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**ANALYSIS OF THE EQUILIBRIUM STATE OF FLUX POWDERS IN THE MOULD DURING CONTINUOUS CASTING OF STEEL**

**ANALIZA STANU RÓWNOWAGI ZASYPEK W KRYSTALIZATORZE PODCZAS CIĄGŁEGO ODLEWANIA STALI**

Mould fluxes in the continuous casting of steel perform a protective function against oxidizing effect of the atmosphere on liquid metal, reduce friction between the solidifying steel shell and the walls of the mould and regulate the transfer of heat to the mould walls. Their chemical composition is crucial as it impacts the determination of the characteristic temperatures. The paper presents calculation results of the equilibrium composition of the selected mould powders in thermodynamic conditions similar to the actual conditions during continuous casting of steel slabs based on FactSage. The calculations were verified by high temperature tests of mould flux powders.

*Keywords:* mould flux, continuous casting of steel, FactSage

Zasyпки krystalizatorowe w procesie ciągłego odlewania stali pełnią funkcję ochronną ciekłego metalu przed działaniem utleniającym atmosfery, zmniejszają tarcie pomiędzy powstającym naskórkim, a ściankami krystalizatora oraz regulującą przenikanie ciepła do ścianek krystalizatora. Kluczowe znaczenie ma ich skład chemiczny, który wpływa na określenie charakterystycznych temperatur. W pracy zaprezentowano wyniki obliczeń składu równowagowego wybranych zasypek krystalizatorowych w warunkach termodynamicznych zbliżonych do rzeczywistych w procesie ciągłego odlewania wlewków przeznaczonych na wyroby płaskie w oparciu program FactSage. Obliczenia zweryfikowano wysokotemperaturowymi badaniami wybranych zasypek krystalizatorowych.

**1. Introduction**

The process of continuous casting of steel is the casting technology that is prevailing throughout the world. The mould is the key component of a continuous casting machine. A number of effects occur within the mould. The control of these effects allows obtaining cast strands without defects, with specific properties and at a cost effective rate. Steel casting and obtaining a cast strand in a solid state involves controlled heat removal by the water that cools the mould and water-air sprays in the secondary cooling zone. Fig. 1 presents a section through the mould and a strand segment under the mould, identifying all crucial zones essential for the heat removal process [1]. Thermal stresses which deform the forming shell disturb heat conduction to the mould walls. The quality of the basic parameters of the mould flux powder is decisive to the stability of heat removal. Under industrial casting conditions, the chemical composition of the mould flux powder changes due to the assimilation of non-metallic inclusions, the impact of liquid steel and reactions which occur during the steel melting. The following influence the cast strand quality:

- the dynamically changing shape of the liquid steel meniscus in the mould,
- the infiltration of the molten mould powder into the gap formed between the strand and the mould wall,

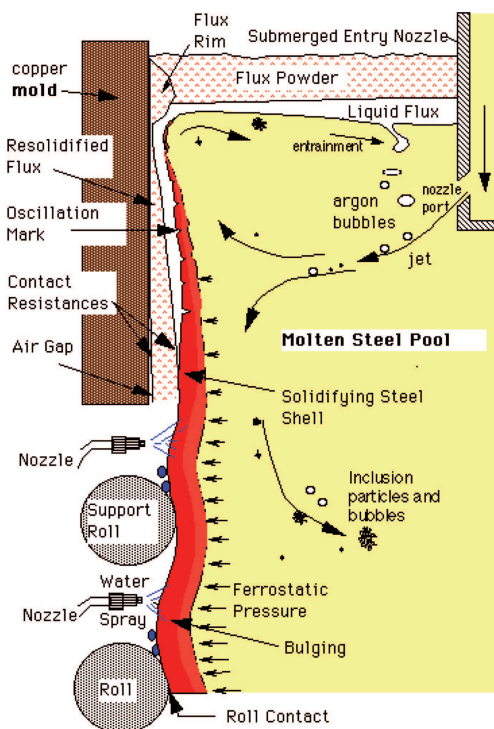


Fig. 1. A section through the mould and the strand segment under the mould [1]

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- steel overheating degree,
- the process of heat conduction through the strand, the liquid and solid mould flux layer and through the formed gap and mould walls.

The study includes an analysis of the equilibrium state of the selected mould flux powders in thermodynamic conditions similar to the actual conditions in the process of continuous casting of strands for flat products. The equilibrium state of mould powders was computed based on the FactSage program. The calculations were verified by tests in a high-temperature microscope by determining characteristic temperatures.

## 2. Significance of mould flux powders in the continuous steel casting process

The mould flux powders are commonly used in the process of continuous casting of steel. They are dispensed onto the surface of liquid steel in the mould and supplemented during the casting process. The following are the most important functions of mould flux powders [2]:

- protection of the liquid steel against oxidation,
- assimilation of non-metallic inclusions,
- protection against heat loss,
- reduction of friction between the formed shell and the mould walls,
- homogeneous and effective heat conduction between the solidifying metal and the inner surface of the mould walls.

The mould flux layer applied on the liquid steel surface in the mould protects the steel against the oxidising effect of the atmosphere. Its high basicity increases its capability to assimilate non-metallic inclusions. The molten flux flows down between the solidifying shell and the mould walls, thus reducing the friction coefficient. The optimal lubrication enables the strand to be pulled out from the mould, thus reducing the hazard of breakout. This effect is additionally enhanced by the oscillating movement of the mould necessary for the correct course of casting. As a result of solidification the metal shrinks and an air gap forms between the shell and the mould walls. After melting, the mould flux fills this gap, thus providing increased and uniform heat removal by the mould walls. The occurrence of the air gap is also compensated by application of a mould with a specific taper. Therefore it is possible to use higher casting speeds, and the occurrence of thermal stresses resulting from the increased temperature gradient on the shell surface is minimised. In order to effectively penetrate the gap the mould flux should have a low viscosity. The following influence the properties of mould flux powders:

- chemical composition,
- mineralogical composition,
- grain size composition,
- manufacturing process,
- drying or roasting method,
- free carbon content.

After being applied onto the liquid steel, the mould powder is subjected to the impact of high temperature. Within a short time chemical reactions and effects occur, which result in the occurrence of diversified layers in terms of phase com-

position and chemistry on the vertical section of the applied mould powder. Fig. 2 presents a model of the structure of a multi-zone mould flux layer on the surface of liquid steel in the mould. The mould flux is typically applied as a powder. The moisture content should not exceed 0.8%, and it is released at a temperature of about 300°C. The applied layer should melt before it has reached the contact surface with the liquid steel. Therefore the liquidus temperature of the mould flux should be lower than the liquidus temperature of the steel cast. The melting temperature of the mould flux depends on its chemical composition, while its meltdown coefficient depends on the content of components that accelerate the melting process. These are mainly sodium, potassium and fluorine carriers. The thickness of the sintered and semi-solid layer depends on the kind and amount of free carbon. Mould fluxes with a higher carbon content, in particular characterised by a combustion temperature under 600°C are distinguished by the occurrence of a visible zone of the sintered and semi-solid layer of the mould flux. However, if mould flux powders with a reduced carbon content are used, characterised by a combustion temperature of about 800°C, the mould flux layer in the sintered and semi-solid state simply does not occur. After reaching the ignition temperature, carbon in the form of graphite burns immediately, thus enhancing the supply of thermal energy to the environment, and, consequently, the mould powder melts immediately [3]. Oxides of most of mould flux components exist in the form of carbonates. Depending on the component type, component decomposition is an endothermic reaction and occurs at various temperatures [4]. These temperatures are between 650 ÷ 900°C. Chemical compositions and melting temperatures of mould fluxes used in Poland are presented in Table 1.

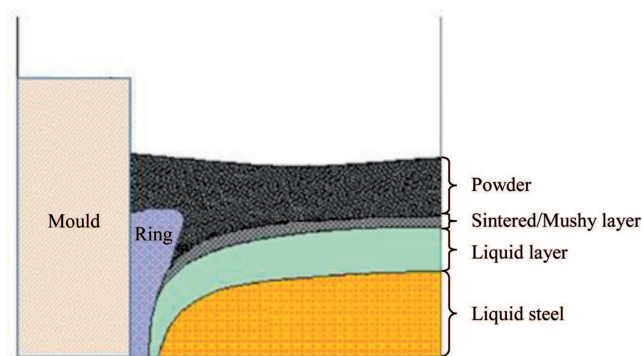


Fig. 2. A model of the structure of a multi-zone mould flux layer on the surface of liquid steel in a continuous casting mould

Samples of mould powders of grades Accutherm ST-SP/222-DS, Scorialit SL470/Si, and Alsiflux GS-MG/22B were taken for tests. Based on the chemical composition of the powders tested, thermodynamic calculations were performed in order to determine the influence of temperature on the formation of the mould flux liquid phase. Also the effect of some mould flux powder components on a change in the melting temperature was checked. The mould flux powders analysed are commonly used for casting low-carbon and peritectic steels.

TABLE 1

## Mould flux powders used in Poland

| Grade                  | Chemical composition [%] |      |                  |                                |                                |   |                  |                  |                    |                 |                    | Melting point °C |
|------------------------|--------------------------|------|------------------|--------------------------------|--------------------------------|---|------------------|------------------|--------------------|-----------------|--------------------|------------------|
|                        | CaO                      | MgO  | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O                       | K <sub>2</sub> O | CaF <sub>2</sub> | C <sub>wolny</sub> | CO <sub>2</sub> | C <sub>total</sub> |                  |
| Accutherm ST-SP/222-DS | 29.1                     | 2.6  | 34.2             | 5.7                            | 1.5                            | 7.9                                     | 0.9              | 6.9              | 4.3                | 7.2             | -                  | 1085             |
| Alsiflux GS-C7.3       | 27.0                     | 3.9  | 34.4             | 4.7                            | 1.6                            | Na <sub>2</sub> O/K <sub>2</sub> O 11.8 |                  | 9.0              | 3.6                | 7.7             | 5.7                | 1050             |
| Alsiflux GS-MC22       | 36.5                     | 2.75 | 27.5             | 4.5                            | 1.5                            | -                                       | -                | 8.0              | 3.25               | 7.5             | 5.25               | 1120             |
| Alsiflux PS-C7.2       | 27.0                     | 4.5  | 30.5             | 5.0                            | 1.75                           | -                                       | -                | 9.5              | 3.5                | 10.0            | 6.25               | 1020             |
| Alsiflux PSS-LC2.2     | 37.0                     | 1.5  | 32.0             | 5.75                           | 1.5                            | -                                       | -                | 9.25             | 4.0                | 4.5             | 5.25               | 1150             |
| Scorialit SL470/M      | 27.0                     | -    | 32.5             | 45                             | 1.0                            | 6.5                                     | 6.0              | 8.0              | 3.0                | 9.0             | 5.5                | 1090             |
| Scorialit SL470/Si     | 27.0                     | -    | 32.0             | 4.5                            | 0.5                            | 3.5                                     | 3.5              | 7.5              | 7.5                | 6.5             | 9.0                | 1020             |
| Scorialit SL679/T1     | 32.0                     | -    | 38.0             | 3.0                            | 0.5                            | 2.75                                    | 2.75             | 8.0              | 1.5                | 3.5             | 2.5                | 1230             |
| Syntherm GS/1220/P     | 37.5                     | -    | 30.9             | 5.9                            | 1.2                            | 6.2                                     | 0.7              | 10.5             | 3.8                | 5.0             | 5.2                | 1150             |
| Alsiflux GS-MG22B      | 37.0                     | 1.8  | 31.5             | 5.5                            | 1.8                            | Na <sub>2</sub> O/K <sub>2</sub> O 6.5  |                  | 10.0             | 4.5                | 5.5             | 5.8                | 1150             |

### 3. Calculations of the thermodynamic equilibrium state

The chemical composition, according to Table 1, was assumed in calculations to determine the equilibrium state of the material tested under specific thermodynamic conditions. The equilibrium state of mould fluxes was computed in the FactSage program. Fig. 3 presents the effect of temperature on the formation of the liquid phase of mould fluxes in the thermodynamic equilibrium conditions at a pressure of 1 atm. Fig. 4 and 5 presents the effect of some components in the mould powder Accutherm ST-SP/222DS on the formation of the liquid phase in the thermodynamic equilibrium conditions at a pressure of 1 atm and at a temperature of 1150°C.

In ideal conditions during heating, the mould flux liquid phase already starts occurring at temperatures between 600÷700°C. Before complete melting, depending on the type of mould flux powder, the share of the liquid phase at a specified temperature varies. The melt down dynamics also varies. The GS-MG22B mould powder is characterised by the highest temperature at which the liquid phase share increases, as compared to the other powders. The chemical composition influences the melting temperature. An increase in the SiO<sub>2</sub> content in the range of 20 ÷40% increases the melting temperature. An increase in the CaO and Al<sub>2</sub>O<sub>3</sub> content increases the melting temperature, however, above a certain level it causes a reduction of the melting temperature. CaF<sub>2</sub> has the opposite effect. Between 1÷2.5% CaF<sub>2</sub> reduces the melting temperature, while above 2.5% it increases the melting temperature. Despite their negative effect, fluorine compounds are fairly often used in industrial practice because they reduce viscosity, and thus improve the liquidity of the fluxes applied.

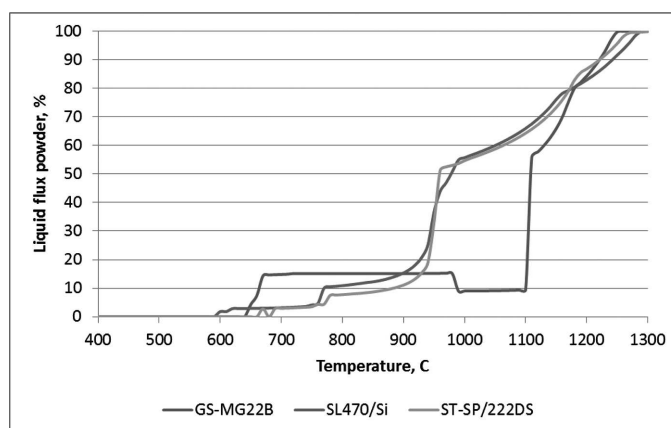


Fig. 3. The effect of temperature on the formation of the liquid phase of mould fluxes in thermodynamic equilibrium conditions at a pressure of 1 atm

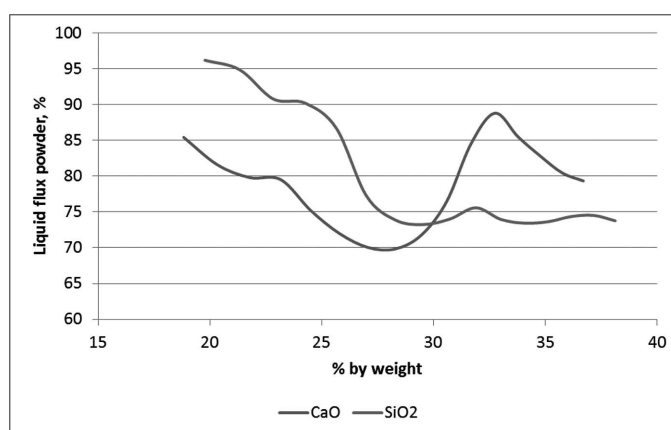


Fig. 4. Effect of CaO and SiO<sub>2</sub> in the mould powder Accutherm ST-SP/222DS on the formation of the liquid phase in thermodynamic equilibrium conditions at a pressure of 1 atm and at a temperature of 1150°C

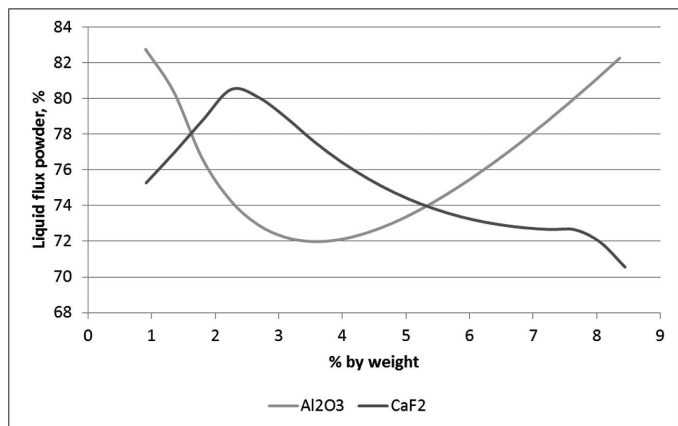


Fig. 5. Effect of CaO and SiO<sub>2</sub> in the mould powder Accutherm ST-SP/222DS on the formation of the liquid phase in thermodynamic equilibrium conditions at a pressure of 1 atm and at a temperature of 1150°C

#### 4. Examination in a high-temperature microscope

In order to verify thermodynamic calculations, the mould fluxes were examined in a high-temperature microscope. Based on these examinations the characteristic temperatures were determined and compared to the manufacturer’s data sheet. The mould powders were homogenised in terms of

chemical composition and the samples were prepared in accordance with the requirements and methodology of testing in a high-temperature microscope [5, 6].

The samples of mould flux powders were pressed into cylindrical pastilles with a laboratory press. The cylinder diameter and height was 3 mm. After drying the sample was placed in a ceramic furnace tube directly on a 96% Al<sub>2</sub>O<sub>3</sub> pad on a thermocouple. The furnace was heated with a constant temperature increment of 20°C/min while blowing the sample atmosphere through with technical air. The test enabled the sample temperature and profile changes to be recorded with a digital camera fitted with a set of diaphragms and optical filters. During heating of the samples in the furnace, distinct changes to their shapes and dimensions were observed. The recorded temperature values determined:

- the sintering temperature, at which the sample shrank while maintaining sharp edges;
- the deformation temperature, at which the profile was clearly rounded, indicating the beginning of melting. This effect is often related to the occurrence of significant quantities of the liquid phase in the sample;
- the sphere temperature, at which the sample tested took on a spherical shape;
- the hemisphere temperature, at which the sample tested took on a hemispherical shape;
- the flow temperature, at which the sample spilt (flew).

TABLE 2

The characteristic temperatures of mould flux powders used for casting of steel for flat products

| Grade                 | Sintering temperature | Deformation temperature | Sphere temperature | Hemisphere temperature | Flow temperature |
|-----------------------|-----------------------|-------------------------|--------------------|------------------------|------------------|
|                       | [°C]                  |                         |                    |                        |                  |
| Alsiflux GS-MG22B     | 932                   | 1090                    | -                  | 1143                   | 1219             |
| Accutherm ST-SP/222DS | 920                   | 1011                    | 1075               | 1094                   | 1134             |
| Scorialit SL470/Si    | 781                   | 950                     | 974                | 1005                   | 1037             |

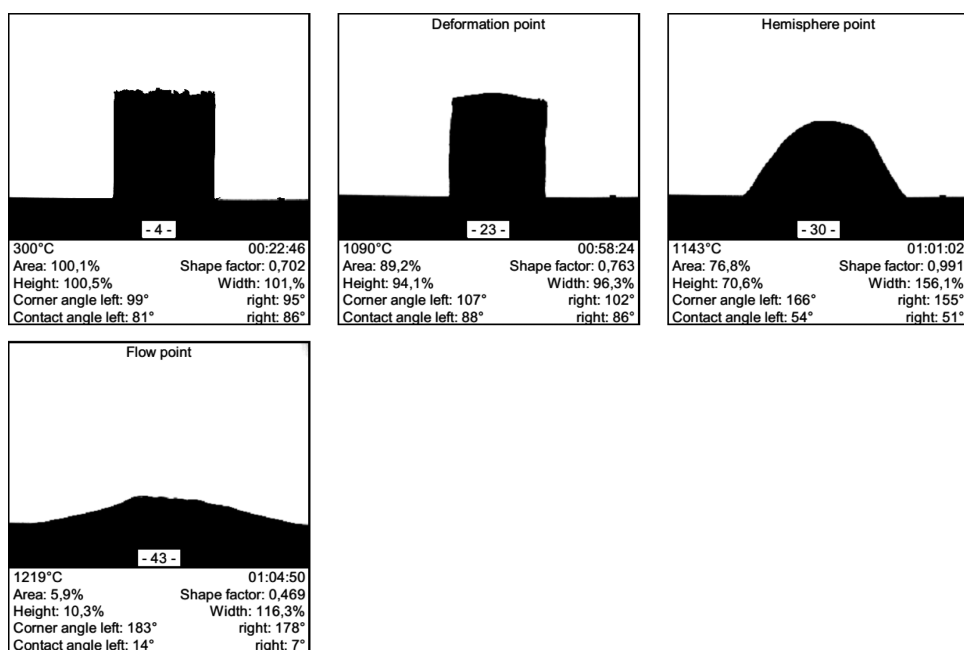


Fig. 6. Photographs of the Alsiflux GS-MG22B mould powder sample at the determined characteristic temperature

This knowledge regarding characteristic temperatures for the mould fluxes is especially useful for determining the behaviour of components of mineralogically complex mould fluxes in the continuous casting process. Table 2 presents the characteristic temperatures of mould flux powders used for the casting of steel for flat products determined on the basis of high-temperature microscope tests. Components with the highest and the lowest melting temperatures influence the defor-

mation, sphere and flow temperatures. The mould flux powder GS-MG2B features the highest temperatures. The mould flux powder SL470/Si features the lowest temperatures. Fig. 6-8 present pictures of samples of the tested mould flux powders at the specific characteristic temperature, whereas Fig. 9-11 show changes in the sample shapes and dimensions during heating.

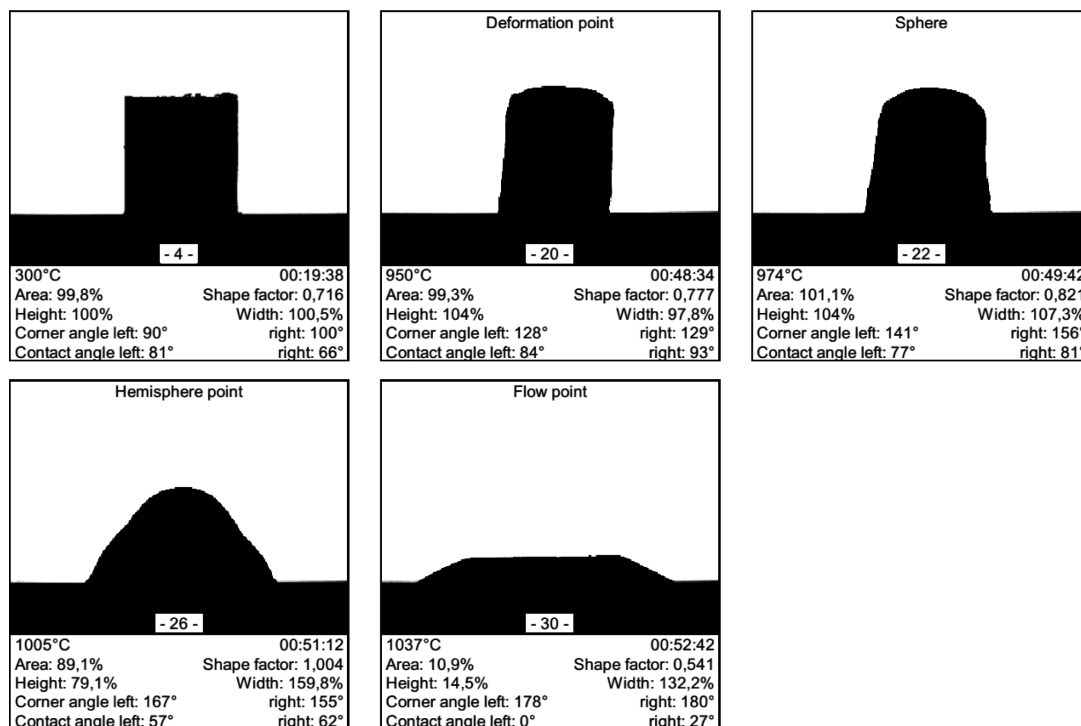


Fig. 7. Photographs of the Scorialit SL470/Si mould powder sample at the determined characteristic temperature

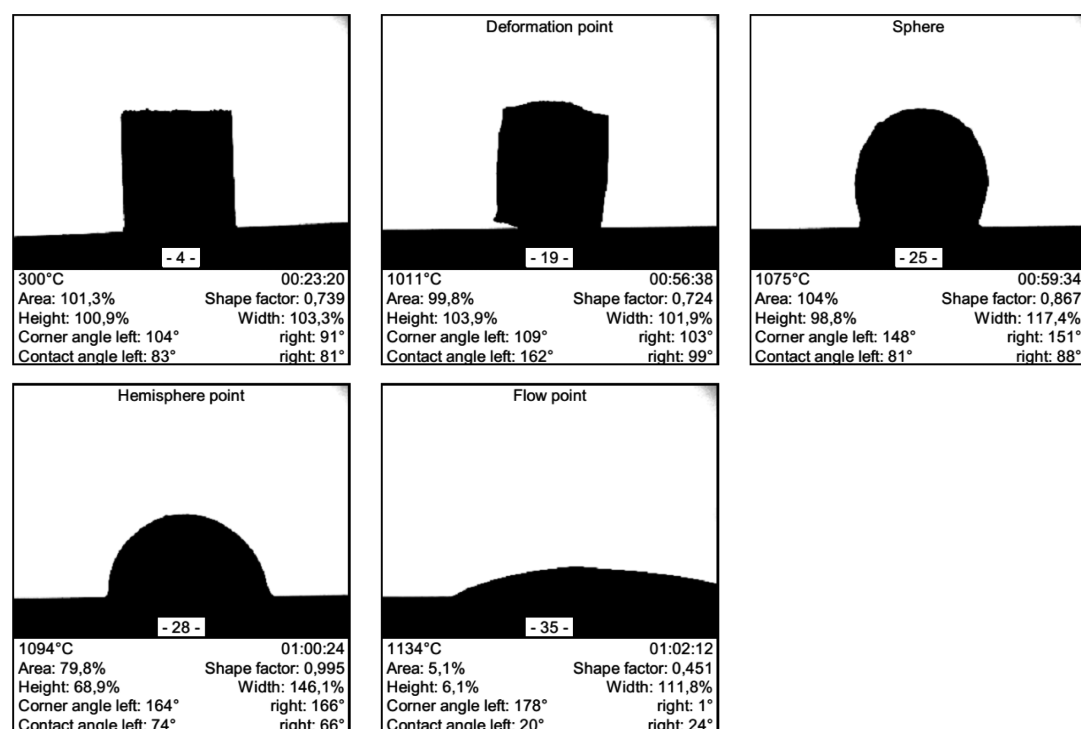


Fig. 8. Photographs of the Scorialit SL470/Si mould powder sample at the determined characteristic temperature

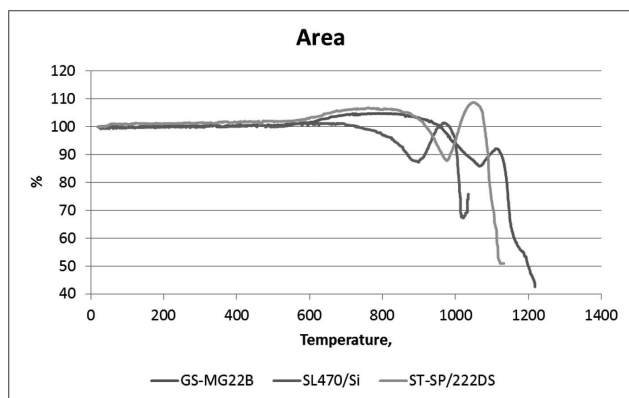


Fig. 9. The change in the surface area of the end view of mould flux powder samples during heating

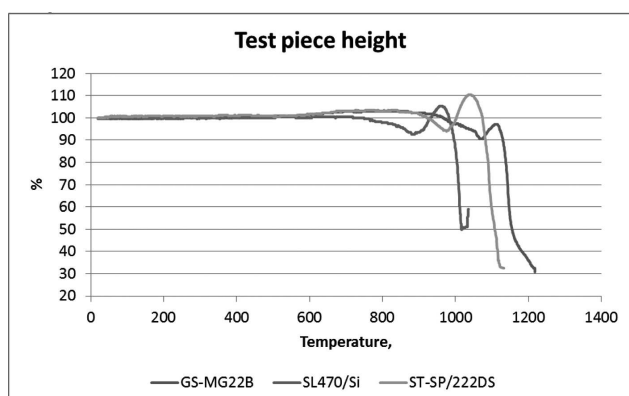


Fig. 10. The change in the height of mould flux powder samples during heating

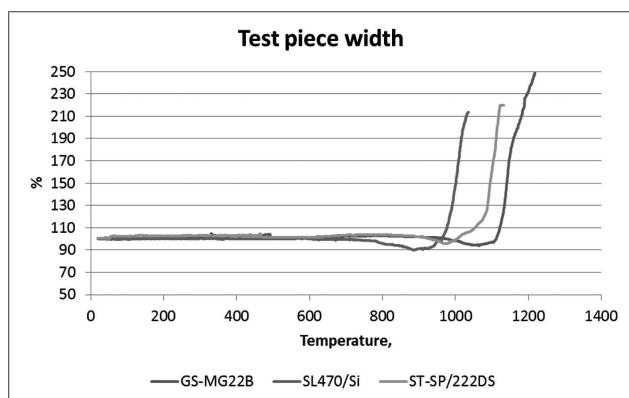


Fig. 11. The change in the width of the mould flux powder samples during heating

## 5. Conclusion

The mould flux powder requirements vary depending on the grade of the steel cast. For casting of peritectic steels, a low heat transfer coefficient should be ensured. In practice, slow cooling is possible thanks to mould flux powders that are rich in the crystalline phase at the vertical section of the layers. Such mould fluxes are characterised by a high  $\text{CaO/SiO}_2$  ratio and a low viscosity. The high meltdown coefficient of a mould flux powder is achieved by the addition of high-temperature

carbon in graphite form and an appropriate mineralogical selection of the mould powder components. Therefore the mould flux powder features a short meltdown time, the occurrence of reactions in the mould flux layer in a solid state is minimised, and the sintered layer and the semi-solid layer virtually do not exist. The application of mould flux powders for casting of peritectic steels does not pose any problems in industrial practice.

A low-carbon steel may be cooled faster during casting. In order to ensure a high heat transfer coefficient, the mould powder should feature vitreous phases at the vertical section of the layers – that is a low  $\text{CaO/SiO}_2$  ratio. Consequently, the mould flux viscosity increases which does not favour filling the air gaps by the liquid flux. At the vertical section the mould flux features the solid, sintered, semi-solid and liquid phases. The use of an increased carbon content restricts the heat transfer in a vertical direction. As a result, the flux is characterised by a low meltdown coefficient. The high viscosity caused by the low  $\text{CaO/SiO}_2$  ratio is unfavourable and is prevented by the application of an increased amount of fluorine, which improves the liquidity of the flux. Due to the harmful effect of fluorine compounds on the environment, attempts to use alternative compounds that can increase the flux liquidity are made. An increase in the  $\text{SiO}_2$  content in the mould flux powder increases the melting temperature. An increase in the  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  content first causes an increase, and subsequently a decrease in the melting temperature. An increase in the  $\text{CaF}_2$  content decreases the melting temperature, however above a certain level it increases it.

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