Prediction of Melting Paths of Wollastonite-Containing Compositions

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Abstract

The article analyzed the main groups of thermal insulation (TIM) and slag-forming (SFM) mixtures produced by leading foreign companies: acidic ones based on the SiO_2–Al_2O_3 system, basic ones based on the CaO–MgO–Al_2O_3 system and medium basic ones based on the CaO (MgO) system–Al_2O_3–SiO_2. It is shown that achieving the necessary properties of the SFM and TIM requires strict observance of the mass content of the components of mixtures produced on the basis of synthetic materials in granular form with a given dispersion. Compliance with a given composition and dispersion is associated with the need to provide a given melting temperature (for intermediate ladles 1 250–1 450 °C, for molds 950–1 150 °C), neutrality to the cast metal, protection of the melt from secondary oxidation, minimization of heat loss from the melt mirror, absorption of non-metallic inclusions of various natures (Al_2O_3, CaO, SiO_2, TiO_2, less often MgO-containing) and sizes; as well as a number of specific requirements: compatibility with the working layer of the lining of the bucket, maintaining the work of the stoppers, minimizing harmful gaseous emissions, *etc*. It is known that Al_2O_3, Ti_xO_y, and CaO refractory inclusions in steel cause the majority of defects on the surface of a cold-rolled sheet, therefore, the aim of the work was to analyze the physicochemical regularities and melting paths of the wollastonite-containing compositions during the assimilation of nonmetallic inclusions by them. To analyze the melting paths of the wollastonite-containing compositions in the CaO–Al_2O_3–SiO_2 system, a diagram of the primary crystallization field of anorthite and the adjacent boundary curves is shown, indicating the directions of temperature drop and designating invariant points. The presented scheme adequately reflects the topological regularities of the state diagram of the CaO–Al_2O_3–SiO_2 system. To analyze the melting paths of the wollastonite-containing SFM compositions during the assimilation of TiO_x impurities from steel melts, a diagram of the primary crystallization field of $CaTiSiO_5$ sphene with adjacent boundary curves, the direction of temperature drop, and the designation of invariant points is presented. It is shown that steric and kinetic factors have a predominant effect on the formation of the three-layer layer in the SFM (molten, partially molten and unmelted layers). The influence will be the lesser, the more uniform the thickness of the entire SFM layer (when it is heated from the melt mirror), and the competing processes of solid–phase interaction will start, which provide a gradual accumulation of more refractory compounds and increase the melting temperature of the SFM.

Key words：wollastonite-containing compositions; slag-forming mixtures; heat-insulating mixtures; solid–phase interaction

1 Introduction

The intensification of the process of continuous casting of steel and the increase in the scale of its implementation in steelmaking are due to the expansion of the field of application of critical metal products from continuously cast billets of various grades, profiles and sizes.

Production of a "clean" steel for responsible purposes[1] provides special requirements not only on the quality of continuously cast and rolled metal, but also on the reduction of

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the production costs and the improvement of environmental conditions. The problems of reducing non-metallic inclusions in steel after out-of-furnace refining, precipitation of residual non-metallic inclusions in the melt and preventing re-oxidation of steel during casting largely determine the quality of the final product and are solved at advanced metallurgical enterprises through the use of slag-forming (SFM) and thermal insulation (TIM) mixtures.

Such mixtures are differentiated by their use in the intermediate ladles and molds of continuous casting machines (CCM), in which they perform different functions. Leading foreign companies have mastered the large-capacity production of TIM and SFM of three groups of compositions[2-11]: acidic (based on the SiO_2–Al_2O_3 system), basic (based on the CaO–MgO–Al_2O_3 system), and medium basic (based on the CaO (MgO)–Al_2O_3–SiO_2 system).

Medium-base compositions are most in demand due to increased versatility; as a separate ingredient, they often contain wollastonite or have a ratio of components close to the stoichiometry of wollastonite.

At the same time, all compositions contain a number of special additives for regulating operational properties and are subdivided into fluoride and fluoride-free, as well as carbon and carbon-free (for the steel with regulated low carbon content—dynamo, transformer, and IF-steel for the automotive industry). For intermediate ladles, a separate two-layer variant of application (a combination of SFM + TIM) is more common, and for crystallizers a single-component variant of the mixture is more preferable[1,3,6].

The most modern compositions have strict limitations on permissible deviations in the content of components and do not include previously widely used ingredients: ash and slag waste, Portland cement, glass break, *etc*.

However, such compositions contain a significant amount of pre-synthesized components (sintered or fused) and are not obtained on grinding and mixing equipment, but pre-granulated, with a given fractional composition and the shape of granules in the form of hollow spherulites obtained in tower spray dryers[9-11]. Accordingly, the task of obtaining modern SFM and TIM has become more complicated at the present stage, it has left the field of solutions by metallurgical specialists and seems relevant for the technology of refractory non-metallic materials.

At its core, the task of obtaining modern SFM compositions is inverse to the tasks traditionally solved by refractory companies. To solve this problem, it is also required to provide a given melting temperature (usually for intermediate ladles 1 250–1 450 °C, for molds 950–1 150 °C), neutrality to the cast metal, protection of the melt from secondary oxidation, minimization of heat loss from the melt mirror, active prolonged interaction and absorption of non-metallic inclusions of various natures (Al_2O_3, CaO, SiO_2, TiO_2, less often MgO–containing) and sizes; as well as a number of specific requirements: compatibility with the working layer of the lining of the bucket, maintaining the work of the stoppers, minimizing harmful gaseous emissions, *etc*.

The purpose of the work was to analyze the physical and chemical regularities and melting courses of the wollastonite-containing compositions as they assimilate non-metallic inclusions, primarily Al_2O_3.

These issues are important for controlling the processes of SFM penetration, selecting the necessary additives for regulating the viscosity and wetting ability of the forming melt, as well as the level of assimilation ability with respect to non-metallic inclusions.

2　Theoretical Statements

The state diagrams of the CaO–SiO_2 and CaO–Al_2O_3–SiO_2 systems are important for the technologies of Portland cement, alumina cement and aluminosilicate refractories. The compounds in these systems have been studied in sufficient details, and modern research mainly addresses the issues of refining the melting points and the nature of the crystalline structure. Fundamentally new information (on solid-phase relationships, the position and shape of the fields of primary crystallization of compounds, *etc*.) in comparison with classical publications[12, 3] in recent years has not been established.

Wollastonite exists in two polymorphic modifications: wollastonite low-temperature β-CS (hereinafter, abbreviations C—CaO, S—SiO_2, A—Al_2O_3 are accepted) and high-temperature α-CS (pseudowollastonite). The polymorphic transformation temperature is 1 125 °C. To achieve the goal of the study, it seems sufficient to use the traditional methods of physicochemical analysis of state diagrams, detailed in the educational literature on the technology of refractory non-metallic materials, for example [14].

Pseudowollastonite melts congruently at 1 544 °C[12], and if there is an excess of SiO_2 in the wollastonite-containing composition in excess of $CaSiO_3$ stoichiometry, the onset melting temperature decreases to 1 436 °C due to the presence of minimal eutectic in the CaO–SiO_2 system. In this case, silica and pseudowollastonite are inert with respect to mutual solid-phase solubility.

The presence of an excess of CaO in the wollastonite-containing composition over the stoichiometry of $CaSiO_3$ will determine the presence of hydraulically active calcium silicates (C_3S, C_2S and, possibly, C_3S_2) in the synthesis of the material, which directly follows from the consideration of the state diagram of the CaO–SiO_2 system[12].

The presence of crystalline hydrate compounds in the composition of the SFM is undesirable because of their decomposition upon contact with the melt and dissolution of the liberated hydrogen in it, which leads to steel embrittlement. In addition, the presence of CaO increases the initial melting temperature (1 460 °C). To analyze the melting paths of the wollastonite-containing composition in the CaO–Al_2O_3–SiO_2 system, a diagram of the primary crystallization field of anorthite, adjoining boundary curves with the directions of temperature drop (indicated by arrows) and the invariant points (a, b, c, d, e, f) and

the corresponding connodes is shown in Fig. 1.
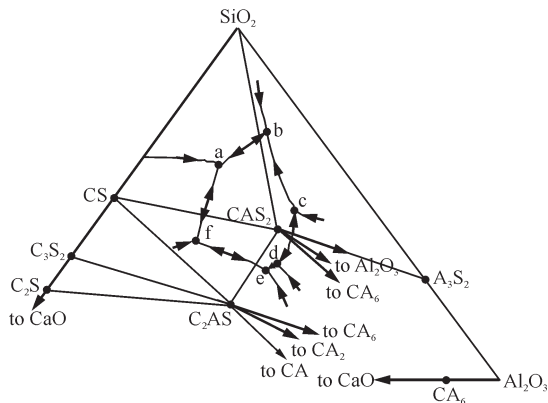
Fig. 1 Field diagram of primary crystallization of anorthite in CaO–Al$_2$O$_3$–SiO$_2$ system

The presented scheme adequately reflects the topological regularities of the state diagram of the CaO–Al$_2$O$_3$–SiO$_2$ system, which follows from the equality of the number of boundary curves (six) making up the primary crystallization field of anorthite CAS$_2$, and the number of connecting connodes (six) from anorthite to the compositions of the compounds whose primary crystallization fields limit the field of anorthite.

When analyzing the melting paths of the wollastonite-containing composition, it will be taken into account that under thermodynamically equilibrium conditions they are strictly opposite to crystallization paths.

Figure 2 shows a diagram of the primary crystallization field of the CaTiSiO$_5$ sphene with adjoining curves, the direction of temperature drop, and the designation of invariant points (l, m, n, p, s). This scheme was used to analyze the melting paths of wollastonite-containing SFM compositions during the assimilation of TiOx impurities from steel melts.
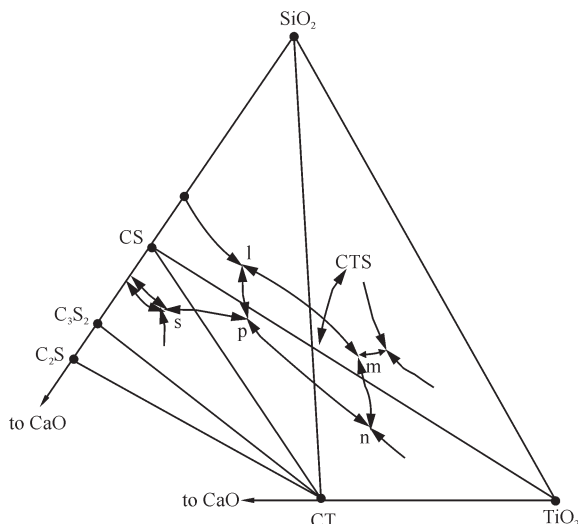
Fig. 2 Scheme of primary crystallization field of sphene in CaO–TiO$_2$–SiO$_2$ system

The analysis technique involved the selection of a figurative point on the CaO–SiO$_2$ side of the concentration triangle of the triple oxide systems under consideration, corresponding to a certain SFM composition.

The assimilation of impurities (Al$_2$O$_3$ or TiO$_2$) by the initial composition of the SFM corresponds to the movement of the figurative point in the direction of the corresponding vertex of the concentration triangle of the analyzed system.

At the same time, structural elements of the state diagram corresponding to specific physicochemical processes change. The vertices of an elementary triangle determine the combination of three compounds with a minimum melting point at an invariant point inside this triangle. The intersection of the connodes during the transition from one elementary triangle to another determines the development of a solid-phase exchange reaction with the participation of compounds whose composition points lie at the ends of the corresponding connodes. The path along the connodes can pass through the "crossing" point (Van Rijn), at which the connode crosses the boundary curve between the fields of primary crystallization, corresponding to a no monotonic change in the melting temperature of the composition.

The analysis results of the above processes were compared with general ideas about the processes in the SFM located on the surface of the steel melt under the assumption that the lower layer of the SFM is represented by the melt, the middle transition layer contains both the melt and the solid grains of the SFM, and the upper one is in the solid state.

3 Results and Discussion

According to literature[1], the main number of defects on the surface of a cold rolled sheet ("veil", "rolled pollution", "rolled crack", "delamination", *etc*.), as well as in a continuously slab cast billet, are caused by refractory inclusions Al$_2$O$_3$, Ti$_x$O$_y$, and CaO in steel.

The reason for the presence of alumina in steel can be not only the lining used and the corundum-containing refractory, but also the use of metallic aluminum for deoxidation of the melt.

Wollastonite-containing SFM compositions are capable of assimilating a significant amount of Al$_2$O$_3$ solids from the melt. This is due to the fact that the connecting line between the compositions CS and C in the state diagram crosses the connodes CAS$_2$ (anorthite)–C$_2$AS (gelenite) and CAS$_2$–CA$_6$, *i.e.* at SFM heating temperatures, solid-phase exchange reactions as follows should occur before melting according to Table 1.

$$3CS+2A=C_2AS+CAS_2 \tag{1}$$
$$2CS+7A=CAS_2+CA_6 \tag{2}$$
$$\text{In total: } 5CS+9A=2CAS_2+C_2AS+CA_6 \tag{3}$$
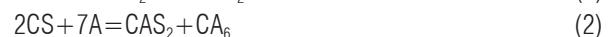
Interaction according to reaction (1) will result in the formation of a three-phase combination, the composition of the compounds in which forms the elementary triangle CS–C$_2$AS–CAS$_2$ with the eutectic present in it at 1 265 °C (point f in Fig. 1). Accordingly, melting will begin at a eutectic temperature, and not yet melted, overlying layers of the SFM will continue to heat up, which will lead to further assimilation of Al$_2$O$_3$ due to the development of reaction (2).

Table 1 Changing path of a figurative point depending on composition

Composition	Type of impurity		Path of a figurative point			
	Al_2O_3	TiO_2	Through elementary triangles	Eutectic temperature in an elementary triangle /℃	Crossing (X) or along (−) the connodes	Temperature of the figurative point /℃
CS	+	-	$CS–CAS_2–C_2AS$ $CAS_2–C_2AS–CA_6$ $C_2AS–CA_6–A$	1 265; 1 380	(X) $CAS_2–C_2AS$, (X) $C_2AS–CA_6$	
	-	+	-	-	(−) CS–CTS, (−) CTS–T	1 353 1 375
CS with excess of C (S 40%–50%)	+	-	$C_3S_2–CS–C_2AS$ $CS–CAS_2–C_2AS$ $CAS_2–C_2AS–CA_6$ $C_2AS–CA_6–A$	1 310; 1 265; 1 380	(X) $CS–C_2AS$, (X) $CAS_2–C_2AS$, (X) $C_2AS–CA_6$	
	-	+	$C_3S_2–CS–CT$ CS–CTS–CT CTS–CT–T	1 398; 1 348; 1 365	(X) CS–CT, (X) CT–CTS	
CS with excess of S (S 50%–65%)	+	-	$S–CS–CAS_2$ $CS–CAS_2–C_2AS$ $CAS_2–C_2AS–CA_6$ $C_2AS–CA_6–A$	1 170; 1 265; 1 380	(X) $CS–CAS_2$, (X) $CAS_2–C_2AS$, (X) $CAS_2–CA_6$	
	-	+	S–CS–CTS S–CTS–T	1 318; 1 365	(X) S–CTS	
CS with excess of S (S>65%)	+	-	$S–CS–CAS_2$ $S–CAS_2–A_3S_2$ $CAS_2–A_3S_2–A$	1 170; 1 345	(X) $S–CAS_2$, (X) $CAS_2–A_3S_2$	
	-	+	$S–CS–CAS_2$ S–CTS–T	1 170; 1 365	(X) S–CTS	

Note: 1) In the compositions with an excess of one of the components, the total SiO_2 content is approximately indicated.

2) In parentheses there are the temperatures of the onset melting of the composition included in the concentration region of the corresponding elementary triangle, as well as the temperatures of the crossing points at the intersection of the boundary curves and the connodes (Van Rijn points).

The initial CS and products of reaction (2) belong to the elementary triangle $CAS_2–C_2AS–CA_6$ with the eutectic present in it (point e in Fig. 1). Accordingly, the melting temperature in such a three-phase combination will shift to a higher eutectic value of 1 380 °C (point e in Fig. 1)[13].

Further heating of the SFM composition based on wollastonite will be characterized by two competing processes: continuing melting with the formation of a melt corresponding to the composition of the eutectic (at point e in Fig. 1), and on the other hand, by the accumulation of refractory compounds: CAS_2 (1 550 °C), C_2AS (1 593 °C), and CA_6 (1 850 °C)[13].

For SFM, the composition of which is enriched in CaO over stoichiometry of wollastonite, a higher initial melting temperature will be observed, since the connecting line with Al_2O_3 crosses the $CS–C_2AS$ connode, and the primary solid-phase interaction will take place between calcium silicate and alumina by the reaction as follows.

$$C_3S_2+A=CS+C_2AS \qquad (4)$$

In this case, the three-phase combination formed by heating the SFM (C_3S_2, CS, and C_2AS) begins to melt at 1 310 °C[13] —in the eutectic lying inside the corresponding elementary triangle.

Only with further assimilation of Al_2O_3 and the development of reaction (4) will conditions be created for the formation of three-phase combinations $CS–C_2AS–CAS_2$, and then $C_2AS–CAS_2–CA_6$, which are characterized by eutectic melting at 1 265 and 1 380 °C (points f and e in Fig. 1).

The non-uniformity of the increase in melting temperatures over the thickness of the SFM layer (1 310, 1 265, and 1380 °C) can be the cause of local melts, the formation of cakes and dense crusts, which negatively affects the thermal stabilization of the steel melt.

On the contrary, the SFM compositions slightly enriched in SiO_2 with respect to stoichiometry of wollastonite will have a wider melting range, since the onset melting temperature decreases (the connecting line between the points of the composition SCO and Al_2O_3 crosses not only the $C_2AS–CAS_2$ and $CAS_2–CA_6$ connodes, but also the $CS–CAS_2$ connode) due to the development of the solid-phase interaction between excess silica, alumina, and CS with the formation of CAS_2.

$$CS+S+A=CAS_2 \qquad (5)$$

Correspondingly, the three-phase combination (CS, S, and CAS_2) belongs to the elementary triangle with the minimum

eutectic at 1 170 °C for the entire CaO–Al$_2$O$_3$–SiO$_2$ system (point a in Fig. 1).

When the SFM composition is enriched with a significant amount of SiO$_2$ in comparison with the stoichiometry of wollastonite, it is possible that the connecting line between the composition SCO and Al$_2$O$_3$ crosses the CAS$_2$–S and CAS$_2$–A$_3$S$_2$ connodes (mullite).

Such compositions will be "acidic" and they are characterized by solid-phase interaction not only by reaction (5), but also by reaction mechanism (6).

$$CS+4A+3S=CAS_2+A_3S_2 \qquad (6)$$

Reactions (5) and (6) together provide the reaction as follows.

$$2CS+5A+4S=2CAS_2+A_3S_2 \qquad (7)$$
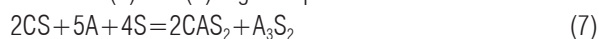
Note that an excess of SiO$_2$ in the reaction zone can be observed due to its input from heat-insulating mixtures of TIM, modern compositions of which are represented by specially heat-treated rice husk with a high content of finely dispersed SiO$_2$ or silica fume. Therefore, SFM melting begins at 1 170 °C, and in the process of heating and development of reactions (5) and (6), conditions are provided for melting the three-phase composition S–CAS$_2$–C$_3$S$_2$ at a eutectic temperature of 1 345 °C (point b in Fig. 1). Further heating of the SFM layer is characterized by competition between the melting and the development of solid-phase interaction (7) with the assimilation of Al$_2$O$_3$ from the steel melt and the accumulation of refractory compounds CAS$_2$ (1 550 °C) and C$_3$S$_2$ (1 850 °C)[13].

It should also be taken into account that the SFM compositions enriched in SiO$_2$ with respect to the stoichiometry of wollastonite have lower thermal conductivity compared with those enriched in CaO, which causes a lesser need for TIS and facilitates the supply of new portions of SFM refining and correcting additives during the casting of a series of steel melts.

The foregoing indicates the obvious advantages of the SFM compositions, slightly enriched in SiO$_2$ with respect to stoichiometry of wollastonite, because solid-phase reactions (5), (1), and (2) will be realized along the depth of the layer, sequentially providing monotonic melting in a wide temperature range due to the eutectics at 1 170, 1 265 and 1 380 °C (points a, f, e in Fig. 1). For such compositions, a reduced demand for fluxing and exothermic additives and a high ability to assimilate the main types of non-metallic inclusions in steel, including titanium oxides are predicted.

The last conclusion obviously follows from a consideration of the CaO–SiO$_2$–TiO$_2$ state diagram[13], in which there is a ternary compound CaTiSiO$_5$–sphene (see Fig. 2).

The sphene composition is located at the intersection of the connodes S–CT and CS–T (hereinafter, the abbreviation: T—TiO$_2$). When using wollastonite-containing SCOs, with the composition enriched in SiO$_2$, melting will occur at a minimum eutectic temperature of 1 318 °C, accompanied by a competing solid-phase interaction (8).

$$CS+C=C_2S \qquad (8)$$

As sphene is formed and CS is consumed, conditions can be provided for melting a three-phase combination of S, CTS, and T in a eutectic at 1 365 °C.

The composition of combinations of wollastonite-containing SFM enriched in CaO with respect to CS stoichiometry, on the contrary, will have a higher melting point of 1 348 °C, because a three-phase combination will form: CS, CT, and CTS or even more refractory: CS, CT, and C$_3$S$_2$ (eutectic at 1 398 °C)[13].

As can be seen, with respect to Ti$_x$O$_y$ assimilation, the composition of wollastonite-containing SFMs enriched in SiO$_2$ is also more preferable (no more than ∼65 *mass*% in the total composition).

4 Conclusions

The melting paths of wollastonite-containing compositions that determine the dominant processes in the composition and the ability to assimilate the main types of non-metallic inclusions in accordance with the state diagrams of physicochemical systems based on the fundamental laws of equilibrium thermodynamics were analyzed. The steric and kinetic factors will have an unconditional influence on these processes during the formation of the characteristic three-layer layer (molten, partially molten and unmelted layers) in the SFM. The influence will be the lesser, the more uniform the thickness of the entire SFM layer (when it is warmed up from the melt mirror), and the competing processes of solid-phase interaction will start, which ensure the gradual accumulation of more refractory compounds and delay the final melting of the SFM to higher temperatures. The wollastonite-containing compositions, slightly enriched in SiO$_2$, have undoubted advantages. They are capable of actively and in a significant amount refining steel melt from the main types of non-metallic inclusions, while maintaining the long-term and reliable heat-insulating ability of the SFM due to the possibility of three different solid-phase interactions providing gradual and increasingly complicated melting over a wide temperature range. For such compositions, lower requirements for TIS and the need for additional modification with fluxes, exothermic and other types of additives are predicted.

In conclusion, it is more expedient to provide insignificant silica enrichment of wollastonite-containing compositions not due to mechanical addition of SiO$_2$, but due to the synthesis of heterophasic material based on pseudo-wollastonite, anorthite, and silica glass. This does not contradict the fact that a component containing an undesirable ingredient (Al$_2$O$_3$) is introduced into the composition since a three-phase combination will form, melting at 1 170 °C, and provide optimal conditions for mass transfer in the resulting melt: Al$_2$O$_3$ will serve as a seed for further steel refining, and unmelted anorthite as a seed for its further solid-phase formation. The heterophasic wollastonite-containing compositions are most perspective as the main component of the SFM in modern steel metallurgy processes.

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