of the wettability test and the contact angle values recorded during this test.

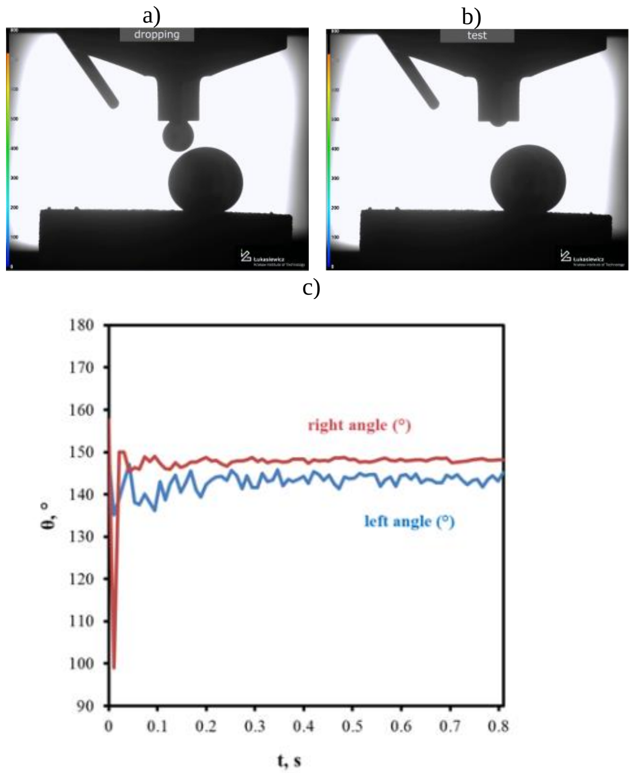


Fig. 2. The results of wettability test carried out on the sand with phosphate binder hardened by MgO: view of the drop at the moment of squeezing it out of the capillary (a,) the squeezed out drop resting on the substrate (b), and the measured contact angle (c)

For the tested moulding sand, the contact angle was within the required range. This means that the molten alloy should not penetrate into the pores of the moulding sand, and the components of the sand should not enter into reaction with the components of the casting alloy.

**Thermal analysis**

Figure 3 shows the cooling curves plotted from the temperature values recorded in moulds during the cooling of castings.

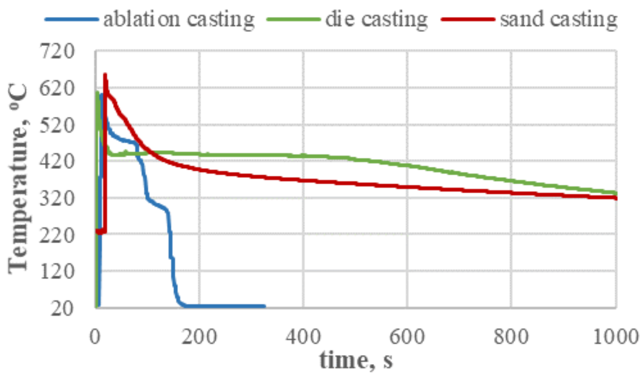


Fig. 3. Cooling curves recorded in moulds during melting

Ablation casting allowed for a significant reduction in the solidification and cooling time of castings. In less than 3 minutes from the moment of pouring the mould, the casting cooled down to room temperature, while half an hour after pouring, the temperature of both die and sand mould castings was still exceeding 200°C.

**Examinations of the casting microstructure**

Figures 4-6 shows the dispersion of the casting structure at 50x magnification. The secondary dendrite arm spacing is presented in Table 2.

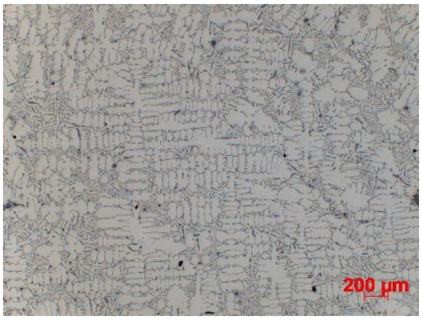


Fig. 4. The dispersion of dendritic structure in the central part of casting, 50x magnification: ablation mould

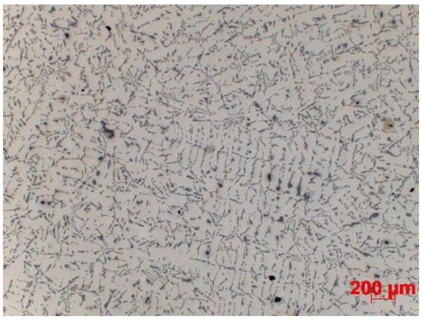


Fig. 5. The dispersion of dendritic structure in the central part of casting, 50x magnification: sand mould

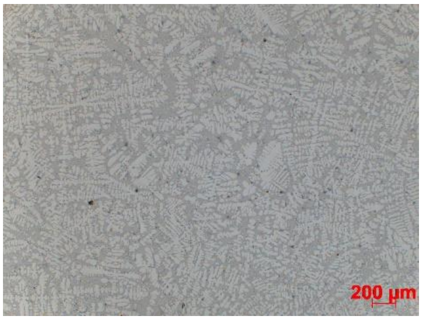


Fig. 6. The dispersion of dendritic structure in central part of casting, 50x magnification: metal mould

Table 3.
The secondary dendrite arm spacing, SDAS, mm (50x, etched, 10 oriented secants)

| **Mould** | **Part of casting** | | | |
|---|---|---|---|---|
| | **bottom** | **top** | **centre** | **Mean** |
| Ablation mould | 57.7 | 71.0 | 66.6 | 65.1 |
| Sand mould | 80.0 | 86.0 | 80.0 | 82.0 |
| Metal mould | 32.0 | 46.0 | 38.0 | 38.7 |

One can trace differences in the cooling speed-related pattern of dendritic structure dispersion occurring between samples of castings poured in different tested moulds and also between different zones in castings, except for the casting poured in a conventional sand mould (Fig. 7-9). The value of SDAS was reduced by more than 20% compared to the traditionally solidifying casting. The sand casting was characterized by an over 50% higher SDAS compared to the die casting, the difference is reduced to 34% after the use of ablative cooling.

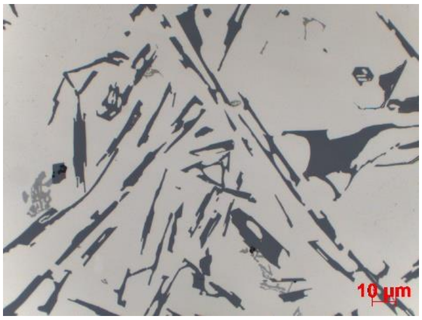


Fig. 7. The morphology of eutectic silicon in the central part of casting, 1000x magnification; ablation mould

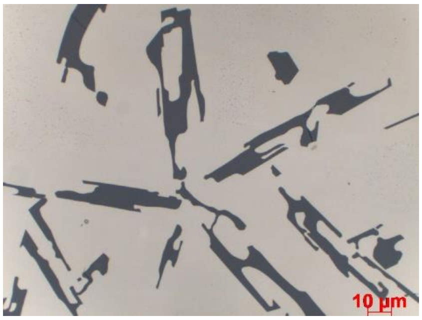


Fig. 8. The morphology of eutectic silicon in the central part of casting, 1000x magnification; sand mould

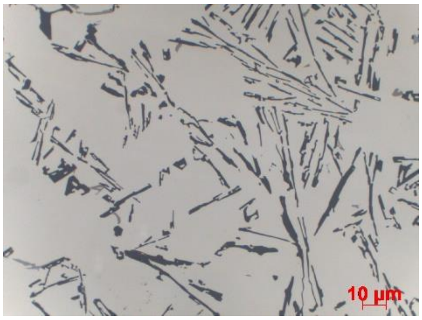


Fig. 9. The morphology of eutectic silicon in the central part of the casting, 1000x magnification; metal mould

The occurrence of different dispersion patterns of the eutectic Si precipitates was also noticed, but no changes in the morphology of individual precipitates related to the cooling rate were observed.

**Testing the strength properties of castings**

Table 3 compares the results of mechanical tests carried out on castings poured from a modified alloy in moulds made from the magnesium oxide-hardened sand mixture with Glifos binder and, for comparison, in metal moulds.

Table 4.
The results of strength testing

| Sample designation | $d_o$, mm | $S_0$, $mm^2$ | $L_0$ mm | $F_{p0,2}$ kN | $R_{p0,2}$ MPa | $F_m$ kN | $R_m$ MPa | $L_u$ mm | A % |
|---|---|---|---|---|---|---|---|---|---|
| Sand mould | 8.0 | 50.2 | 40.0 | 3.35 | 66.8 | 6.45 | 129 | 40.97 | 2.4 |
| Metal mould | 8.0 | 50.2 | 40.0 | 3.18 | 63.4 | 7.13 | 142 | 41.23 | 3.1 |
| Ablation mould | 8.0 | 50.2 | 40.0 | 3.20 | 63.7 | 7.86 | 156 | 40.67 | 2.7 |

Rapid ablative cooling enabled obtaining properties similar to or even higher than the properties of a die casting. The tensile strength of the casting made by the ablation technology was higher by about 20% and 9% compared to the common sand casting and die casting, respectively, while the elongation *A* was lower by about 13% compared to the die casting.

**Testing the moulding sand and wastewater**

Table 4 shows the results of measurements of the concentration of various pollutants in the wastewater compared with the results obtained for freshwater from the supply network used in the process.

Table 5.
Water test results

| Parameter | Pre-process sample | Post-process sample |
|---|---|---|
| | Concentration of pollutants (mg/l) | |
| $BOD_5$ | <3 | 4 |
| COD | 2 | 17 |
| Suspension | <4 | <4.0 |
| Total nitrogen | 1.60 | 1,5 |
| Total phosphorus | <0.05 | 180 |

The wastewater meets most of the requirements. The concentration of the majority of pollutants is far below the permissible level. The only exception is phosphorus, the content of which has been exceeded 180 times. Therefore it is not possible to safely discharge this water into a combined sewage system. An additional post-process water purification installation is required, which can significantly increase the cost of the technology when applied in an industrial plant.

Figures 10-12 shows the scan images of fresh sand, fragmented sand mould used for the process and sand mould after the ablation casting process.

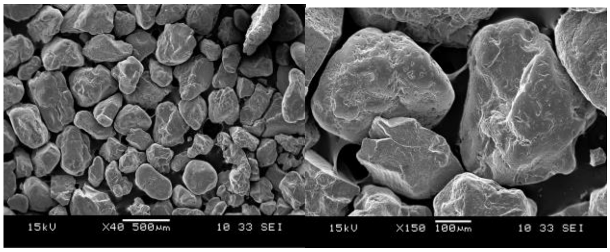


Fig. 10. Sand grains at 40x and 150x magnification: fresh sand

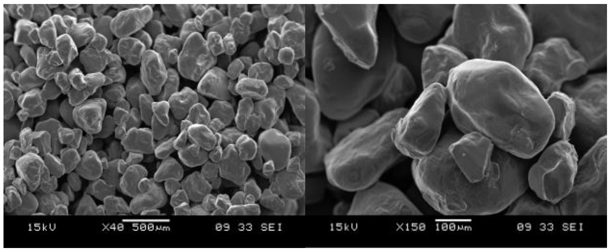


Fig. 11. Sand grains at 40x and 150x magnification: moulding sand for the process

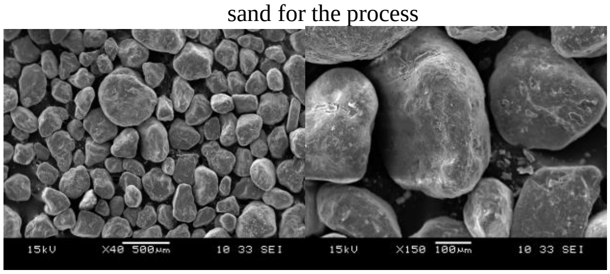


Fig. 12. Sand grains at 40x and 150x magnification: ablation post-process sand

Local EDS analysis of the chemical composition was performed at several points on each of the sand samples. This allowed for an assessment of whether the ablative washing process has removed binding materials from the sand grains. The spots where the analysis was performed are shown in Figures 13-15. Table 6 shows the results of the chemical composition analysis.

Table 6.
The results of chemical composition analysis

| Spot | C | O | F | Na | Mg | Al | Si | P | K | Ca | Cr | Fe | Zr | Ti | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fresh sand** | | | | | | | | | | | | | | | |
| 1 | | 54.0 | | | | | 46.0 | | | | | | | | 100.0 |
| 2 | | 56.9 | | | | 0.2 | 42.8 | | | | | | | | 100.0 |
| 3 | | 65.7 | | | | 2.6 | 23.0 | | 0.2 | 0.1 | | 6.2 | 0.9 | 1.3 | 100.0 |
| 4 | | 65.3 | | | | | 34.7 | | | | | | | | 100.0 |
| Max | | 65.7 | | | | 2.6 | 46.0 | | 0.2 | 0.1 | | 6.2 | 0.9 | 1.3 | |
| **Moulding sand** | | | | | | | | | | | | | | | |
| 1 | | 66.5 | | | 2.7 | 5.3 | 4.0 | 17.7 | 0.3 | | 2.8 | 0.6 | | | 100.0 |
| 2 | | 61.6 | | | 1.6 | 2.9 | 22.8 | 9.6 | 0.1 | | 0.8 | 0.5 | | | 100.0 |
| 3 | 5.2 | 62.9 | | | 3.1 | 5.4 | 1.7 | 19.6 | | | 1.9 | 0.3 | | | 100.0 |
| 4 | | 65.5 | | | 0.6 | 1.2 | 29.1 | 3.3 | | | 0.2 | | | | 100.0 |
| Max | 5.2 | 66.5 | | | 2.7 | 5.3 | 4.0 | 17.7 | 0.3 | | 2.8 | 0.6 | | | |
| **Moulding sand after the ablation casting process** | | | | | | | | | | | | | | | |
| 2 | | 62.0 | | | 0.3 | 7.4 | 17.1 | 9.7 | 0.3 | 0.4 | 2.0 | 0.9 | | | 100.0 |
| 3 | | 60.0 | | 6.7 | 0.3 | 8.4 | 23.3 | | 0.1 | 0.6 | 0.1 | 0.3 | | | 100.0 |
| 4 | | 64.1 | | | 0.5 | 9.1 | 13.3 | 8.6 | 0.8 | 0.4 | 1.6 | 1.7 | | | 100.0 |
| 5 | | 45.5 | 5.0 | | 0.4 | 3.1 | 44.1 | | 0.2 | 0.7 | 1.0 | | | | 100.0 |
| Max | | 64.1 | 5.0 | | 0.5 | 9.1 | 44.1 | 9.7 | 0.8 | 0.7 | 2.0 | 1.7 | | | |

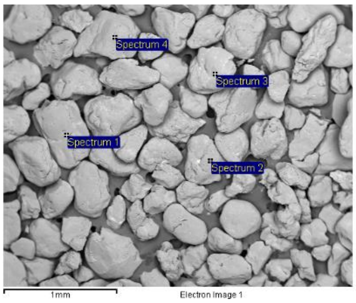


Fig. 13. Spots where the chemical composition was analyzed for fresh sand

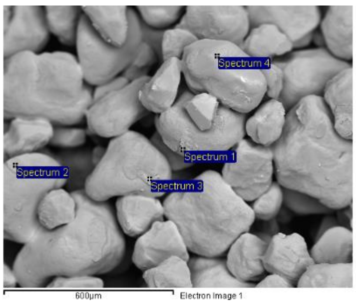


Fig. 14. Spots where the chemical composition was analyzed for tested moulding sand

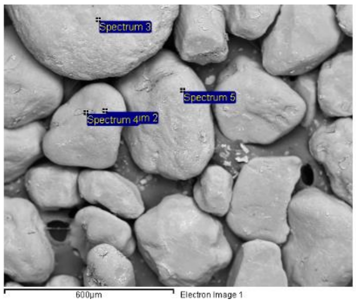


Fig. 15. Spots where the chemical composition was analyzed for moulding sand after the ablation process

The examination of moulding sand grains before and after the ablation process has suggested the full removal of binder from the sand grains. However, local analysis of the chemical composition combined with EDS has shown the presence of the residual chemical compounds left by the binder on the surface of the grains. The low carbon content results from the sample preparation used (carbon tape) and from the common phenomenon of contamination in SEM microscopes (contamination e.g. due to the presence of oil vapors from vacuum pumps)

## 4. Conclusions

The research has shown that foundry mould made from the magnesium oxide-hardened sand with phosphate binder was easily and quickly disintegrated by the ablation agent (11s), thus ensuring quick heat dissipation from the casting. This refined the casting microstructure (SDAS reduced by 20% compared to the casting made in a conventional sand mould), which directly resulted in higher strength properties of the casting. The tensile strength of the casting made by the ablation process was 9% higher than the tensile strength of the die casting.

Tests of the post-process water showed that safe discharge of this water into a combined sewage system was not possible, mainly because of the phosphorus concentration significantly exceeding the permissible level, i.e. 180 times.

Scanning of the sand used for the ablation casting process showed that most of the binder was removed from the sand grains during ablation. Unfortunately, the ablation process did not allow for the complete removal of binder, as further confirmed by the local analysis of chemical composition which revealed the presence of large amounts of phosphorus on the surface of the grains (even up to 10%).

Despite the very satisfactory strength properties of casting made by the ablation casting technology, the lack of the possibility to discharge the post-process wastewater into a combined sewage system makes the entire process much less cost-effective as it is necessary to either dispose or purify the wastewater.


## Acknowledgements

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