

INVESTIGATION OF THE MELTING BEHAVIOUR OF MOULD POWDERS

Nathalie Kölbl, Irmtraud Marschall & Harald Harmuth
University of Leoben, Austria

ABSTRACT

The melting behaviour of mould powders has a major impact on the stability of casting conditions and the quality of strand surface. Therefore the melting behaviour of six commercial mould powders having a CaO/SiO₂ ratio in the range of 0.61-1.34 and a carbon content between 5.2 and 15.2 wt% was investigated mineralogically using several methods. All methods applied yielded supplementary details. Therefore only the combination of the results of each method offers a global characterisation of the reaction mechanisms during heating. Based on the results taken from the DTA the specimens were annealed and quenched at selected temperature levels and afterwards investigated mineralogically using X-ray diffraction, reflected light and scanning electron microscopy including electron probe microanalysis. For the in situ observation of the melting behaviour a hot stage microscope was applied. Even though the mineralogical composition of the six mould powders as received differs there are still similarities. The main components of the mould powders as received are wollastonite, fluorite, carbon, carbonates, silicates, synthetic glasses like fly ash, blast furnace slag and/or glass scraps. Because these minerals are not in chemical equilibrium reactions take place during heating. These may be the decompositions of several phases and the formation of cuspidine by solid-solid reactions of wollastonite and fluorite or by participation of a liquid phase and the formation of intermediate phases like nepheline, rankinite, diopside and alkali-silicates in dependence on the mineralogical composition. Further rise of temperature leads to the formation of a homogeneous liquid phase. The liquidus temperature varies between 1040°C and 1270°C.

INTRODUCTION

In the continuous casting process mould powders are added to the top of the steel meniscus in the mould where they have to fulfil requirements concerning casting condition stability and strand surface quality [1]. To meet these requirements the mould powder ought to have a suitable melting behaviour which depends on the casting conditions and the steel grade. Therefore several investigations have been carried out to describe this feature using the differential thermal analysis (DTA) [2, 3, 4] and other phenomenological methods [5, 6, 7, 8]. Because their results do not give information about the mineralogical composition in dependence on the temperature also investigations on annealed and quenched samples using x-ray diffraction (XRD) have been carried out [2, 9, 10, 11, 12]. This enabled the detection of both the raw materials and the minerals which were formed after the heat treatment. Natural silicates and silica SiO_2 , synthetic silicates, calcite CaCO_3 , magnesite MgCO_3 , sodium carbonate Na_2CO_3 , potash K_2CO_3 , fluorite CaF_2 , cryolite Na_3AlF_6 , borates and different kinds of carbon which may be graphite, carbon black and/or coke breeze are used as the main raw materials [13]. The formation of cuspidine $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$, wollastonite CaSiO_3 , anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$, gehlenite $\text{Ca}_2\text{Al}_2\text{SiO}_7$, carnegieite NaAlSiO_4 , pectolite $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$, combeite $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$, akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and villiaumite NaF , the combustion of carbon during heating and its effect on the melting rate have already been reported [2, 9, 10, 11, 12]. Even though the XRD was enhanced by the integration of a heating chamber which enables measurements on one specimen every 50°C during heating [14] no direct observation of the sample is possible and therefore very little is known about the reactions taking place with increasing temperature. For this reason the aim of the present work is the application of further investigation methods based on the identification of the mineralogical composition to characterise the melting behaviour of mould powders by identifying the reactions taking place during heating.

METHODOLOGY

Samples

For the characterisation of the melting behaviour of mould powders six commercial mould powders have been investigated. Half of them are powders (MP 3-5) and the others are granules (MP 1-2 and MP 6). Their CaO/SiO_2 ratio is in the range of 0.61-1.34 and their carbon content lies between 5.21 and 15.2 wt%. The detailed chemical compositions of the investigated mould powders are given in the table below. All figures are without loss of ignition.

Table 1: Chemical composition of the investigated mould powders in wt%

	MP 1	MP 2	MP 3	MP 4	MP 5	MP 6
F	6.24	4.26	5.06	4.79	5.56	8.01
SiO_2	33.24	35.53	39.19	36.09	39.18	31.17
Al_2O_3	5.13	6.17	6.12	15.11	2.02	3.00
CaO	36.45	25.98	23.75	29.13	37.83	41.91
MgO	1.42	3.35	2.33	4.33	4.20	1.37
Na_2O	5.77	7.18	4.86	3.83	6.69	7.67
K_2O	0.16	0.19	0.08	0.09	0.12	0.14
MnO	0.98	<0.01	0.61	<0.01	<0.01	0.06
Fe_2O_3	2.09	1.51	1.95	0.88	0.78	0.41
TiO_2	0.22	0.31	0.09	0.35	0.09	0.03

SO ₃	0.15	0.92	0.40	0.15	0.08	0.45
BaO	0.27	0.07	0.18	0.03	0.11	0.03
B ₂ O ₃	0.03	0.03	0.08	0.01	<0.01	<0.01
P ₂ O ₅	<0.01	<0.01	<0.01	<0.01	0.77	0.93
ZrO ₂	<0.01	<0.01	<0.01	<0.01	0.33	<0.01
C	7.79	14.50	15.20	5.21	2.24	4.71
total	100.00	100.00	100.00	100.00	100.00	100.00
CaO/SiO ₂	1.1	0.73	0.61	0.81	0.97	1.34

Investigation of Annealed Samples

For the first characterisation of the mould powders as received a DTA including thermogravimetry (TG) was carried out. The heating rate for these investigations was 5°C/min up to 1400°C. Based on these results the samples were annealed at selected temperature levels using a laboratory kiln. Therefore also a heating rate of 5°C/min was used. After a dwell time of 30 min at the relevant temperatures the samples were quenched to room temperature by dipping them into water.

To get a general idea about the mineralogical composition of the mould powders as received and after annealing the specimens were investigated using XRD. Afterwards polished samples were prepared to detect the phases in more detail using reflected light and scanning electron microscopy including electron probe microanalysis.

In-situ Observation of the Melting Behaviour

For the in-situ observation of the melting behaviour of mould powders the hot stage microscope shown in Figure 1 was implemented. It consists of the following devices: A commercial available reflected light microscope with a gimbal-mounted table in order to align the specimen surface perpendicular to the incident light has been applied. On the table a gas tight heating chamber which houses a 60 watt electrically heated corundum furnace is situated. The platinum crucible and the sample can be inserted from the top. To reduce the thermal radiation a corundum aperture partially shields the quartz window which enables observation of the specimen. The heating chamber is water cooled in order to protect the objectives and can be flushed with gas to select the dedicated atmosphere for the measurement. Special precautions were necessary in order to enable the in-situ observation until the complete melting of the sample [15]. Two thermocouples are applied, one for the furnace and an additional one for the actual specimen temperature.

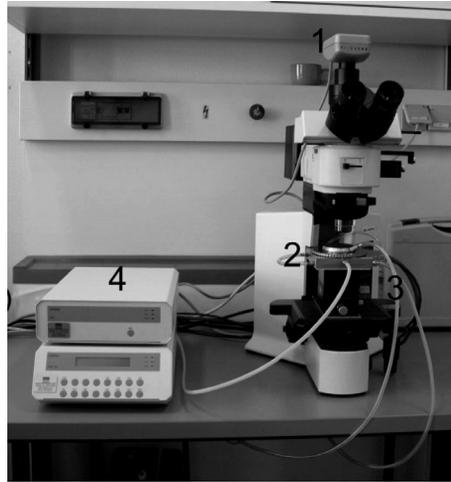


Figure 1: Hot stage microscope 1: CCD camera, 2: water-cooled heating stage, 3: gimballed table, 4: control unit

Uncompacted specimens showed not to be suitable. Therefore the mould powder was pressed to pills with a height of about 1 mm to get a planar surface. Afterwards a sample suitable for the size of the platinum crucible was cut out. In addition the investigations were also carried out on polished specimens. This enables the accurate observation of phase transformations. The specimen was heated with a rate of 10°C/min until complete liquefaction.

RESULTS AND DISCUSSION

Mineralogical Composition of the Original Mould Powders

Even though the investigated mould powders differ in their chemical and mineralogical composition there are still similarities: Among the main components are wollastonite CaSiO_3 , fluorite CaF_2 , in two cases a slag showing crystals of cuspidine $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$ and wollastonite in a glassy matrix and in one case albite $\text{NaAlSi}_3\text{O}_8$. In lower amounts calcite CaCO_3 , quartz SiO_2 , corundum Al_2O_3 , periclase MgO , carbon and synthetic glasses like fly ash, blast furnace slag and/or glass scraps are present. In MP 3 and MP 5 cryolite Na_3AlF_6 is used as flux material besides fluorite. All powders investigated are also composed of alkali-silicates and alkali-carbonates in different minor proportions. MP 6 is the only one showing low amounts of barite BaSO_4 . Hematite Fe_2O_3 and diopside $\text{CaMgSi}_2\text{O}_6$ were detected sporadically in MP 1 and MP 2.

Dissociation of the Carbonates

In MP 3, MP 5 and MP 6 lower amounts of sodium bicarbonate (NaHCO_3) are present. Based on the results of the DTA including TG its dissociation starts at approximately 80°C. In the case of MP 2 instead of sodium bicarbonate sodium calcium carbonates related to shortite $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ and nyerereite $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ can be detected. Most likely these minerals are formed during the production process: Sodium bicarbonate dissolves in the water slurry and reacts with calcium out of the slags and maybe wollastonite.

During heating the dissociation of these minerals takes place at around 600°C according to the DTA and mineralogical investigations.

The dissociation of further alkali carbonates cannot be detected using the DTA, because the exothermic effect of the combustion of carbon interferes with the endothermic effect of the dissociations. It can only be observed by the investigation of the stepwise annealed specimens. In the case of MP 1 the dissociation of calcite can be detected at 500°C according to observations of Schwerdtfeger, *et al.* [12]. Because this low temperature was not expected thermochemical calculations were carried out which showed that in the case of the presence of silicates and carbon a lowering of the dissociation temperature takes place.

Combustion of Carbon

Considering the aforementioned investigation methods the most suitable one for the observation of the combustion of carbon is the hot stage microscopy. Carbon has a yellow and metallic appearance in the dark light microscopy and in the reflected light microscopy (Figure 2). Therefore it can easily be distinguished from other phases.

Each of the investigated mould powders consists of various carbon carriers. These can be for example graphite or petroleum coke. In dependence on the kind of carbon in the mould powder the combustion of the carbon particles takes place at different temperatures. Using the hot stage microscopy the combustion of the carbon particles can be observed by the decrease due to the oxidation process starting at the polished surface and the margin (Figure 2). Pores are left after the complete decarburisation, and the associated specimen temperature may be registered. Considering the six mould powders the combustion takes place in the temperature range between 420-830°C based on the results of the hot stage microscopy. Contrary to this using the DTA this effect can only be detected up to 710°C. This is due to the fact that at higher temperatures the carbon content is very small and its combustion results in no distinguishable effect any more. Therefore it can only be observed by microscopically means.

Stability of the Original Glasses, Halogenides, Oxides and Silicates

The first minerals which change their composition are the synthetic glasses. In most cases they absorb alkalis, particularly sodium resulting from the dissociation of carbonates and cryolith, in the temperature range between 500-750°C. In the case of MP 5 also the barium diffuses into the slags. The absorption of the alkalis causes a lowering of the melting point of these phases. The following ascending order concerning the melting point can be given: glass scraps and the slag containing also wollastonite and cuspidine form the first melting phases, then blast furnace slag and at last fly ash which can be detected up to 900°C in the case of MP 2.

In the temperature range of 600-750°C quartz is also observed to take part in formation of a silicate melt with considerable amounts of calcium and sodium.

Periclase is observed up to 750°C. At approximately this temperature it reacts with other raw materials to form a *feldspatoid* and *fluorrichterite* (see section *intermediate phases*). If albite is used as raw material for the mould powders it can be detected up to 880°C based on the results taken from the mineralogical investigations of the stepwise annealed samples. Fluorite is stable up to 900°C. In the case of MP 1 showing the highest wollastonite content fluorite is even present at 1000°C. Corundum is observed up to 900-1050°C depending on its original content and the original mould powder composition.

Intermediate Phases

The most important intermediate phase which is formed during the heating of fluoride containing mould powders is cuspidine. There are two different mechanisms: In the first case the formation of cuspidine is already observable at around 600°C. It is formed by solid-solid reactions between wollastonite, slag, fluorite, albite and alkali carbonates. Then cuspidine is situated either at the boundaries of the wollastonite, the slags or the albite and in lower amounts at the boundaries of the fluorite. Its crystal size is very small and according to the XRD results its crystal structure is imperfect because of the integration of foreign ions like sodium and/or aluminium. When the sample is heated to higher temperatures (900-1200°C) where a liquid phase is already present the cuspidine is formed by the reactions of the residuals of fluorite, cryolithe, calcium silicates, sodium aluminium silicates and the liquid. In this case it shows a larger crystal size and is purer than when it is formed at lower temperatures. Microanalyses show that Na₂O, MgO and Al₂O₃ remain dissolved in the liquid phase which is in a glassy state after the quenching to room temperature.

Using hot stage microscopy the formation of cuspidine can be investigated in situ. In the case of polished samples the reactions can be observed at first by the change of the boundaries of the minerals, especially of fluorite. With increasing temperature the reaction zone heads towards the centre until it is also completely transformed. At the same time an obvious brightening of the minerals take place which is related to the formation of cuspidine. This process can be seen in Figure 2 where at 580°C the fluorite is still present in the centre but at the boundary the formation of cuspidine already took place.

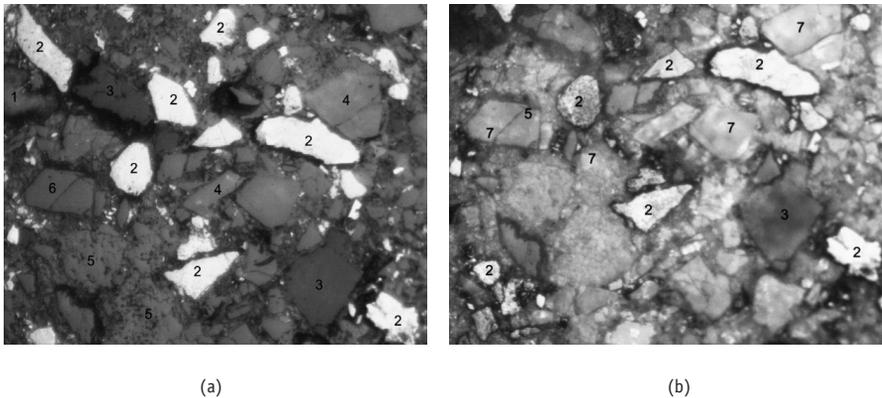


Figure 2: Formation of cuspidine and beginning of the combustion of carbon in a polished sample of MP 3 at (a) room temperature and (b) 580°C. 1: residual soda, 2: carbon, 3: fluorite, 4: glassy phase, 5: albite, 6: calcite, 7: cuspidine

In most cases the cuspidine generated via solid-solid reactions is accompanied by the formation of rankinite Ca₃Si₂O₇. It also occurs in the circumference of fluorite and can be detected in the samples annealed between 600-900°C.

During heating also several different sodium calcium silicates are formed in dependence on the mineral composition of the mould powder. In MP 3 combeite Na₂Ca₂Si₃O₉ and other non-stoichiometric sodium calcium silicates are detected at 670°C. These minerals result from the reactions of sodium and calcium containing components with the glass scraps and quartz. In the case of MP 1 and MP 2 having the highest natural wollastonite content a reaction zone of combeite is formed around the wollastonite particles separating them from the cuspidine. This can first be observed in samples annealed at 700°C (MP 1) and 750°C (MP 2) respectively where the size of cuspidine is quite small. With

rising temperature the wollastonite is only stable in the centre and both the content of combeite and cuspidine increase clearly. Wollastonite can be observed up to 900°C in the case of MP 2. Because MP 1 shows a higher wollastonite content it can be detected up to 1000°C. In MP 5 and MP 6 sodium calcium silicates are formed, too. Here fluorine containing slags are used as components which bring some fluorine to the sodium calcium silicates. They are formed from a glassy component of the original mould powder containing wollastonite as well as cuspidine together with Na₂O rich minerals, quartz and fluorite in the temperature range between 550-750°C. The analyses of their chemical compositions show that they can be related to pectolite with fluorine instead of the OH-group. Thus they may be called fluorpectolite NaCa₂Si₃O₈F. Furthermore fluorrichterite Na(NaCa)Mg₅Si₈O₂₂F₂ is formed which also contains magnesium.

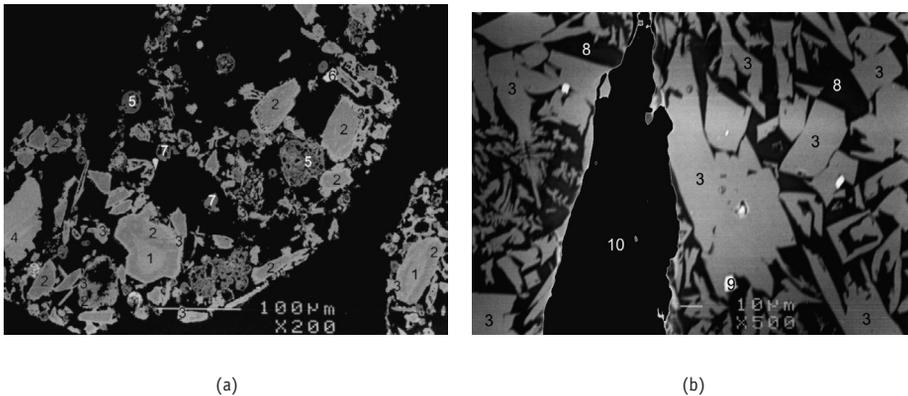


Figure 3: Microstructure of MP 1 after annealing at (a) 800°C and (b) 1200°C (SEM backscattered electron image)
1: wollastonite, 2. combeite, 3: cuspidine, 4: fluorite, 5: nepheline, 6: hematite, 7: glass phase 8: glassy solidified matrix, 9: metallic inclusion, 10: pore

A further intermediate phase is nepheline (NaAlSi₃O₈) which is almost free of potassium and stable in two of the investigated mould powders in the temperature range between 700°C and 1050°C. Because of the fact that MP 1 shows only small amounts of alumina the nepheline content is also very low. By contrast in MP 4 having the highest Al₂O₃ content a lot of nepheline is formed. The stepwise annealed specimens of MP 3 which is composed of albite as one main component show no nepheline formation. Instead of it a liquid matrix is formed.

In the case of MP 6 feldspathoid and two different liquid phases result from the reaction of albite, cryolite, Na₂CaSi₂O₆ which crystallised from a liquid at 620-660°C, fluorite and glass phase. Regarding the sample annealed at 900°C the feldspathoid is situated at the boundary of the cuspidine crystals and the liquid.

Diopside CaMgSi₂O₆ which is also sometimes used as raw material in minor proportions can only be detected in the samples of MP 2 and MP 5 annealed at 900°C.

Formation of Liquid Phases

According to the investigations of MP 6 the first liquid phase can be observed from 540°C upwards as a by-product of the formation of intermediate phases from wollastonite, glass phase, quartz, fluorite and already dissociated calcite and cryolite in very small amounts. In the case of glass scraps (MP 2) the first liquid occurs at 670°C because of the

absorption of alkalis. Contrary to this the other specimens show the first liquid phases at 750° in the case of MP 2 and MP 5 and in the case of MP 1 and MP 6 at 900°C according to the mineralogical investigations. From this temperature onwards sodium, magnesium, aluminium and iron are not longer dissolved in cuspidine and are present in the liquid phase. If the specimens are quenched to room temperature they solidify in a glassy state.

Applying hot stage microscopy the first cohesive liquid phase containing residual solids can be detected between 720-1060°C depending on the mould powder. Here MP 5 shows the lowest temperature.

Cuspidine and in one case wollastonite are melting at last. The formation temperature of a homogeneous cohesive liquid (no solids present any more) varies between 1040°C and 1270°C. It could not be correlated with the CaO/SiO₂ ratio of the mould powders.

Comparison of the Investigation Methods

Most of the temperatures determined by the three methods (stepwise annealed specimens, DTA, hot stage microscopy) for particular processes characterising the melting behaviour of mould powders are comparable. The differences between the investigations of stepwise annealed specimens and the other methods can be explained by the defined gap between the investigated temperatures. Temperature measurements differ for DTA and hot stage microscope. In case of DTA the furnace temperature, and in case of the hot stage microscope the specimen temperature are registered. Therefore during the heating procedure the same effect may be observed at apparently lower temperature with the hot stage microscope.

CONCLUSIONS

The investigations show that there is no method to favour and only the combination of all methods offers a global characterisation of the melting behaviour of mould powders, because all of them result in additional information.

Even though the mineralogical composition of the mould powders as received differs there are still similarities. Wollastonite, fluorite, carbon, carbonates, silicates, synthetic glasses like fly ash, blast furnace slag and/or glass scraps are used as raw materials. During heating reactions take place because the components are not in chemical equilibrium. At first the decompositions of several phases like carbonates occur. Afterwards cuspidine is formed either by solid-solid reactions of wollastonite and fluorite or by participation of a liquid phase. Additionally intermediate phases like nepheline, rankinite, diopside and alkali-silicates in dependence of the mineralogical composition of the mould powders are detected. Further rise of temperature leads to the formation of a liquid phase. The temperature where a cohesive homogeneous liquid without any solid phases emerges varies between 1040°C and 1270°C.

Further application of these results is planned in the following respect. On the one hand when compared with the structure of slag rims they help to understand the process and conditions of their formation. On the other hand they should help to clarify the suitability of mould powders for different steel grades and the reasons for undesired casting conditions and possible material defects.

ACKNOWLEDGMENTS

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NOMENCLATURE

DTA = Differential thermal analysis.
 MP = Mould powder.
 XRD = X-ray diffraction.

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