Effects of Substituting SiO_2 with Oxidisers on the Reaction Performance and Physical Properties of Mould Flux for High Ti-bearing Steel

Zhuo CHEN,¹⁾ Weitong DU,¹⁾ Min ZHANG,²⁾ Qian WANG^{3)*} and Shengping HE³⁾

1) College of Metallurgical and Materials Engineering and Industrial Technology Research Institute, Jiangsu University of Science and Technology, Zhangjiagang, People's Republic of China.

2) Pangang Group Research Institute Co., Ltd., Panzhihua, People's Republic of China.

3) College of Materials Science and Engineering, Chongqing University, Chongqing, People's Republic of China.

(Received on August 2, 2020; accepted on November 25, 2020; J-STAGE Advance published date: January 23, 2021)

In order to eliminate the TiN inclusion emerging from the molten steel and maintain the stable performance of mould flux during continuous casting of high Ti-bearing steel, the influence of extra oxidisers, such as Mn_2O_3 , Mn_3O_4 , and Fe_2O_3 substituting SiO_2 , on the reaction performance and physical properties of CaO– SiO_2 type mould flux was investigated in this study. A detailed study using thermodynamic calculation, X-ray diffraction, and thermogravimetric analysis shows that the oxidisability of oxidisers to TiN, ranging from strong to weak, is Fe_2O_3 , Mn_2O_3 , Mn_3O_4 , and SiO_2 . The oxidisability of SiO_2 in the mould flux is much weaker than that of Mn_2O_3 and Fe_2O_3 . Results show that the precipitation of solid iron after the reaction between the CaO– SiO_2 – Al_2O_3 type or CaO– Al_2O_3 type mould fluxes with Fe_2O_3 and TiN worsens the liquidity of the mould flux and further deteriorate its physical properties. Mn_2O_3 is the best option, with a sustainable change in the physical properties at less than 10 wt.%. Moreover, following the reaction with TiN, the physical properties of the CaO– SiO_2 – Al_2O_3 type mould flux with 15 wt.% Mn_2O_3 show an acceptable change for the application of casting.

KEY WORDS: TiN inclusion; mould flux; high Ti-bearing steel; oxidisers.

1. Introduction

The addition of titanium as a stabiliser is commonly used to bond with residual carbon and nitrogen to stabilise certain stainless steels and some corrosion-resistant alloys to strengthen their corrosion resistance.^{1,2)} However, this process is also accompanied by a significant increase in clogging or mould floater events.^{3–7)} Titanium nitride (TiN) inclusion is precipitated inevitably during the continuous casting owing to the character of titanium which can react with nitrogen at temperatures approaching the liquidus temperature of the steel.⁸⁾ The TiN inclusion derived from the steel rises to the steel-slag interface in mould and changes the properties of mould flux and then impairs the surface appearance of initial solidified shell as a result of the entrapment of mould flux.^{9–11)}

The solubility of titanium nitride in CaO– SiO_2 type mould fluxes is small, at less than 0.5 wt.% at 1 600°C,¹²⁾ despite it exhibiting a slight increase with the increasing SiO_2 con-

tent. Further, TiN was found to react with the composition of mould flux, especially for SiO_2 content in CaO– SiO_2 type mould flux.^{9–11,13)} During the contact between TiN and CaO– SiO_2 type mould flux processing, SiO_2 can act as an oxidising agent and react with TiN to form titanium oxide. In our previous work¹⁰⁾ we investigated the change in the composition of mould slags with different SiO_2 contents following the reaction with 321 stainless steel samples. Additional thermodynamic calculations were performed to verify the experiments. The analysis showed that except for the reaction between TiN and SiO_2 , TiN inclusion also reacted with B_2O_3 , Fe_2O_3 , and Na_2O constituents in mould flux. Meanwhile, SiO_2 would react with [Ti] and [Al] only in case of the slag with higher SiO_2 . For high Ti-bearing steel, a significant concentration of TiN in the liquid steel is precipitated, and the mould or tundish flux will become saturated quickly with respect to TiN, leading to a two-phase slurry of liquid flux and solid TiN. The result would be a further increased viscosity of the mould flux due to solid precipitates of TiN. The assimilation of the TiN inclusion by mould flux is a dominant method for its control or

* Corresponding author: E-mail: q_wang@cqu.edu.cn

removal during the casting process.

TiO₂ formed by the reactions will dissolve within the mould flux. The effect of the TiO₂ contents on the properties of the CaO–SiO₂ type mould flux, such as its viscosity and crystallisation has been studied intensively. Referring to the phase diagram of the CaO–SiO₂–TiO₂ system,¹⁴⁾ the formation of perovskites is strongly dependent on the CaO/SiO₂ ratio. For the CaO–SiO₂ type mould flux, the precipitation of TiO₂ perovskites was observed and a strong effect on viscosity can be the result of the losses of SiO₂ due to the interfacial reaction.^{10,11,13,15)} For the basicity of mould flux of less than 1, the viscosity increases gently with the addition of TiO₂ at less than 10 wt.% and cuspidine is substituted with perovskites or anorthite, which is detrimental to the heat transfer and lubricating properties. For the basicity of mould flux in the range between 1 and 1.5, the viscosity increases sharply with the addition of TiO₂ at more than 10 wt.%.^{16–20)}

While several relevant studies have been conducted, most of these focused on the CaO–SiO₂ type mould flux and its interfacial interaction between the inclusions comprising TiO₂ or TiN, and on the mould flux or the evolution behaviour of non-metallic inclusions of Ti-bearing steel.^{21–23)} No relevant study involved the component optimisation of mould flux for Ti-bearing steel. This study focuses on the assimilation of TiN for high Ti-bearing steels by the addition of extra oxides in the mould flux instead of SiO₂ to avoid affecting the basicity and physical properties. The physical properties were measured for the mould flux with the extra oxides and the effect on the assimilation of TiN was evaluated by thermodynamic calculation and laboratory-scale experiments.

2. Experiments

Analytical-grade Mn₂O₃, Fe₂O₃, Mn₃O₄, B₂O₃, TiO₂, SiO₂, MgO, Al₂O₃, Na₂CO₃, CaCO₃, CaF₂, Li₂CO₃ and Ba₂CO₃ were selected as raw materials in this experiment, with Na₂CO₃, CaCO₃, Li₂CO₃ and BaCO₃ being substituted for Na₂O, CaO, Li₂O and BaO respectively.

2.1. Reaction between Pure Oxidisers and TiN

Pure Mn₂O₃, Mn₃O₄, Fe₂O₃, and SiO₂ were compared and analysed in this study due to their suitable dissolution in the mould flux, absence of environmental hazards and low-melting-point of reaction products. In the case of CaO–SiO₂ type mould flux, the associated loss of SiO₂ is greater, accompanied by an increase in basicity, as discussed in the Introduction. Hence, SiO₂ was considered herein.

The oxidisers and TiN were roasted in a muffle furnace at 200°C for 1 h to remove moisture, and then well mixed in an agate mortar. The mass ratios of mixture are presented in **Table 1**. Due to the multi-valence of manganese, two ratios

of Mn₂O₃ and Mn₃O₄ were investigated herein.

About 10 g of the mixture was compacted into a pure Fe crucible (outside diameter 12 mm, inside diameter 10 mm and height 20 mm). Four samples with the same ratio were heated in a vertical tube furnace with silicon carbide elements, and a sintered alumina working tube (outside diameter 130 mm and inside diameter 110 mm) at fixed 1 350°C for desired reaction time. The samples were taken out one by one after the reaction for 25, 45, and 80 min, respectively. The samples were cooled down to room temperature, subsequently crushed and milled for XRD analyses. In addition, the phases present in samples after mixing was also analysed using XRD method and marked as 0 min. The whole reaction process was carried out under inert argon atmosphere at a flow rate of 600 mL/min. The measurements of reaction rate were taken by thermogravimetric technique and the mixture of 1 g was heated at 20°C/min under inert argon atmosphere at a flow rate of 300 mL/min.

2.2. Reaction between Mould Flux and TiN

The main chemical composition of the experimental mould flux with three different types (three different basicity) are presented in **Table 2**. The traditional CaO–SiO₂ type mould flux with high SiO₂ content was applied for the Ti-bearing steel during continuous casting and marked as CS mould flux herein. About 10 wt.% of bulk sample of TiN was added into mould fluxes directly for the investigation of the reaction between mould flux with oxidiser and TiN. For comparison, CSA mould flux (CaO–SiO₂–Al₂O₃ type mould flux) and CA mould flux (CaO–Al₂O₃ type mould flux) with extra Mn₂O₃ or Fe₂O₃ were studied for the oxidant of TiN in slag system. The properties of CSA mould flux and CA mould flux are designed for the requirement of continuous casting of Ti-bearing steel.

The three different type mould fluxes were prepared by mixing chemical reagents in a mixer. Then, 200 g of the mixture was melted in an induction furnace for 30 min to decompose carbonates and homogenise its chemical composition. Thereafter, the oxidiser was mixed into the fundamental mould flux in a mixer. Part of the mixture was investigated for the reaction experiments and the other part was applied to evaluate the properties of viscosity, melting temperature, and the break point temperature.

2.3. Measurements of Physical Properties

Viscometry was performed with a rotating pure iron bob

Table 1. Mass ratio (wt.%) of oxidisers and TiN.

Sample	Fe ₂ O ₃ :TiN	SiO ₂ :TiN	Mn ₂ O ₃ :TiN	Mn ₃ O ₄ :TiN
Ratio	1.7:1	0.96:1	1.87:1 23.64:1	1.85:1 7.3:1

Table 2. Main compositions (wt.%) and properties of fundamental mould fluxes.

Mould flux	R=CaO/SiO ₂	SiO ₂	CaO	Al ₂ O ₃	MgO	Fe ₂ O ₃	F [−]	Na ₂ O	B ₂ O ₃	η _{l, 300°C, Pa. s}	T _{br} , °C	T _m , °C
CSA	1.97	10.7	21.08	23.66	/	/	14.28	/	2.82	0.114	1 175	1 095
CS	1.18	33.2	39.18	7.22	1.76	0.57	7.29	10.71	/	0.178	1 110	1 105
CA	15.1	3.53	53.30	17.7	1.42	/	7.07	/	1.77	0.166	1 195	1 129

(15-mm diameter) in a pure iron crucible using a viscometer. The viscometer was calibrated at room temperature with standard oils. The break point of viscosity is when crystallisation of mould flux becomes significant during cooling. As a convention, the break point temperature was determined from the viscosity–temperature curve of mould flux in which there is an explicit turning point at a certain temperature. However, for the ambiguous break point in the curves, the temperature was determined from the tangent point of the arc. The melting temperature of mould flux was conducted in the furnace by obtaining the temperature of the hemisphere point. To control the atmosphere inside viscometer and melting temperature furnace, high-purity argon gas (99.9999%) was filled into the chamber at a flow rate of 600 and 300 mL/min, respectively. During the casting of high Ti-bearing steel, the larger titanium pickup is in the accordance with the greater propensity for titanium nitride formation in that steel. While the effect of oxidisers on the physical properties of mould fluxes was measured herein, the effect of TiN and TiO₂ on physical properties was also investigated. The crystallisation ratio of samples on cooling refer to the structure of samples at room temperature, which was approximately obtained by calculating the cross-sectional area of crystal in this study.

3. Results and Discussion

3.1. Thermodynamic Calculation

Thermodynamic calculations with FactSage 7.0 using the databases Fact-PS and FT-oxid were performed to study the reaction of TiN with different oxidisers. Based on the aforementioned literature review, the reaction with SiO₂ was the focus of interest during the casting of Ti-bearing steel. **Table 3** summarises the oxidisers investigated in the present study. Since manganese and iron are multi-valent elements, different mass ratios of oxidisers and TiN were calculated from 1 000 to 1 400°C. The thermodynamics characteristic of the Gibbs free energy for the reaction of TiN and different oxidisers are summarised in **Fig. 1**. It can be seen that the SiO₂ is expected not to react with TiN in the range of 900–1 800°C, and the other three oxidisers, in order of decreasing potency, are Fe₂O₃, Mn₂O₃ and Mn₃O₄, in sequence. The phases after TiN reacting with oxidisers assuming equilibrium conditions are displayed in **Fig. 2**. The equilibrium phase of the SiO₂ and the TiN is coincided to the Gibbs free energy in **Fig. 1**. As shown in **Fig. 2(b)**, Fe₂O₃ was reduced to Fe, and TiN was not found and oxidised to TiO_x which are composed of Ti₄O₇, TiO₂, Ti₃O₅, and FeTi₂O₅. For the Mn₂O₃ and Mn₃O₄, the equilibrium phase of manganese is TiO₂ and Mn₂TiO₄ as shown in **Figs. 2(c) and 2(d)**, implying that the Mn(II) is the stabilised

valence in the equilibrium system. In order to improve the oxygenation efficiency of TiN, the mass ratio of Mn₂O₃ or Mn₃O₄ and TiN should be much higher than that of Fe₂O₃ and TiN.

$$\Delta G^0 = 295\,577 - 86.3T$$

$$\Delta G^0 = -97\,592 - 119.9T$$

$$\Delta G^0 = -100\,455 - 63.2T$$

$$\Delta G^0 = -142\,068 - 52.8T$$

3.2. Reaction between Pure Oxidisers and TiN

The reaction products between pure oxidisers and TiN were investigated for different reaction times. **Figure 3(a)** shows that SiO₂ could not react with TiN at 1 350°C. During the reaction between Fe₂O₃ and TiN, Fe and Fe₃Ti₃O₁₀ were observed at 20 min, and subsequently Fe₃Ti₃O₁₀ was transformed into FeTi₂O₅, as shown in **Fig. 3(b)**. TiN was fully oxidised into TiO₂ and then combined with FeO to form ferrous titanate. As shown in **Figs. 3(c) and 3(d)**, when the mass ratio of Mn₂O₃: TiN was 1.87, Mn(II) was in the equilibrium as Mn₂TiO₄ and MnO phase after the designed reaction time. TiN was oxidised into TiO₂ and combined with MnO to form Mn₂TiO₄ phase, with relatively small amounts of residual TiN remaining in production. When the mass ratio was 23.64:1, excess Mn₂O₃ was present in the initial reactants and was in the equilibrium as Mn₃O₄. However, TiN was fully oxidised into TiO₂ under this mass ratio. As shown in **Figs. 3(e) and 3(f)**, MnO and Mn₂TiO₄ were also observed during the reaction between Mn₃O₄ and TiN. However, the remaining TiN shown in **Fig. 3(e)** proved that the oxidisability of Mn₃O₄ for TiN was fairly inferior to that of both Mn₂O₃ and Fe₂O₃. Hence, Mn₃O₄ will not be considered as an oxidiser in mould flux in the following experiments.

Figure 4 shows the thermogravimetric curves along with an increase in temperature for the reaction of oxidisers and

Table 3. Mass ratios (wt.%) of oxidisers and TiN.

Oxidisers	oxidisers: TiN			
SiO ₂	0.97	/	/	/
Fe ₂ O ₃	0.27	1	1.7	/
Mn ₃ O ₄	0.5	1.85	4	7.3
Mn ₂ O ₃	1.87	2.87	3.87	4.87

Fig. 1. Gibbs free energy for reaction between TiN and different oxidisers. (Online version in color.)

Fig. 2. Thermodynamic calculation results for reaction between TiN and different oxidisers by FactSage. (Online version in color.)

Fig. 3. XRD patterns of reaction products between oxidisers and TiN at different reaction times. (a) $\text{SiO}_2\text{:TiN}=0.96\text{:}1$; (b) $\text{Fe}_2\text{O}_3\text{:TiN}=1.7\text{:}1$; (c) $\text{Mn}_2\text{O}_3\text{:TiN}=23.64\text{:}1$; (d) $\text{Mn}_2\text{O}_3\text{:TiN}=1.87\text{:}1$; (e) $\text{Mn}_3\text{O}_4\text{:TiN}=7.3\text{:}1$; (f) $\text{Mn}_3\text{O}_4\text{:TiN}=1.85\text{:}1$.

TiN. While the sample mass began to decrease at 600°C for both Mn_2O_3 and Fe_2O_3 , nitrogen was released during the reaction. If the TiN was totally oxidised by Mn_2O_3 and

Fe_2O_3 , approximate 6.6 and 7 wt.% decrement could be exhibited in the bulk sample respectively. However, for the curve of the mass change, the maximum values of 2.3 and

3.6 wt.% for the sample were decreased, which proved that 46 and 57 wt.% TiN was oxidised by Mn_2O_3 and Fe_2O_3 and reaction rate was calculated as 0.055 and 0.075 wt.%/min, respectively. Therefore, the oxidation rate and oxidation ratio of Fe_2O_3 are slightly higher than those of Mn_2O_3 . During the later period, the sample mass clearly increased, which implied that the residual TiN might be oxidised by air.

3.3. Reaction between Mould Flux with Different Oxidisers and TiN

Based on the calculation and experiments of the reaction

Fig. 4. Thermogravimetric curves of Mn_2O_3 and Fe_2O_3 reacting with TiN. (Online version in color.)

between oxidisers and TiN, the lower mass ratio (1.87:1) of Mn_2O_3 and TiN in Table 1 were investigated herein, and meanwhile the mass ratio of Fe_2O_3 or SiO_2 and TiN were 1.7 and 0.97, respectively. The main phases of mould flux following the reaction with TiN (as determined by XRD) are shown in Figs. 5(a)–5(d). For the reaction between CSA mould flux with Mn_2O_3 and TiN, small amount of TiN was found at 1 000°C and then disappeared at 1 300°C and 1 400°C, resulting in the formation of titanate phases (BaTiO_3 , CaTiO_3 , NaTi_2O_4). Reduction of the Mn_2O_3 yielded the MnAl_2O_4 phase. For the reaction between CA mould flux with Mn_2O_3 and TiN, TiN and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{F}_2$ were observed after cooling the samples held at 1 000–1 400°C invariably, which illustrated that the majority of TiN could not be oxidised effectively in this slag. However, CaTiO_3 disappeared at 1 400°C and manganese-based phases was not found because these phases were not the main phase in the slag and could not be analysed accurately by XRD analysis.

However, the suspended solid (about 13 g) was precipitated unexpectedly during the reaction between CSA or CA mould flux with Fe_2O_3 and TiN, and separated with liquid slag. SEM analyses indicated that bulky pure iron remained in the high-melting-point material as well as with TiN and slag phases, as shown in Fig. 6. This means that Fe_2O_3 reacted with TiN in mould flux and was reduced to Fe which is expected to decrease the fluidity of mould flux, and then lowered the oxidation of TiN. For the CSA mould flux with Fe_2O_3 , the main phase of residual liquid slag with high viscosity was composed of CaTiO_3 , Fe, and $\text{Ca}_4\text{Ti}_9\text{O}_{17}$,

Fig. 5. XRD patterns of slag after reaction between mould flux with oxidisers and TiN. (a) CSA mould flux + Mn_2O_3 ; (b) CA mould flux + Mn_2O_3 ; (c) CSA mould flux + Fe_2O_3 ; (d) CA mould flux + Fe_2O_3 .

Fig. 6. SEM analysis of high-melting material during reaction between mould flux with Fe_2O_3 and TiN at 1400°C; (a) CSA mould flux; (b) CA mould flux.

Fig. 7. XRD patterns of slag after reaction between CS mould flux and TiN.

whereas following the reaction between CA mould flux with Fe_2O_3 and TiN with relatively lower viscosity the residual liquid slag was mainly composed of CaF_2 , $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{F}_2$, and LiAlO_2 .

The suspended solid also emerged in CS mould flux during the contact with TiN. As shown in Fig. 7(a) and Table 4, the oxidation products TiO_2 combined with CaO in mould flux to form CaTiO_3 . TiN appeared in liquid slag at 1000°C and 1300°C, probably because the high viscosity of mould flux after the reaction offers a weak flow performance and then prevents the oxidation of TiN. The phase of $\text{Fe}_{0.5}\text{Si}_{0.5}$ in Fig. 7(b) shows that this indeed is the result of the reaction between Fe_2O_3 or SiO_2 and TiN.

3.4. The Effects of TiN and TiO_2 on the Physical Properties of Mould Flux

Figure 8 illustrates the effects of TiN on viscosity at 1300°C ($\eta_{1300^\circ\text{C}}$), melting temperature (T_m), break point temperature (T_{br}) and crystal ratio of mould flux with different basicity. It is clear that the viscosity of the CS mould flux is notably impressionable to the TiN content, which also increase the crystal ratio to a certain extent with the increase of TiN. This implies that in this case the SiO_2 content in the CS mould flux is reduced by TiN, and the precipitated CaTiO_3 phase increases the crystal ratio of the mould flux. The yield of titanium oxide has similar amphoteric characteristics with Al_2O_3 in CS mould flux.^{24,25)}

Table 4. Compositions of slag phase in Fig. 6 detected by EDS analysis.

Slag	O	Si	Al	Ca	Ti	Mg	Fe	Ba
CSA mould flux	40.65	12.34	5.97	23.84	5.33	/	1.45	10.42
CA mould flux	57.87	/	16.64	24.13	0.46	0.90	/	/

Hence, the variation in these properties shows a somewhat similar trend.

For CSA and CA mould flux, with the addition of TiN of less than 8 and 5 wt.%, respectively, the $\eta_{1300^\circ\text{C}}$ showed a steady change, and then increased markedly. The crystal ratio decreased slightly with the increase of TiN, probably because a limited amount of SiO_2 in CSA mould flux was reduced which increased the basicity of the mould flux. The crystal ratio of CA mould flux stayed at 100% with the increase of TiN, which indicates that TiN did not react with SiO_2 so the basicity was well maintained for the CA mould flux.

The viscosity-temperature curves show an explicit tendency of viscosity and break point temperature, as shown in Fig. 9. For the CS mould flux, the measured increase in the viscosity is hence much higher than the weak solubility of TiN, probably because the large amounts of perovskite precipitates offer a much larger hindrance to flow. This means that the properties change during casting of high Ti-bearing

Fig. 8. Effect of TiN on viscosity at 1300°C, melting point, break point temperature, and crystallization ratio of mould fluxes. (Online version in color.)

Fig. 9. Effect of TiN on viscosity-temperature curves of mould fluxes. (a) CSA mould flux; (b) CS mould flux; (c) CA mould flux. (Online version in color.)

steel (since, at the later period of casting, the CS type mould flux and, hence, the shim start to precipitate the perovskite and form crust).

As an amphoteric substance, the role of TiO₂ exhibits both network forming and network breaking properties. With the different slag components, the content of various coordination states of Ti⁴⁺ will change significantly.^{26,27} The effect of TiO₂ on the physical performance of mould flux is shown in Fig. 10. With TiO₂ increasing, the viscosity of CSA and CS mould flux at 1300°C mildly decreases by depolymerising the complex Si-O-Si structure, which agreed with the findings of other studies.^{17,19,26} Hence, a higher amount of F⁻ in the CSA mould flux is beneficial to the solubility of TiO₂. With more than 6 wt.% and 10 wt.% of TiO₂ added in CA and CS mould fluxes, respectively, the viscosity of both mould fluxes increases significantly since the perovskite, instead of the cuspidine, begins to precipitate, with a lower crystallisation temperature. The viscosity

of CA mould flux decreases gently with the increase in TiO₂ content, when it is less than 6 wt.%, and then deteriorates sharply, with a higher TiO₂ content. Based on the previous study of molecular dynamics analysis,²⁶ Al-O-Al might replace with Ti-O-Al bond resulting in the depolymerisation of [AlO₄]⁵⁻ network at lower TiO₂ content. With TiO₂ up to 6 wt.%, 12CaO·7Al₂O₃ replace by perovskite gradually.

The effect of TiO₂ on the break point temperature of the three mould fluxes shows a descending trend at first followed by a rising trend, as shown in Fig. 10(c). The viscosity-temperature curves in Fig. 11 it can be assumed that TiO₂ display as depolymerisation of Si-O-Si network in the CSA mould flux, and the Al-O-Al network in the CA mould flux. However, when TiO₂ is more than 4 wt.%, the break point temperature will increase due to the precipitation of CaTiO₃ in the CSA and CA mould fluxes. The change in the viscosity of CaO-SiO₂ slag is much more

Fig. 10. Effect of TiO_2 on viscosity at 1300°C, melting point, break point temperature, and crystallization ratio of mould fluxes. (Online version in color.)

Fig. 11. Effect of TiO_2 on viscosity-temperature curves of mould fluxes. (Online version in color.)

obvious. According to the phase diagram of CaO-SiO₂-TiO₂, we discovered the presence of perovskite formation area, which proves that perovskite has a crucial effect on the viscosity of mould flux.

With the increase in the amount of TiO_2 , its influence on the melting temperature showed a uniform trend of increase. The melting temperature of the CSA and CS mould fluxes did not significantly change, and the melting temperature of CA mould flux increased linearly due to the great influence caused by the precipitation of perovskite. These results are consistent with the viscosity-temperature curve.

Similar to the effect of TiN, the crystal ratio of CS mould flux gradually increases with an increase in TiO_2 as shown in Fig. 10(d). If 3 wt.% TiN is fully oxidised, 4 wt.% TiO_2 can be achieved in mould flux. Hence, the crystal ratio of CS mould flux with 4 wt.% TiO_2 is close to that with 3 wt.% TiN, whereas the crystal ratio of CS mould flux with 5 wt.% TiN is smaller than 6.5 wt.% TiO_2 , which implies

that 3 wt.% < TiN < 5 wt.% in the CS mould flux could be almost completely oxidised to TiO_2 . For the CSA and CS mould fluxes with less than 6.5 wt.% TiO_2 , the decrement of crystal ratio is smaller than that of the equivalent TiN in the mould flux, which also proves that a small amount of TiN was oxidised. In contrast, the CSA and CS mould fluxes with less than 6.5 wt.% TiO_2 can accelerate the precipitation of perovskite and increase the crystal ratio simultaneously.

3.5. The Effects of the Oxidisers on Physical Properties of Mould Flux

Figures 12 and 13(a)–13(d) shows the measured effect of increased Mn_2O_3 and Fe_2O_3 on the physical properties of the CSA and CA mould fluxes. Clearly, increases in Mn_2O_3 and Fe_2O_3 content of up to 17 wt.% gives noticeable lower viscosities. Hence, it is possible that Mn_2O_3 or Fe_2O_3 can eliminate the deterioration in the viscosity with the ascending pickup of TiN in the mould flux. With the higher Mn_2O_3

Fig. 12. Effect of different oxidisers on physical properties of CSA mould flux and CA mould flux. (Online version in color.)

Fig. 13. Effect of different oxidisers and TiN on viscosity-temperature curves of CSA mould flux and CA mould flux. (Online version in color.)

addition, the break point temperature of the CSA mould flux increases and that of the CA mould flux decreases in the case of less than 10 wt.%, and then increases sharply. Comparatively, the effect of Fe_2O_3 on the break point temperature of the CSA and CA mould fluxes is weak. Fe_2O_3 has the effect of lowering the melting point of the CSA and CA mould fluxes, which is consistent with the results of Wang.²⁸⁾ The melting point has a reasonable increase with the increase in Mn_2O_3 concentration, in the range of

0–10 wt.%. When the addition of Mn_2O_3 exceeds 10 wt.%, the change in the melting point is similar to the change of the break point temperature, which increases remarkably, resulting in a serious deterioration of the performance of the mould flux.

Given the low solubility of titanium nitride, the absence of titanium nitride as a separate phase implies that the titanium is present in the mould flux as an oxide, hence titanium pickup by the mould flux occurs by the reactions between

Table 5. Effect of different oxidisers and TiN on properties of mould fluxes.

Mould flux	$\eta_{1300^\circ\text{C}}$, Pa.s	T_{br} , °C	T_{m} , °C
CSA mould flux+15%Mn ₂ O ₃ +9%TiN	0.052	1 176	1 095
CSA mould flux+15%Fe ₂ O ₃ +9%TiN	0.944	1 200	1 242
CA mould flux+15%Mn ₂ O ₃ +9%TiN	0.056	1 236	1 184
CA mould flux+15%Fe ₂ O ₃ +9%TiN	0.85	1 198	1 251

oxides and TiN. Hence, the physical properties of the mould flux with Fe₂O₃ or Mn₂O₃ were investigated following the reaction with TiN, as shown in **Table 5** and Figs. 13(e)(f). In both cases, steady properties were achieved for the mould flux with Mn₂O₃ due to the effective oxidation and solubility of oxidative products. However, the properties of both mould fluxes with Fe₂O₃ deteriorate dramatically. From the analysis of XRD, Fe as a reduction product was precipitated in the mould fluxes and hence physically deteriorated their apparent properties.

4. Conclusions

The physical properties of the mould flux with extra oxides were investigated in this study. Based on the experimental results and thermodynamic calculation, the following conclusions can be drawn:

(1) The ability of SiO₂ to oxidise TiN from strong to weak, was as follows: Fe₂O₃, Mn₂O₃, Mn₃O₄, and SiO₂. For pure SiO₂, the reaction with TiN cannot occur. The oxidation rate of Fe₂O₃ is slightly faster than that of Mn₂O₃, and the oxidisability of SiO₂ in the mould flux is much weaker than that of Mn₂O₃ and Fe₂O₃.

(2) While pickup of TiN by the mould flux is inevitable during the casting of high Ti-bearing steel, this can deteriorate the heat transfer and lubrication conditions. For CaO–SiO₂ mould flux with a lower basicity, not only the loss of silica is greater but also the amount of titanium oxide is substantially larger due to the oxidation of TiN, resulting in an increased basicity and susceptible precipitation of perovskite in this mould flux. The solidification of solid phase in the mould flux causes an irretrievable deterioration in the apparent viscosity, melting temperature, and break point temperature.

Although Fe₂O₃ can lower the viscosity and melting temperature of the CSA and CA mould fluxes, the precipitation of solid iron following the reaction between the CSA or CA mould fluxes with Fe₂O₃ and TiN should be responsible for the sharp increase in physical properties. Hence, selection of Fe₂O₃ as an oxide for the mould flux is inappropriate during the casting of high Ti-bearing steel.

In this study, Mn₂O₃ was found to be the best option from

the used oxidisers, resulting in a sustainable change in the physical properties of less than 10 wt.%. Moreover, following the reaction with TiN, the physical properties of the CSA mould flux with 15 wt.% Mn₂O₃ showed an acceptable change for the application of casting.

Acknowledgements

The authors gratefully express their appreciation to National Natural Science Foundation of China (No. 52074054 and No. U1660204) and the fourth batch of major science and technology projects in panxi experimental base (low cost manufacturing technique of titanium alloyed high-strength and high-toughness steel and its application).

REFERENCES

- 1) M. B. Leban and R. Tisu: *Eng. Fail. Anal.*, **33** (2013), 430.
- 2) J. Cavazos, I. Gomez and M. Guerrero-Mata: *Mater. Sci. Technol.*, **27** (2011), 530.
- 3) Y. Gao and K. Sorimachi: *ISIJ Int.*, **33** (1993), 291.
- 4) S. Basu, S. K. Choudhary and N. U. Girase: *ISIJ Int.*, **44** (2004), 1653.
- 5) J. Y. Li, G. G. Cheng, Q. Ruan, J. X. Pan and X. R. Chen: *Metall. Mater. Trans. B*, **50** (2019), 2769.
- 6) Z. Chen, M. Li, X. F. Wang, S. P. He and Q. Wang: *Metals*, **9** (2019), 635.
- 7) J. H. Lee, M. H. Kang, S. K. Kim, J. H. Kim, M. S. Kim and Y. B. Kang: *ISIJ Int.*, **59** (2019), 749.
- 8) M. T. Nagata, J. G. Speer and D. K. Matlock: *Metall. Mater. Trans. A*, **33** (2002), 3099.
- 9) L. J. Zhou, Z. H. Pan, W. L. Wang, J. Y. Chen, L. W. Xue, T. S. Zhang and L. Zhang: *Metall. Mater. Trans. B*, **51** (2020), 85.
- 10) Z. Chen, Y. B. Zhang, S. P. He, Z. R. Li and Q. Wang: *Can. Metall. Q.*, **58** (2019), 464.
- 11) H. Todoroki, T. Ishii, K. Mizuno and A. Hongo: *Mater. Sci. Eng. A*, **413** (2005), 121.
- 12) B. Ozturk: *Metall. Trans. B*, **23** (1992), 523.
- 13) R. Nunnington and N. Sutcliffe: *Proc. 59th Electric Furnace Conf., (Phoenix, AZ), Iron and Steel Society, Warrendale, PA*, (2001), 361.
- 14) V. Daněš and I. Nerád: *Chem. Pap.*, **56** (2002), 241.
- 15) S. K. Michellic and C. Bernhard: *Scanning*, **2017** (2017), Article ID 2326750.
- 16) T. Kishi, H. Takeuchi, M. Yamamiya, H. Tsuboi, T. Nakano and T. Ando: *Nippon Steel Tech. Rep. Overseas*, (1987), No. 34, 11.
- 17) A. Arefpour, A. Monshi, T. Khayamian and A. Saidi: *Engineering*, **4** (2012), 435.
- 18) L. F. Sun, H. P. Wang, M. F. Jiang, Q. Z. Lin, C. L. Liu and Y. Zou: *Adv. Mater. Res.*, **287–290** (2011), 227.
- 19) Z. Wang, Q. F. Shu, X. M. Hou and K. C. Chou: *Ironmaking Steelmaking*, **39** (2012), 210.
- 20) J. Y. Li, G. G. Cheng, Q. Ruan, J. X. Pan and X. R. Chen: *Ironmaking Steelmaking*, **47** (2020), 31.
- 21) S. K. Michellic, D. Loder, T. Reip, A. A. Barani and C. Bernhard: *Mater. Charact.*, **100** (2015), 61.
- 22) D. C. Park, I. H. Jung, P. C. Rhee and H. G. Lee: *ISIJ Int.*, **44** (2004), 1669.
- 23) M.-A. V. Ende, M. X. Guo, R. Dekkers, M. Burty, J. V. Dyck, P. T. Jones, B. Blanpain and P. Wollants: *ISIJ Int.*, **49** (2009), 1133.
- 24) B. Mysen and D. Neuville: *Geochim. Cosmochim. Acta*, **59** (1995), 325.
- 25) P. P. Bihuniak and R. A. Condrate: *J. Non-Cryst. Solids*, **44** (1981), 331.
- 26) J. B. Kim and I. Sohn: *ISIJ Int.*, **54** (2014), 2050.
- 27) J. L. Li, Q. F. Shu and K. C. Chou: *ISIJ Int.*, **54** (2014), 721.
- 28) H. M. Wang, L. L. Yang, G. R. Li, X. Zhu, H. Zhu and Y. T. Zhao: *J. Iron Steel Res. Int.*, **20** (2013), 21.