Effect of liquefaction controlling components in carbon-free mould powder for the continuous casting of ultra-low carbon steels

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ABSTRACT

In the continuous casting of ultralow carbon (ULC) steels, free carbon is used to control the melting behaviour of mould powders. If the carbon is not completely removed during melting, it is enriched at the top of the slag pool. Liquid steel may come into contact with this layer because of the turbulence of the molten metal, resulting in its recarburisation, which negatively affects the desired product quality. Thus, a reduction in carbon input is desirable. For this purpose, SiC and/or Si_3N_4 with and without antioxidants were selected as melt-control additives to replace carbon in the mould powders. Thermodynamic calculations were performed to quantify their effect on the melting behaviour based on the chemical composition of a flux already applied to ULC steels. To experimentally assess the liquefaction behaviour, laboratory mould powders were prepared and annealed in steel crucibles closed with a lid. Crucibles were inserted into a furnace that was already preheated to selected temperatures between 900–1200 °C for 10 min and quenched to room temperature. Subsequently, the samples were mineralogically investigated. The results confirmed those obtained from the thermodynamic calculations. Si_3N_4, and SiC in particular, are suitable raw materials for delaying the solid-solid reactions of raw material components during melting. Owing to their stability at high temperatures, the necessary SiO_2 content to form a liquid phase is not available, resulting in lower amounts of the liquid phase. The addition of antioxidants to delay the oxidation of SiC further reduces this positive effect. Attempts to decrease the SiC content without negatively affecting the melting behaviour resulted in a reduction in the CO_2 emission by at least 27 g CO_2/kg of mould powder when compared to the carbon-containing standard mould powder. These investigations revealed differences in the melting behaviours of granules and loose powders, which are related to their respective production processes.

INTRODUCTION

In the continuous casting of steel mould powders added to the liquid steel pool form different horizontal layers during melting, a homogeneous liquid layer exists in contact with the steel, and the original mould powder is still present on the upper surface. In between a sintered layer owing to the formation of liquid and new solid phases exists. The slag infiltrates the gap between the steel and the mould. A liquid layer is in contact with the strand, a glassy layer is close to the mould, and a crystalline layer lies in between. In particular, the structure of the crystalline layer affects heat transfer from the strand to the mould (Mills, Fox, Thackray and Li, 2004).

A common approach for controlling the melting behaviour of mould powders is the addition of carbon particles of different types and sizes, for example, graphite or carbon black, to a mixture of raw-material components. At lower temperatures, they reduce the contact between raw material particles and delay solid-solid reactions. A liquid phase is formed with increasing temperature. Because of the nonwetting carbon particles, the liquid droplets remain separated, and a continuous liquid is prohibited. This phenomenon is known as the skeleton effect (Mills, 1990; Kawamoto, Nakajima, Kanazawa and Nakai, 1994; Kölbl, Marschall and Harmuth, 2009; Kromhout, 2013). After the carbon is burned off, which depends on the oxygen supply in the high-temperature areas of the mould powder layers, a homogeneous liquid is formed. If the carbon is not completely oxidized, it accumulates on top of the liquid slag layer, resulting in a carbon-rich layer with a carbon content of more than 20 wt.% for mould powders with carbon contents of solely 3.5 wt.% when delivered (Supradist, Cramb and Schwerdtfeger, 2004). This effect has also been confirmed by laboratory investigations (Yan, Yang, Chen, Barati and McLean, 2015). Owing to the oscillation of the mould and the turbulence of the steel flow from the submerged entry nozzle, liquid steel may come into contact with the carbon-enriched layer, resulting in its recarburisation. In particular, for ultralow-carbon steels, this reaction changes the steel properties, which reduces the strand quality. Various approaches have been proposed to inhibit this reaction. A thicker slag layer increases the distance between the carbon-rich layer and steel bath, making contact more difficult. Furthermore, different efforts have been made to improve the raw material composition of the powders. Graphite is replaced by quick-burning or activated carbons to support its oxidation, and oxidising agents such as MnO_2 or catalysts such as Fe_2O_3 for reactions at low oxygen activity and high temperatures are added (Yi, Song and Peng 2013; Terada, Kaneko, Ishikawa and Yoshida, 1991; Han, Wen, Tang and Chen, 2023; Nakato, Takeuchi, Fujii, Nozaki and Washio, 1991). Another approach is the replacement of free carbon in the mould powder by using alternative raw material components showing similar properties as carbon (Takeuchi, Nishida, Ohno, Kataoko and Hikara, 1976; Takeuchi, Mori, Nishida, Yanai and Mukunashi, 1978; Debiesme, Radot, Coulombet, Lefebvre, Pontoire, Roux and Damerval, 1996; Debiesme, Radot, Coulombet, Lefebvre, Pontoire, Roux and Damerval, 1998). With respect to the skeleton effect, the nonwettability of slags is in the focus of these studies. In the first attempt, nitrides were added to the mixture instead of carbon and tested. For this purpose, BN, Si_3N_4, MnN, CrN, FeN, AlN, TiN, or ZrN were suggested (Terada, Kaneko, Ishikawa and Yoshida, 1991; Takeuchi, Nishida, Ohno, Kataoko and Hikara, 1976; Takeuchi, Mori, Nishida, Yanai and Mukunashi, 1978). Boron nitride is the most appropriate option owing to its similarity to carbon in terms of crystalline structure and wetting behaviour. Mould powder investigations in the laboratory showed that the sintering tendency of fluxes containing BN was reduced. The minimum amount required to effectively control the melting behaviour of the mould powders depends on the sizes of the BN particles and the oxidic and fluoridic base materials. A decrease in the raw material particle size resulted in decreased melting rates, which also accounted for the BN. The fusion rates were determined for the original mould powder with carbon and for mixtures containing different amounts of BN in the laboratory. Those containing 2.10 wt.% of BN showed similar behaviour to the original sample. Furthermore, compared with carbon black, BN exhibited a reduced sintering tendency and reduced gas formation. In contrast, during the oxidation of boron nitride, B_2O_3 is formed, acting as a fluxing agent and causing the formation of the first liquid phase. Thus, antioxidants such as Al or CaSi were added to the samples to impede its oxidation at lower temperatures. However, boron oxide not only improves the sintering tendency but also lowers the slag viscosity. Therefore, solely for samples showing a CaO/SiO_2 (C/S) ratio of 0.9, proper viscosities for the continuous casting process were obtained. Based on the laboratory results, the mould powder was selected for testing with a defined steel grade in a continuous caster. After the trial, the surface of the strand was analysed with respect to surface quality. The results revealed that an increase in nitrogen content on the strand surface being as detrimental as the effect of recarburisation. Therefore, this amount must be reduced. The realization was achieved by deliberating retaining some carbon from the mould powder to ensure controlled melting behaviour (Terada, Kaneko, Ishikawa and Yoshida, 1991; Takeuchi, Nishida, Ohno, Kataoko and Hikara, 1976; Takeuchi, Mori, Nishida, Yanai and Mukunashi, 1978).

Additionally, Si_3N_4 was considered to effectively control the melting of mould powders. The benefit compared with BN is that SiO_2, which is already included in the original mould powder composition, is formed during oxidation. Thus, the viscosity of the slag does not change after liquification. Investigations in the laboratory suggested a particle size of 5 μm and a specific surface of 2.5–3.5 m^2g^{-1} to meet the required demands. Subsequently, a mould powder was prepared for industrial trials. During operation, suitable melting rates were observed, but the surface of the steel strand also showed considerable nitride absorption (Debiesme, Radot, Coulombet, Lefebvre, Pontoire, Roux and Damerval, 1996; Lefebvre, Radot, Pontoir and Roux, 1996; Debiesme, Radot, Coulombet, Lefebvre, Pontoire, Roux and Damerval, 1998; Sun, Liu, Fang, Zhang and Lu, 2019).

The concept of associating specially coloured mould powders with steel grades to facilitate onsite identification during operation requires the elimination of carbon from the mould powder composition. Carbon-free samples were investigated using a heating microscope. The results showed that the softening, melting, and flow points agreed with those of the carbon-containing products. In contrast, the melting rate increased considerably. The authors (Macho, Hecko, Golinmowski and M. Frazee, 2005) assumed sufficient thermal insulation of the steel in the mould, as long as a sufficiently thick mould powder layer rests on the mould slag.

Efforts have also been made by various research groups to replace free carbon with SiC (Lefebvre, Radot, Pontoir and Roux, 1996; Maillart, Chaumat and Hodaj, 2010; Ning and Jinghao, 1998; Safarian and M. Tangstad, 2009; Park, Jeon, Lee, Park and Chung, 2016). Similar melting rates were achieved for mould powders containing 2–2.5 wt.% of carbon or 5–6% SiC. A detailed investigation of the layers formed during the experiment revealed three layers. Contrary to the standard, solely carbon-containing product, the sintered layer increased considerably, whereas the original sample layer remained very thin. This was explained by the oxidation of SiC, resulting in a decrease in the basicity of the mould powder, thus accelerating liquid-phase formation. Consequently, carbon was partially replaced by SiC. These products, which contained different ratios of free carbon to SiC, were then tested in contact with liquid steel. Analysis of the chemical compositions of the steel samples indicated an increasing tendency for recarburisation when the carbon content exceeded 1 wt.%.

In the investigations quoted above, phenomenological methods were primarily used to compare the melting behaviour of mould powder compositions where carbon was partially or totally replaced as the melt-control additive. However, the effect of these additives during melting has not yet been described. Thus, in this study, SiC and/or Si_3N_4, with and without the addition of antioxidants, were selected to replace carbon in a mould powder already used for the continuous casting of steels for investigation in laboratory experiments.

EXPERIMENTAL

Mold powder, already used in the continuous casting of ultralow-carbon steels, was selected (hereafter denoted as MP0). Based on its chemical composition, this mould powder was reproduced as a mixture of raw material components that are generally used for the production of mould powders (MP2). As a reference, a sample without melt-controlling additives was prepared (MP1). Subsequently, to substitute the carbon content of MP2, SiC (MP3–6) and/or Si_3N_4 (MP9/MP8) were added to control the melting behaviour of the mixture. For this purpose, the composition was modified to achieve the chemical composition of MP1 after total oxidation of the carbide and nitride phases. An amount of 25 wt.% of the total SiO_2 content in the mould powder was substituted by SiC and/or Si_3N_4. For refractory materials, the addition of antioxidants is the most common technology to prevent carbon oxidation and increase service lifetime owing to enhanced corrosion resistance. Additionally, the desired properties of the product, such as the mechanical properties, are improved (Ghosh, Jagannathan and Ghosh, 2001; Wang and Yamaguchi, 2001; Dai, L, Xiao, G and Ding, D, 2021). Laboratory mould powders MP4–MP6 contain Si and/or Al in addition to SiC, which prohibits the premature oxidation of SiC. A similar addition of Si and Al serves to protect carbon in refractories; so-called antioxidants (Ghosh, Jagannathan and Ghosh, 2001; Wang and Yamaguchi, 2001; Dai, L, Xiao, G and Ding, D, 2021).

Prior to laboratory investigations, thermodynamic calculations of the phase distribution with respect to temperature were performed using FactSage®. The mineral composition and possible liquid phase of each sample were calculated in equilibrium state up to 1550 °C, which corresponds to the steel bath temperature in mould, while maintaining the total initial oxygen amount constant (no oxidation). As a result, the quantities of the phases formed in dependence on temperature are depicted in diagrams, and the amount of liquid phase at 1000 °C was calculated, indicating the melting tendency of each sample for comparison. The experimental investigations of MP1–MP3 aimed to assess the effect of the additives used on the liquefaction behaviour, and it was revealed that, contrary to the calculations performed here, partial oxidation reactions occurred. To minimize the discrepancy between the chemical composition of the as-received commercially fabricated mould powder and the mixtures prepared in this study, the quantity of each raw material component was calculated based on its chemical composition. Quartz, feldspar, calcite, magnesite, fluorite, carbon, wollastonite, soda, corundum, fly ash, glass, blast furnace slag, and hematite were used as base materials, and SiC, Si, Al, and Si_3N_4 were added to control the melting behaviour of the specimen. The mixtures were prepared as listed in Tables 1 and 2. After homogenising, 20 g of each loose mould powder mixture were filled into steel crucibles ($30 \cdot 30 \cdot 40$ mm³) closed by a steel lid and inserted into the furnace preheated to a selected temperature between 900 and 1200 °C. Melt-control additives are expected to be partially oxidized in the crucible atmosphere. At least at lower temperatures, this reaction was incomplete. The oxygen supply was hindered by the lid, simulating the oxygen support under service conditions by diffusion. The crucibles were kept in the furnace for 10 min before being removed and quenched at room temperature. Mineralogical investigations were conducted on polished sections using reflected light microscopy and scanning electron microscopy coupled with energy-dispersive X-ray microanalysis. The latter enables the identification of phases that are stable in dependence on temperature. The samples were ground for X-ray analysis. Finally, the results of the thermodynamic and laboratory investigations were compared.

TABLE 1 – Raw material compositions of MP1 – MP9 (in wt.%)

	MP1	**MP2**	**MP3**	**MP4**	**MP5**	**MP6**	**MP7**	**MP8**	**MP9**
	no melt-control additive	*with carbon*	*with SiC*	*SiC, antiox. Si*	*SiC, antiox. Al*	*SiC, antiox. Si and Al*	*antiox. Al*	*with Si_3N_4*	*with Si_3N_4 and SiC*
Quartz	6.8	6.9	6.3		4.9	0.3			
Feldspar	4.3	4.9	3.8			3.6			
Calcite	2.1	3.3	17.8	7.6		12.0		3.0	15.3
Fly ash	13.3	11.1	13.0	7.4				16.0	7.7
Glass						8.1	22.7		15.3
Magnesite	9.4	9.1	8.1	9.5	10.9	9.3	9.9	9.3	7.7
Fluorite	19.5	18.7	18.7	19.5	20.4	19.2	20.3	19.8	19.1
Carbon		4.4							
Wollastonite	38.1	35.7	20.0	34.0	45.5	28.6	39.9	37.1	19.7
Soda	5.3	4.9	5.1	6.1	6.3	4.0	2.5	6.2	3.4
Corundum				2.4		0.7		0.5	1.7
Blast furnace slag				2.7	0.5	2.8			2.5
SiC			6.0	6.5	6.8	6.4			4.8
Hämatite	1.3	1.2	1.2	1.7	2.4	2.3	2.4	1.2	1.6
Si metallic				2.60		1.3			
Al metallic					2.3	1.3	2.3		
Si_3N_4								6.9	1.7

Owing to the suitable application of SiC to delay the reactions of the raw materials (Results), further attempts were made to reduce the SiC content of MP3 without negatively affecting its melting rate. For MP3, 25 wt.% of the total SiO_2 content in MP0 was replaced with SiC. For MP10–MP13, this amount was continuously reduced. Mixtures were prepared according to Table 2, homogenized, and granulated using a bottle roller to compare their melting behaviours. Subsequently, they were annealed in a preheated furnace according to the procedure described above.

TABLE 2 – Raw material compositions of MP10–MP13 (in wt.%)

	MP10	**MP11**	**MP12**	**MP13**
	20 wt.% SiO_2 replaced by SiC	*15 wt.% SiO_2 replaced by SiC*	*10 wt.% SiO_2 replaced by SiC*	*5 wt.% SiO_2 replaced by SiC*
Quartz			1.6	3.7
Feldspar	4.1	7.9	5.0	4.7
Calcite	4.14	3.5		
Fly ash	16.6	13.4	15.3	15.3
Magnesite	10.1	10.3	10.3	10.3

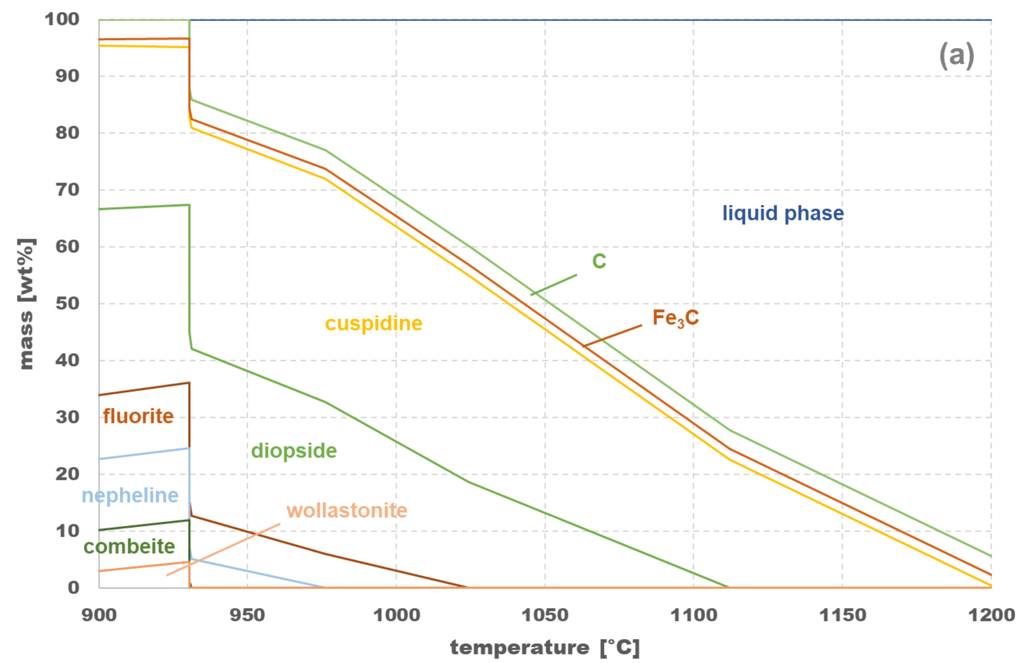
Fluorite	21.7	21.5	21.5	21.2
Wollastonite	40.1	41.2	44.1	43.9
Soda	6.0	5.3	5.8	5.8
SiC	5.8	4.3	2.8	1.4
Hämatite	1.3	1.5	1.3	1.4

RESULTS AND DISCUSSION

Thermodynamic calculations

Figure 1 summarizes the phase compositions of MP0=MP2, MP3, and MP9 with increasing temperature. As expected, the phases differed only slightly among the calculated compositions; however, their stability ranges varied considerably. In all specimens, cuspidine ($Ca_4(Si_2O_7)(F,OH)_2$), formed by the reaction of the raw materials during heating, is the last solid phase that forms before a homogeneous liquid. If the iron oxide in the mould powder is reduced by another component, solid iron and iron silicide with diverse Fe/Si ratios are also formed. At low temperatures, nepheline ($Na_3KAl_4Si_4O_{16}$) is observed in all mixtures, and combeite ($Na_2Ca_2Si_3O_9$) and fluorite (CaF_2) are observed in MP0–MP3 and MP8–MP9. MP3, MP8, and MP9 represent magnesium-fluoride silicates ($Mg_5F_2Si_2O_8$ or $Mg_9F_2Si_4O_8$).

In comparison to the carbon-containing mould powder, the replacement of SiO_2 by SiC and/or Si_3N_4 caused an increase in the quantity of cuspidine (MP3, MP8, and MP9). Owing to the incomplete oxidation of the melt-control components, the availability of SiO_2 was reduced in these samples. Thus, the formation of phases with a higher SiO_2 content was prohibited. Although diopside ($CaMgSi_2O_6$) can be found in MP0 and MP1, it is not stable in the samples containing SiC and/or Si_3N_4. The same applies to mixtures of SiC and antioxidants. Cuspidine and merwinite ($Ca_3Mg(SiO_4)_2$), olivine ($(Mg,Fe)_2SiO_4$), and melilite ($(Ca,Na)_2(Al,Mg,Fe^{2+})(Al,Si)SiO_7$) were present instead of clinopyroxene. Compared with the carbon-containing samples, the quantity of cuspidine did not increase significantly. Furthermore, because of the stability of SiC, particularly at lower temperatures, the CaO/SiO_2 ratio is low, and the formation of the liquid phase shifts to higher temperatures, where SiC oxidation is promoted, thus increasing the C/S ratio. This behaviour was not observed in the samples containing free carbon.



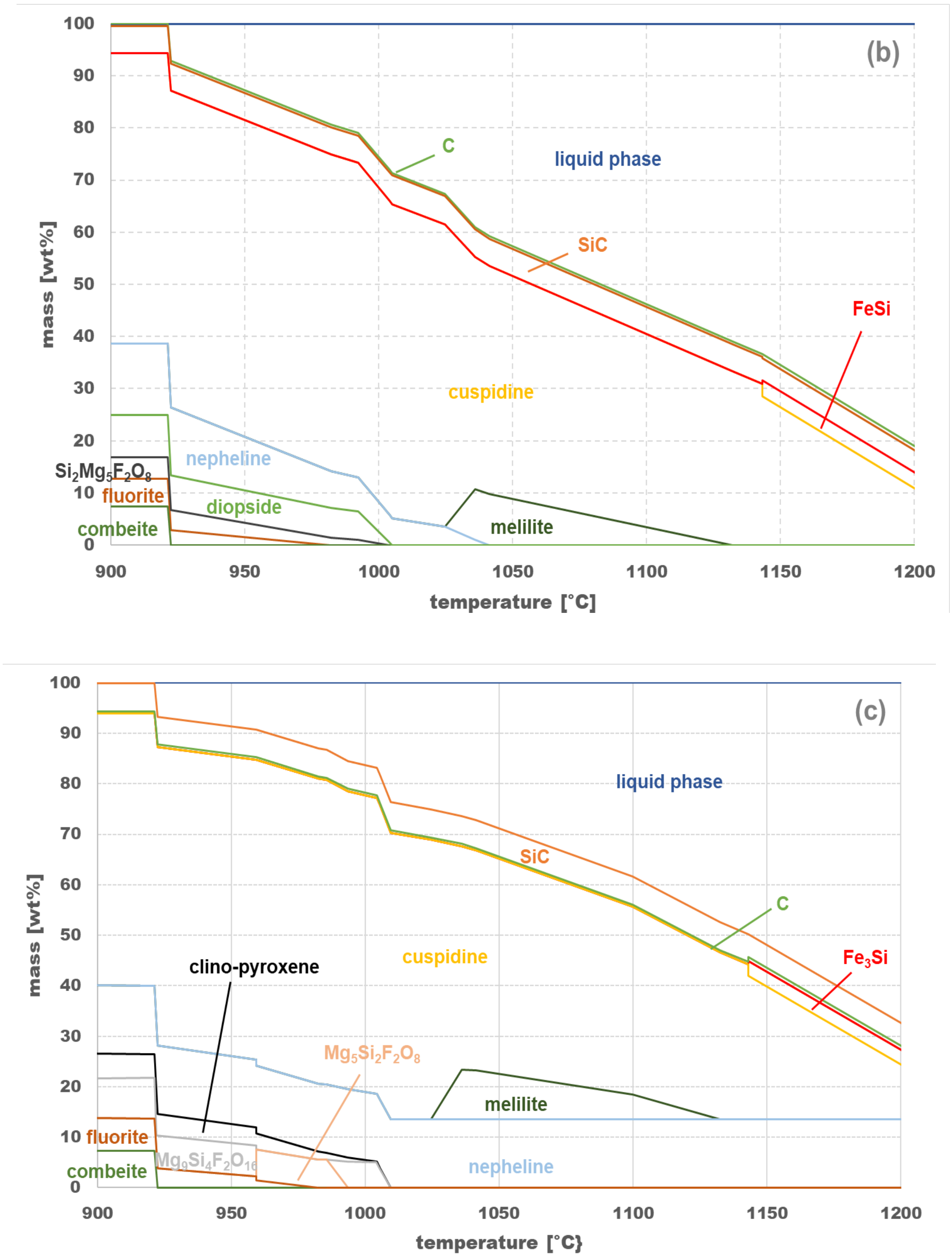


FIG 1 – Mineral compositions as a function of temperature for (a) MP0 and MP2, (b) MP3, and (c) MP9

For all the mould powders, the solidus (T_s) and liquidus (T_l) temperatures were determined using calculations. Additionally, the calculated amounts of liquid phase present at 1000 °C (l_{1000}) were compared to enable the evaluation of the melting tendencies. The results are summarized in Table 3. In the equilibrium state, the temperature of the first liquid phase is not affected by the melting-controlling components. The amount of liquid phase at 1000 °C is not significantly different for all mixtures, with the exception of MP5, which shows the lowest value. A more significant difference was observed in the liquidus temperature. The sample containing SiC (MP5) as the melt-control additive exhibits the highest T_l. By contrast, further addition of antioxidants results in an opposite effect and decreases the liquidus temperature by approximately 80 °C again. In these samples, liquid phase formation is promoted, but its amount at 1000 °C is only slightly higher and still lower than that of MP0 and MP2. The thermodynamic calculations do not end in a total liquefaction of the mould powders up to 1550 °C because the melt-control additives (carbon, SiC, Si_3N_4) are not totally oxidized. Therefore, they are still stable at 1550 °C. In Table 3, they are indicated by the subscript “residual.” Additionally, their initial amount is given, which is marked by “initial.”

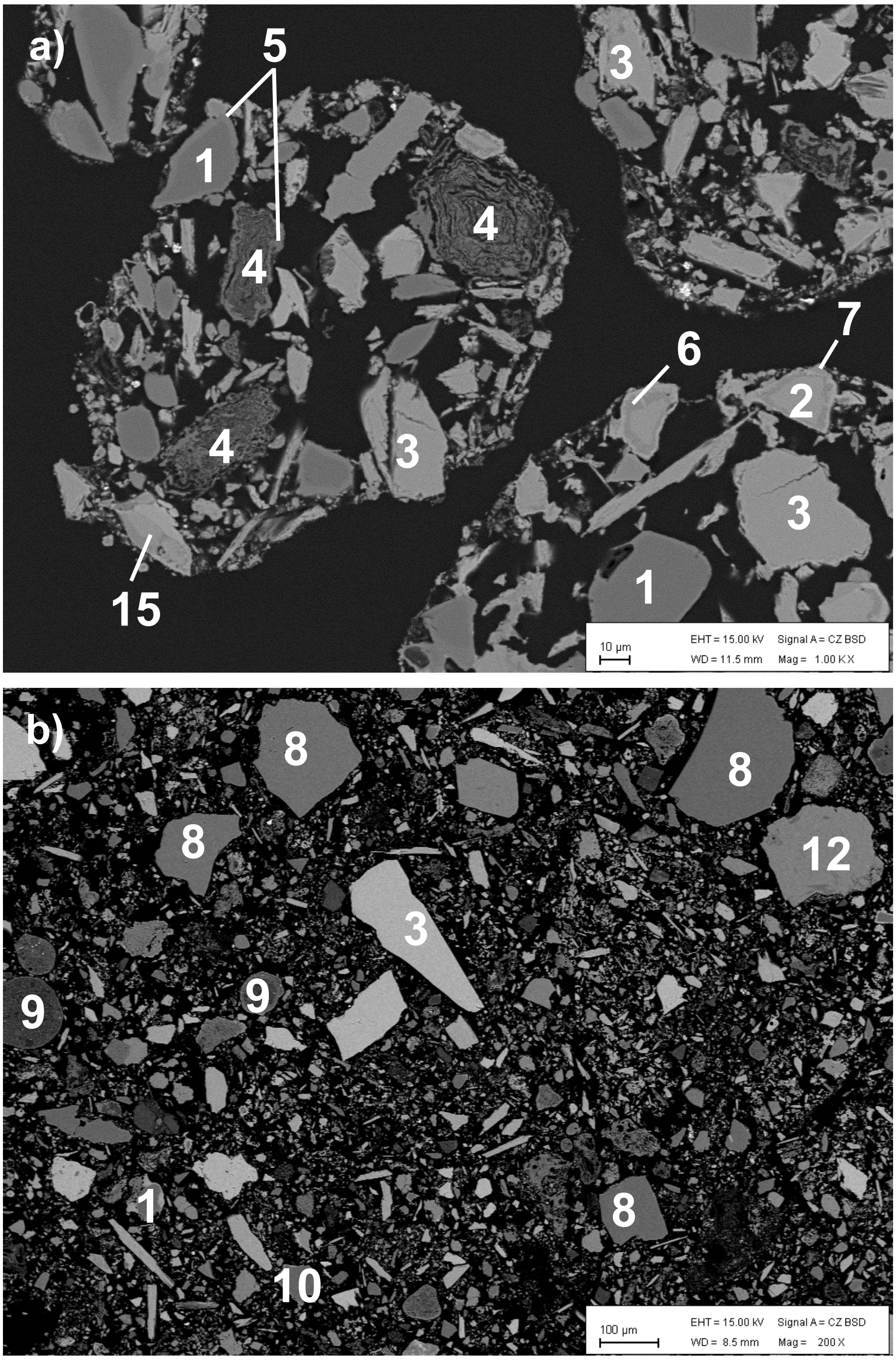
TABLE 3 – Melting tendency based on thermodynamic calculations

	$l_{1000\ °C}$ [wt.%]	T_s [°C]	T_l [°C]	$C_{residual}$ [wt.%]	$SiC_{residual}$ [wt.%]	$SiC_{initial}$ [wt.%]	$Si_3N_{4\ residual}$ [wt.%]	$Si_3N_{4\ initial}$ [wt.%]
MP 0	28.3	931	1202	3.2				
MP 1	26.7	923	1190					
MP 2	28.3	931	1202	3.2				
MP 3	24.2	922	1235	0.8	4.3	6.0		
MP 4	26.8	847	1209		7.1	7.1		
MP 5	18.8	852	1225		7.0	7.0		
MP 6	24.3	852	1210		7.0	7.0		
MP 7	27.5	927	1216					
MP 8	25.1	922	1235				4.9	6.9
MP 9	23.8	921	1235	3.2	4.4	4.8	1.2	1.7

$l_{1000\ °C}$	amount of liquid phase at 1000 °C
T_s	solidus temperature
T_l	liquidus temperature
$_{residual}$	quantity of the respective melt-control additive at 1550 °C
$_{initial}$	initial quantity of the respective melt-control additive in the sample

Laboratory investigations of different mould powder compositions

The microscopical investigations of the standard mould powder MP0 after heat treatment at 900 °C revealed the beginning reactions of the raw material components to form new phases. In this sample, the formation of cuspidine on the surface of the wollastonite particles is observed. The diffusion of Na_2O into the wollastonite results in the formation of sodium calcium silicates that separate the wollastonite in the centre from the cuspidine rim (Figure 2 a). Fluorine does not only diffuse into wollastonite but also into albite to form fluorpectolite ($NaCa_2Si_3O_8F$) and into the partly decarburized magnesite (Figure 2 a). Similar reactions were observed in MP1 and MP2. In addition, diopside ($CaMgSi_2O_6$) was formed. In contrast, no reaction between the raw material particles was observed in the sample containing SiC as the melting-control component (Figure 2 b). However, this beneficial effect was reduced when antioxidants were added to the mixture. Al and/or Si are oxidized even at low temperatures. Furthermore, their oxides contribute to the melting of the raw materials, particularly fines. Thus, for MP4–MP6 liquid phase was already present owing to the reactions of the fines (Figure 2 c). The cuspidine and sodium calcium silicate phases had already formed. The replacement of carbon with Si_3N_4 did not produce the desired effect. Due to the diffusion of Na_2O into glassy phases, their melting temperature is reduced, which results in the formation of small amounts of liquid phase even at 900 °C. Diffusion of F into the dissociated magnesite was also observed. When silicon nitride and silicon carbide were added together (MP9), the reactivity of the raw material components was marginally reduced. However, the diffusion of F into the magnesite and the diffusion of CaO, MgO, and Na_2O into Si_3N_4 still occurred.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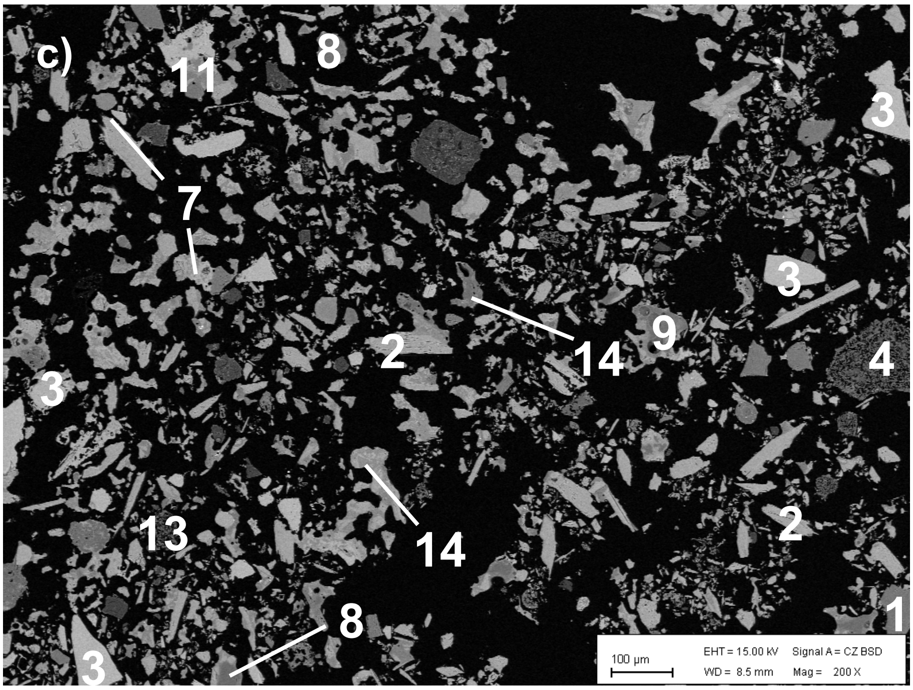
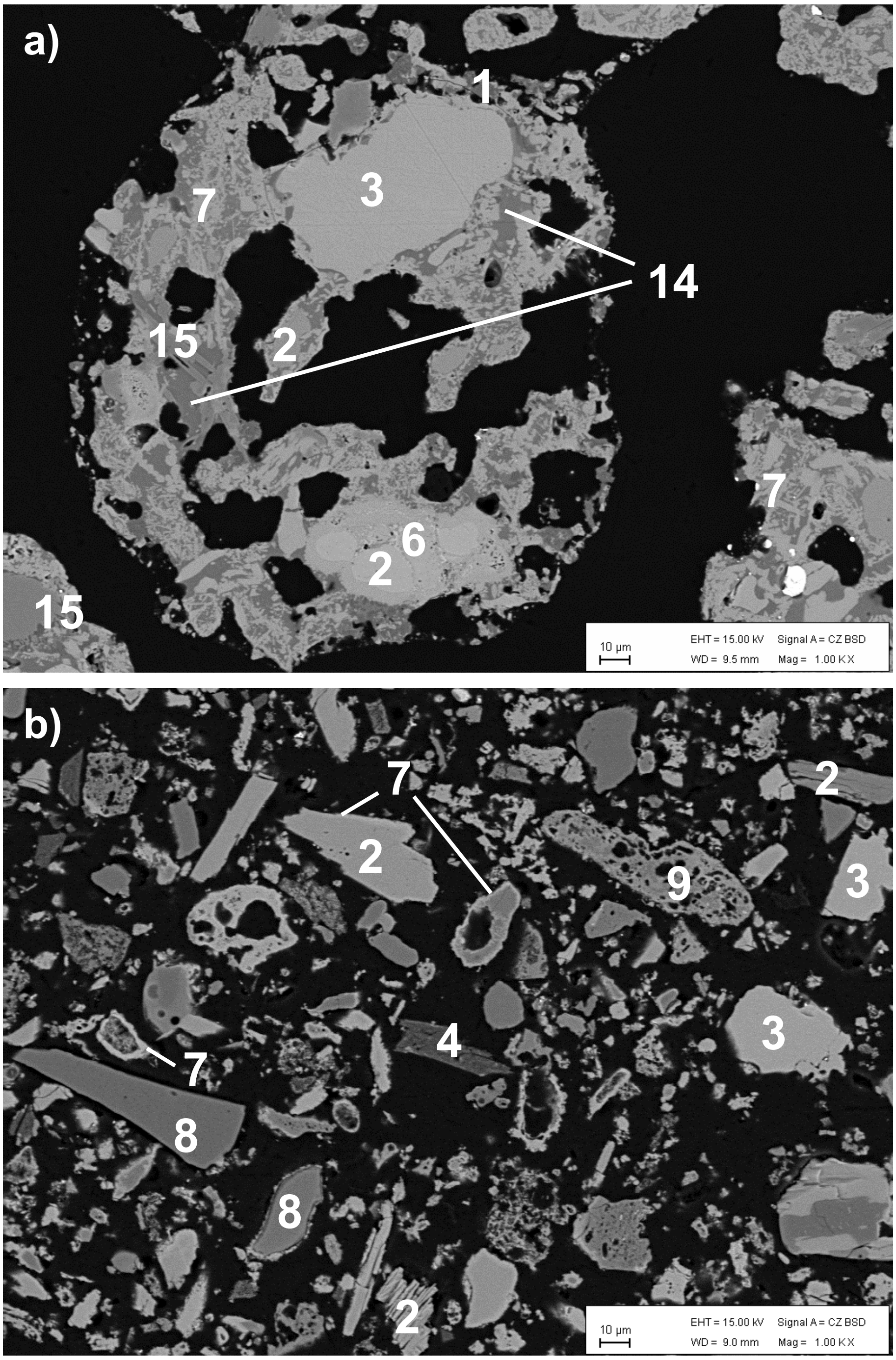


FIG 2 – Backscattered electron image of (a) MP0, (b) MP3, and (c) MP4 after temperature treatment at 900 °C for 10 min

(1) albite, (2) wollastonite, (3) fluorite, (4) dissociated magnesite, (5) fluorpectolite, (6) sodium calcium silicate, (7) cuspidine, (8) SiC, (9) fly ash, (10) quartz, (11) slag, (12) calcite, (13) corundum, (14) liquid phase, and (15) diopside

Comparing the samples after the temperature treatment at 1000 °C, considerable differences in the appearance of the respective mixtures could be observed. The mould powder MP0 used in the continuous casting process contained only the residuals of the initially larger raw material particles (Figure 3 a). These were wollastonite, fluorite, and albite. The cuspidine rim at the boundaries of the wollastonite and the area of the sodium calcium silicate separating the wollastonite in the centre increased. Furthermore, owing to the reaction of the fines, a considerable amount of liquid phase in contact with the newly formed cuspidine is observed. MP1, which contained no melt-control additives, exhibited the diffusion of primarily Na_2O and F into the other raw materials. The residuals of the decarburized magnesite are enriched in F, and silica-containing particles, especially at their surfaces, in Na_2O, but the liquid phase is hardly present. A similar behaviour was observed for MP2. In the SiC-containing sample (MP3), only small amounts of cuspidine were formed (Figure 3 b). SiC inhibits the solid-solid reaction between the components. Thus, the formation of the new phases shifted to higher temperatures. The appearance of MP4 confirmed the previously described effect of Si addition, which resulted in an increased sintering tendency compared with MP3. New solid- and liquid-phase formations are observed. In contrast, if Si is replaced totally or at least partly by Al (MP5 and MP6), the amount of liquid phase is reduced, but is still higher than in MP3. Furthermore, the quantity of raw material particles increased at this temperature, as shown in Figure 3 c. The use of Al alone as an additive resulted in the highest amount of the liquid phase, which is in accordance with the highest sintering tendency (Table 3). In MP8, silicon nitride also delays the solid-solid reactions of the raw materials but is less efficient than SiC. Hence, raw materials and new phases, such as cuspidine, are present. The MP9 showed a similar appearance (Figure 3 d). For both MP8 and MP9 specimens, the oxidation of a substantial amount of Si_3N_4 was detected.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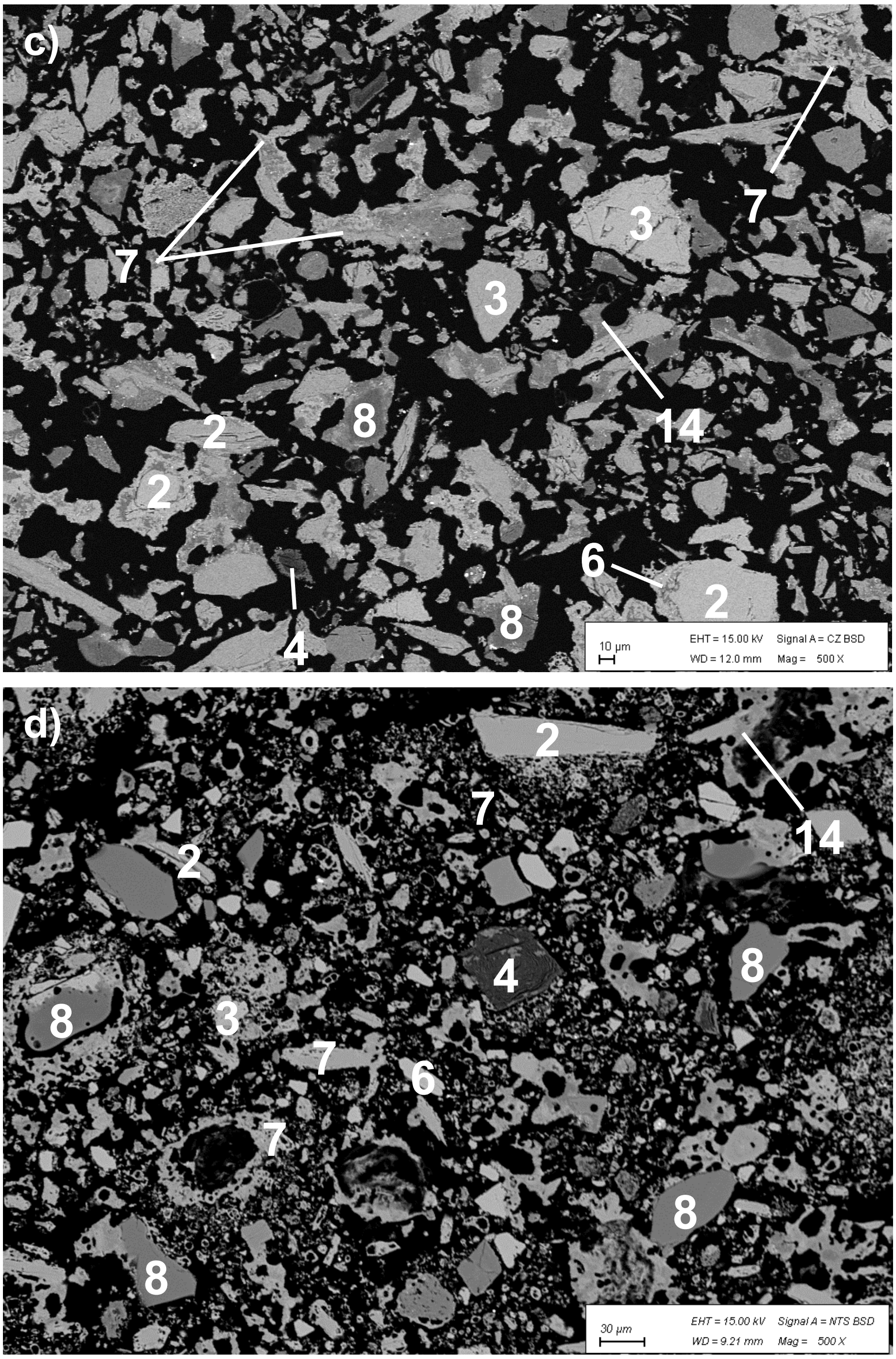
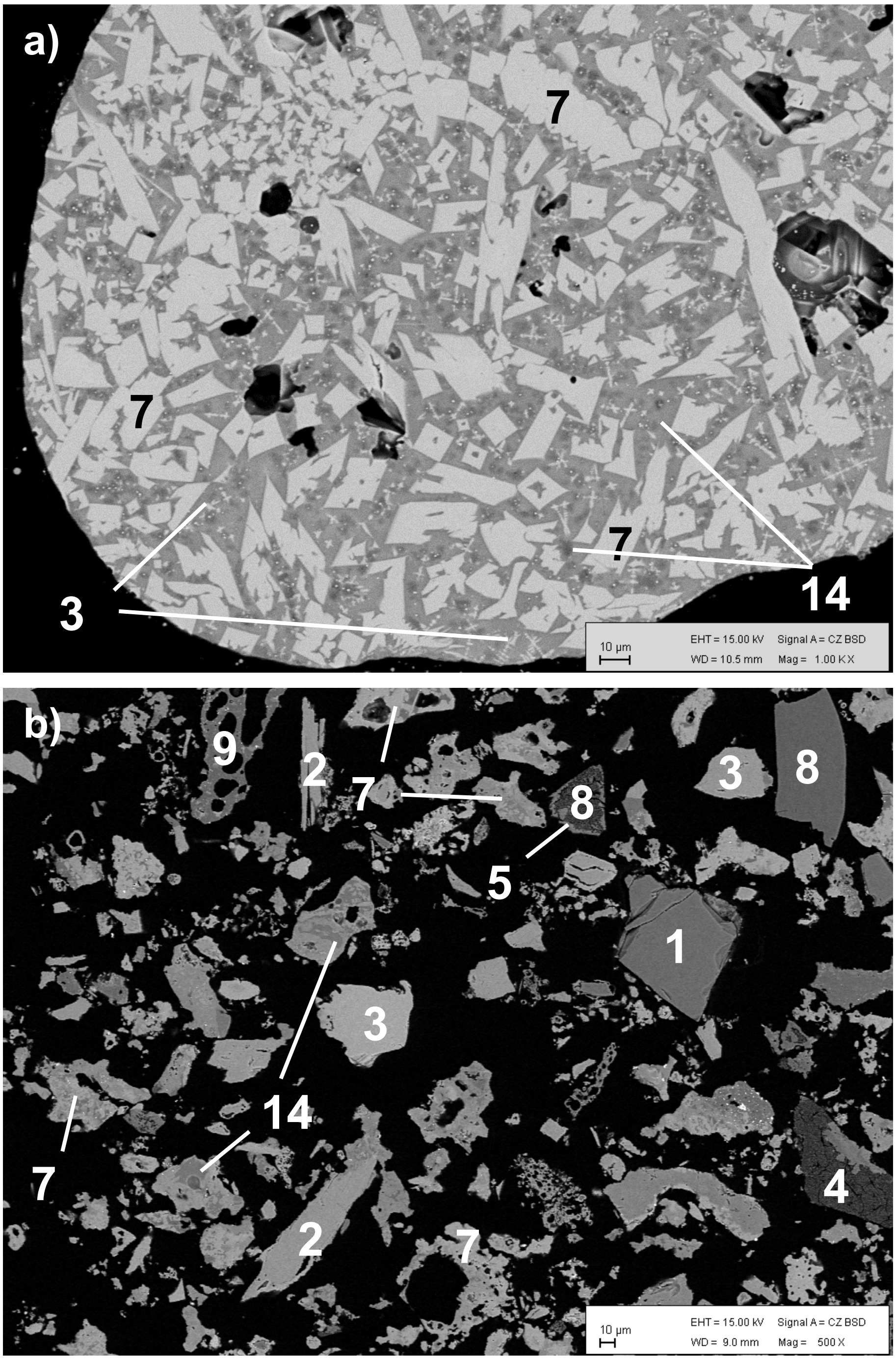


FIG 3 – Backscattered electron image of (a) MP0, (b) MP3, (c) MP6, and (d) MP9 after temperature treatment at 1000 °C for 10 min

(1) Albite, (2) wollastonite, (3) fluorite, (4) dissociated magnesite, (6) sodium calcium silicate, (7) cuspidine, (8) SiC, (9) fly ash, (14) liquid phase, and (15) diopside

After heat treatment at 1100 °C, the samples contained mainly liquid phase and cuspidine (Figure 4). Residuals of large raw material particles were also observed. In MP1, additional fluoride dendrites were observed, which formed during quenching of the samples. A different appearance was observed for MP3 containing SiC. Large raw material particles showed small reaction boundaries on their surfaces, indicating a slow reaction rate. A liquid phase was present but was not coherent (Figure 3 b). SiC was also detected in the samples containing additional antioxidants or silicon nitride (MP4–MP6 and MP9). In these specimens, SiC remained in direct contact with the already formed continuous liquid phase (Figure 4 c). Locally, the SiC particles accumulated. Through oxidation, the melt-control additives caused the formation of pores in the liquid slag in all samples. This was particularly observed in MP8 and MP9, in which Si_3N_4 was used (Figure 4 d).



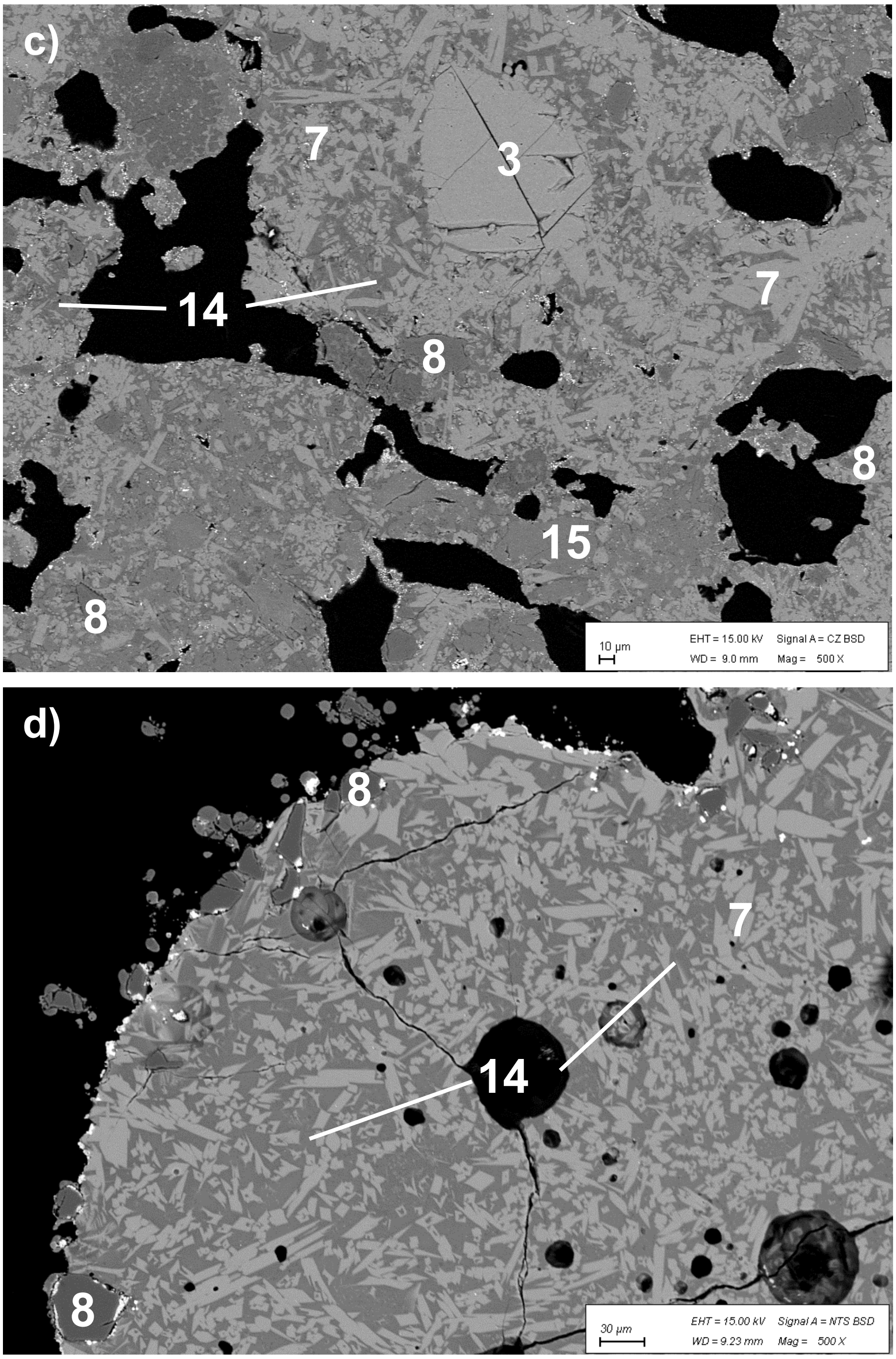
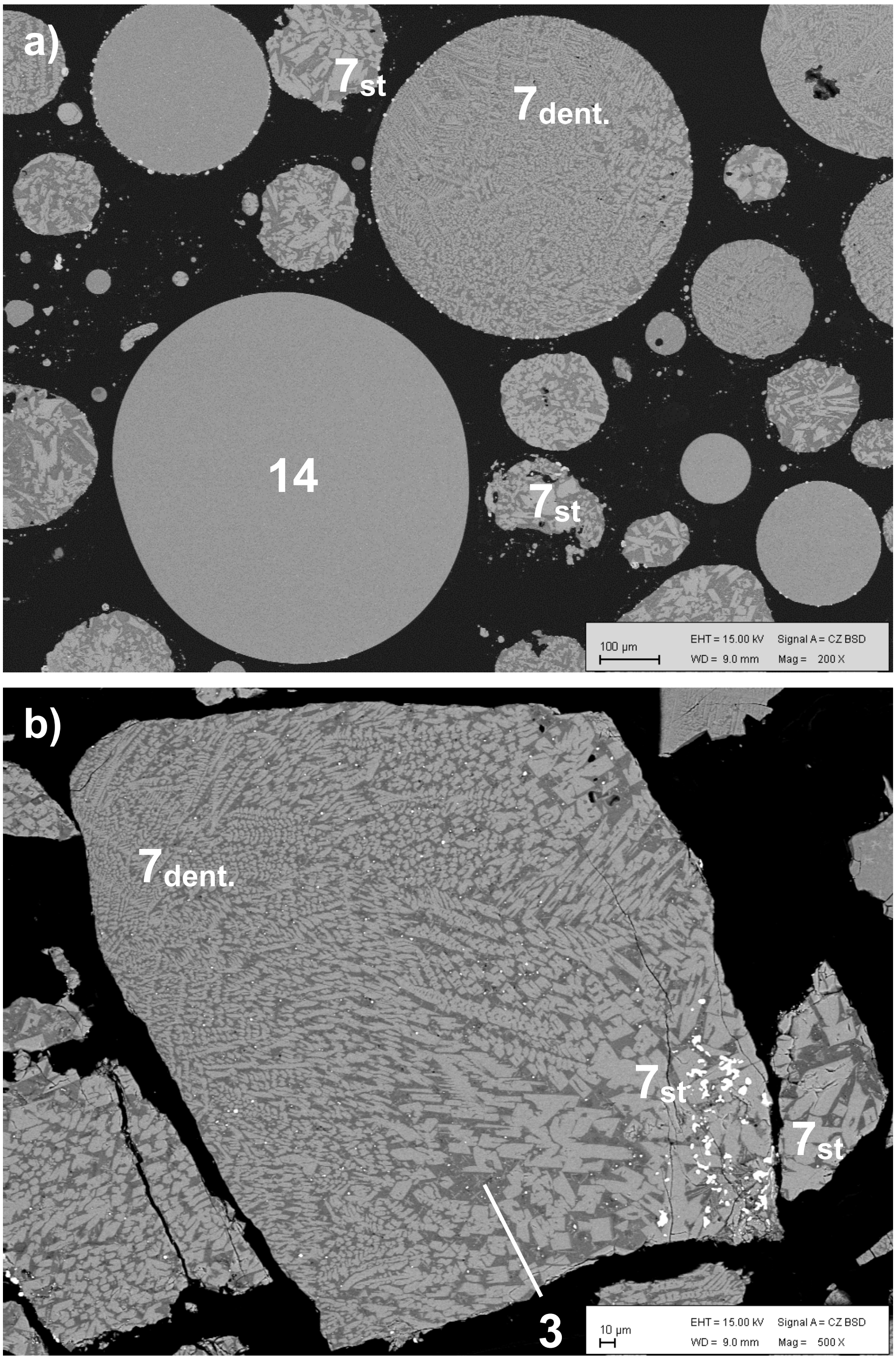


FIG 4 – Backscattered electron image of (a) MP0, (b) MP3, (c) MP4, and (d) MP9 after temperature treatment at 1100 °C for 10 min

(1) albite, (2) wollastonite, (3) fluorite, (4) dissociated magnesite, (5) fluoropectolite, (7) cuspidine, (8) SiC, (9) fly ash, (14) liquid phase, and (15) diopside

After the treatment of the mould powder MP0 as received at 1200 °C, the mineralogical investigations revealed the independent melting of each granule (Figure 5 a). No continuous liquid phase was formed, even though all granules were at least partly liquefied. Some still showed cuspidine in the solid state, whereas others consisted only of the liquid phase. This can be explained by the slightly different chemical compositions of the granules with respect to their F and/or Na_2O contents, which influenced the melting temperature of the granules.

In general, the appearance of the mixtures was very similar. Except for MP0, MP3, and partly MP5, where small quantities of cuspidine in a stocky shape were still present (Figure 5 a,b), a homogeneous liquid phase was formed (Figure 5 d). Nevertheless, cuspidine was found in all other samples. But due to its dendritic shape, it is indicated that it crystallized during cooling and was not present at 1200 °C in the solid state (Figure 5 a,b,c). When SiC was used, some residuals still existed within the liquid slag at this temperature. It was also present in samples containing antioxidants, but its particle size was smaller. This confirms the previously suggested assumption that the addition of Al and especially Si to SiC counteracts the beneficial properties of SiC by promoting reactions between the components. This was also observed when silicon carbide and silicon nitride are used together (MP9).



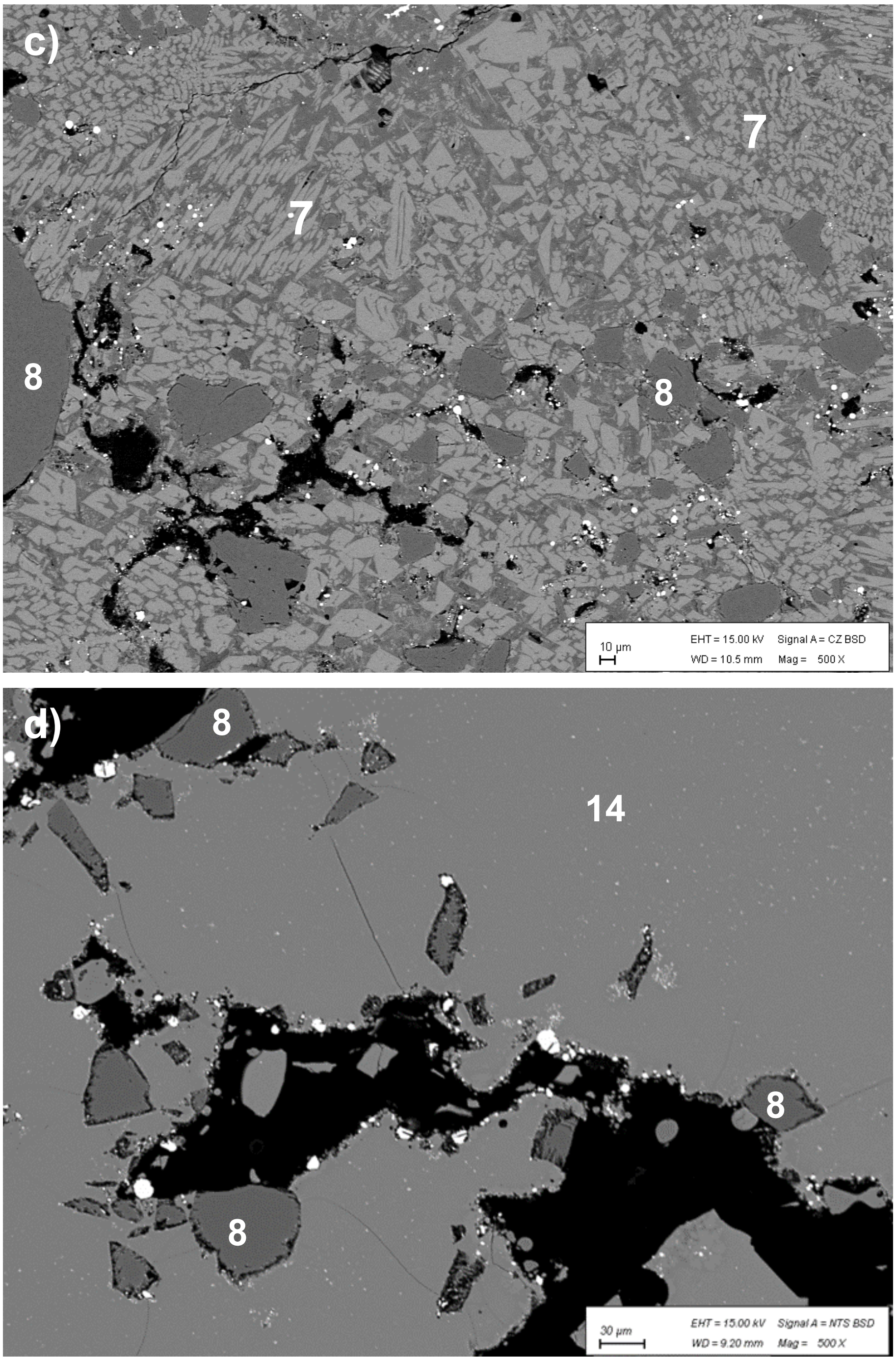


FIG 5 – Backscattered electron image of (a) MP0, (b) MP3, (c) MP5, and (d) MP9 after temperature treatment at 1200 °C for 10 min

(3) fluorite (7) cuspidine: stocky (st.) and dendritic (dent.), (8) SiC, and (14) liquid phase

Reduction of the SiC content

To investigate the effect of the SiC content on the melting behaviour of the mould powder, mixtures were prepared according to the raw material composition given in Table 2. The investigations revealed that for this mould powder composition, SiC content >2.8 wt.% did not have a significant further effect on reducing the reactions of the raw material particles. SiC particles were still present in the samples after the heat treatment at 1200 °C. In contrast, the sample containing solely 1.4 wt.% SiC (MP13) showed the same melting tendency as the mould powder without melt-control additives.

On comparing the results of MP12 with those of the standard carbon-containing mould powder, it is evident that the residuals of the raw materials are detected at only higher temperatures and the amount of the liquid phase is reduced. This indicates that even small amounts of SiC partially inhibited the reaction between the raw material particles and shifted the formation of new solid and liquid phases to higher temperatures. At 1200 °C, SiC is the only solid phase, but its amount is considerably reduced.

CONCLUSIONS

Different melt-control components used to replace carbon in mould powders were investigated. Thermodynamic calculations and laboratory experiments at selected temperatures, together with mineralogical investigations, were conducted to compare their effects. The melting behaviours of the different mixtures were compared with those of the mould powder already used in the continuous casting of steel. These investigations revealed that SiC is a promising substitute for controlling the melting rate of mould powders. For temperatures below 1100 °C, a reduced solid-solid diffusion was observed. This shifted the formation of new solid and liquid phases to higher temperatures and increased the stability of the raw material particles. Owing to its high oxidation resistance, SiC initially remains in a solid state. Thus, the amount of SiO_2 required to form the liquid phase is not available. With increasing temperature, SiC is partially oxidized, and the availability of SiO_2 increases. This influences the formation of new phases. At lower temperatures, where SiC is unoxidized, phases with lower SiO_2 contents are formed. Comparing the amounts of liquid phase with those of the standard mould powder at temperatures below 1000 °C, a lower value was obtained for the SiC-containing samples, even though their solidus temperatures were lower. This agrees with the thermodynamic calculations. Due to the oxidation of Al and Si at lower temperatures, the formation of new phases is supported, which also explains the higher amount of liquid phase at 900 °C. In a subsequent study, the SiC content could be considerably reduced, which could lead to a reduction of at least 27 g CO_2/kg of mould powder compared to the carbon-containing product.

Another possible carbon replacement is silicon nitride. However, its effect is weaker than that of SiC. At temperatures below 1100 °C the reactions between particles were prohibited, but with increasing temperatures, the appearance of the samples after heat treatment was similar to that of the standard mould powder (MP0), because it shows a lower stability than SiC and the necessary SiO_2 amount to form the liquid phase is available at lower temperatures. In addition, the combination of silicon nitride and silicon carbide did not meet expectations with respect to controlling melting behaviour.

The present investigations revealed that the melting rate was lower for loose powders. This can be explained by the close contact between the raw material particles in the case of granules and their production processes. During the production of granulated mould powders, raw material particles are added to a water/binder mixture and homogenized. Sodium carbonate is dissolved and distributed over the entire volume (Han, Wen, Tang and Chen, 2003). Thus, the formation of new phases during heating is promoted. Furthermore, the independent melting of the granules during temperature treatment at 1100 °C and 1200 °C is explained by the diffusion of Na_2O to the surface of the granules during spray drying. Owing to the increased sodium oxide content, the melting temperature is reduced, and the granules start sintering from the boundaries. With an increasing amount of liquid phase, a nearly spherical drop is formed with minimal surface energy. The surface energy would further be reduced by the formation of a coherent liquid phase from single drops. However, owing to the lack of residence time at the annealing temperature, this process was only partially observed during the experiment

The possible pick-up of carbon or nitrogen into the liquid steel during casting, if SiC or Si_3N_4 is used to control the melting behaviour is discussed below. In previous studies, carbon was only partly substituted by nitrides to prevent renitriding of the liquid metal (Debiesme, Radot, Coulombet, Lefebvre, Pontoire, Roux and Damerval,1998). Thus, if Si_3N_4 is used to totally substitute carbon, nitriding will most probably take place during casting. Nevertheless, it was shown that its effect to control the melting rate of a mould powder is weaker than that of SiC being the preferred substitute for carbon. Even for this carbide, only partial substitution of carbon was suggested to ensure the same melting behaviour. If 3 wt.% SiC was used, the carbon content was defined to be <1 wt%. Experiments in contact to the steel revealed a lower effect on recarburisation of the liquid metal (Ning and Jinghao, 1998). As shown in the present paper, similar melting rates were achieved by using solely 2.8 wt.% SiC, which is even lower than in the samples mentioned before. Consequently, recarburisation is not expected to take place. Nevertheless, this assumption has to be confirmed by industrial trials.

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