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Thermochimica Acta 318 (1998) 131–136
thermochimica acta

An application of differential thermal analysis to determine the change in thermal properties of mold powders used in continuous casting of steel slabs

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Received 3 November 1997; accepted 15 March 1998

Abstract

In continuous casting of steel slabs, all the processing steps have as their objective the attainment of the best superficial quality. The selection of an optimized mold powder is an important goal in attaining the best operating conditions. Therefore, the study of the main thermal properties of this raw material, which regulates the heat transfer between the steel plate and the mold and the lubrication of this interface during slab casting, needs special attention, as well as the additional problems due to the absorption of non-metallic materials from the fused steel and from the corrosion of the refractory materials of the equipment. These impurities change the properties of the fluxing material and its performance. If not controlled, they can cause the loss of the quality of the steel produced, and even the interruption of the process.

In this work, samples of processed mold powder, taken directly from the top of the mold during continuous industrial casting of steel slabs, were analyzed by differential thermal analysis (DTA), to determine the changes in thermal properties at different processing times. There is an increase of 41°C in both, the crystallization and melting temperatures after 140 min of processing. From DTA curves it can be seen that the original mold powder has only one crystallization peak and all the contaminated samples present two peaks. In spite of that, in both samples, pure and contaminated mold powders, cuspidine ($Ca_4Si_2O_7F_2$) and nepheline ($NaAlSiO_4$) were identified by X-ray diffraction after thermal treatment that induced the crystallization. © 1998 Elsevier Science B.V.

Keywords: Continuous casting; DTA; Mold powder; Steel slabs; Thermal properties

1. Introduction

Mold powders are fluxing agents used as raw materials in the steel industry, composed mainly of oxides of silicon, aluminium, alkaline and alkali-earth metals, with minor contents of fluorides and carbon [1]. They are used in continuous casting of steel slabs, where they play a very important role on the processing stability and on the final surface quality of the product. As the casting proceeds, the mold powder is poured on the top mold over the molten steel and, due to the high temperatures to which it is exposed (up to

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PII S0040-6031(98)00337-2

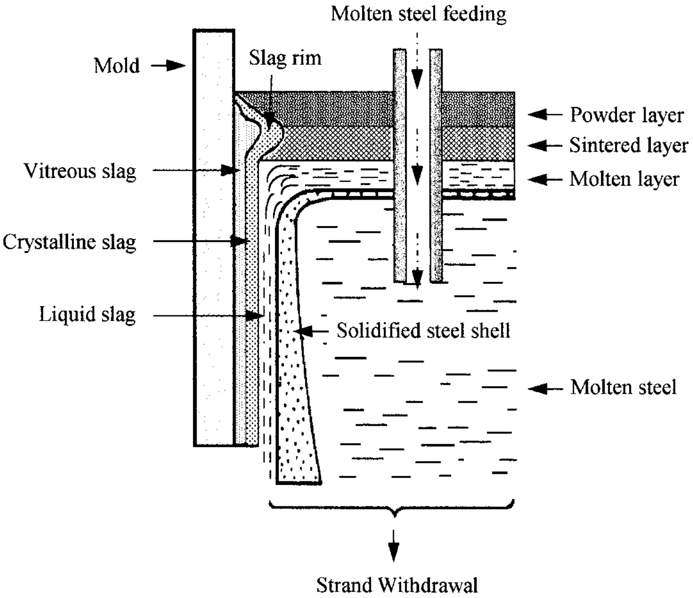

Fig. 1. Schematic representation of the various mold powder phases during continuous casting.

ca. 1500°C), it is subjected to a series of different phase changes as shown in Fig. 1, as well as to chemical reactions, in which fluoride gases, such as SiF_4 and AlF_3, are evolved [2], until a pool of the molten material is formed. This pool will act as a reservoir which continuously feeds the space between the steel slab and the mold with a uniform slag film, composed of the mold powder contaminated with the non-metallic inclusions from the molten steel and from the corrosion of the refractory materials of the equipment. It is important that the pool be as deep as necessary in order to feed the interface in a suitable and continuous way, which depends on the rate of the slag consumption and on the melting rate of the mold powder [3,4].

At the top of the mold, the mold powder, in its different physical states, acts as an insulating material, preventing the premature cooling of the steel during casting, and protecting it from reoxidation. The molten mold powder interacts with the non-metallic inclusions which float on the molten steel, and its capacity to absorb and dissolve them is extremely relevant to prevent fractures and the loss of the plastic properties of the steel [5].

The non-metallic inclusions originate from the reducing agents and from the corrosion of refractories. Among them, inclusions of alumina (Al_2O_3) are most frequent because elemental aluminium is used in excess of stoichiometric amounts to deoxidize the steel (it is possible to attain <5 ppm of oxygen). Because of its low price and its very good efficiency, aluminium is most often used as a reducing agent. When used under stoichiometric quantities, aluminium usually forms mixed oxides with iron [6].

If the fluxing agent acts well as an absorbent of the inclusions, its functions as a lubricant and as a controller of the heat transferred between the steel plate and the mold can be harmed. The slags generated by the molten mold powder are usually formed by systems of the type $CaO–SiO_2–Al_2O_3–Na_2O–K_2O–CaF_2$, which are excellent lubricants with optimized viscosity for each type of steel and predetermined operating conditions of slab casting. When the slag penetrates the metal/mold interface, part of it solidifies, and may crystallize, depending on its chemical composition, and the rest remains in the liquid phase which allows the sliding of the metal plate through the mold. The introduction of the inclusions, formed by the oxides, into the resulting mold powder slag can change its structural properties, as is the case of alumina and zirconia, which tend to increase the crystallization temperature [7], and this causes a decrease of the heat flux between the steel and the mold. Results obtained by Ichikawa et al. [8] show that the heat flux can decrease by 4 kJ m^{-2} h^{-1} for an increase of 10°C in the crystallization temperature. On the other hand, an increase in the alumina content increases the viscosity of the mold powder slag [9] and the magnitude of this interference also depends on other parameters, such as the volatilization of fluorides. This effect certainly changes the appropriate operating conditions and is one of the main causes of the interruption of the industrial casting process, because of the sticking of the solidified steel shell to the mold wall [10].

The objective of this work is to determine by differential thermal analysis (DTA) the main changes in thermal properties of industrial samples of contaminated mold powder, taken directly from the top of the mold during continuous casting of steel slabs at different processing times, when compared with the properties of the original material.

2. Experimental

Mold powder formulated for continuous casting of medium carbon steel was used in this study. The samples were taken from the pool formed in the top of the mold, and the mass percent composition of the original powder is: humidity (0.14%), total carbon (5.33%), SiO_2 (32.34%), CaO (35.12%), Al_2O_3 (8.19%), Na_2O (8.05), K_2O (0.10%), fluorine as F^- (5.80%). The first contaminated mold powder (slag) sample was collected after the casting operating conditions were stabilized. This usually occurs ca. 15 min after the machine starts up, when all the powder added for this specific procedure ought to have been consumed. The other samples were taken at 50, 120 and 140 min. All samples were collected from the same place, at half the distance between the submerged entry nozzle and the mold's narrow face. X-ray diffraction (XRD) analysis revealed that all the samples had vitreous structures.

In order to compare the mold powder free of contaminants and its slag collected during continuous casting, a glass piece of the former was prepared. The first stage of its manufacture involved the decarbonization of the mold powder for 15 h in a porcelain crucible in a furnace at 700°C. The decarbonized material was then melted in a platinum crucible at 1300°C for 10 min in an electric furnace, and poured into a metallic mold in order to obtain the glassy piece.

Samples of 20 mg were analyzed in a Perkin–Elmer differential thermal analyzer DTA 7, at a heating rate of 20°C/min with a 25 cm^3 min^- oxygen flow, in a platinum pan using alumina as the reference material.

Induced crystallization of the initially vitreous samples was taken into account when investigating the development of the crystalline phases by XRD. For this purpose, the samples were heated for 1 h at 760°C, which is a temperature higher than the maximum crystallization temperature observed by DTA for all the samples.

The analyses of the samples of pure mold powder and its slag collected from the top mold after 140 min of operation were done by energy dispersion X-ray fluorescence (EDX), in an Oxford Link ISIS-L300 instrument. The samples were coated with carbon in an atmosphere of argon prior to the analysis.

3. Results and discussion

In Fig. 2, the DTA curves of the original mold powder and of the slags, taken from the top mold during the continuous slab casting, show that the original crystallization properties of the powder are definitely affected by the contaminating inclusions which either come from the steel or from corrosion of the machine's refractory material. It can be seen that while the original powder has only one crystallization peak, the other samples present two peaks, which can be better observed for the sample collected at 50 min after the machine's start up. Both crystallization peaks are shifted to higher temperatures as more impurities are included in the slag. From Table 1, after 140 min of casting this increase is 41°C for the first peak, whereas for the second peak it is lower, estimated as 10°C. This increase of crystallization temperature gives rise to a change of heat-flux conditions between the slab and the mold, because the crystallization of vitreous slag close to the mold wall tends to decrease the radiation heat flux [11]. Consequently, the conduction heat flux becomes the main form of heat transfer leading to milder thermal-exchange conditions.

It is interesting to note that for the same sample of slag collected at 140 min, the onset of the glass-

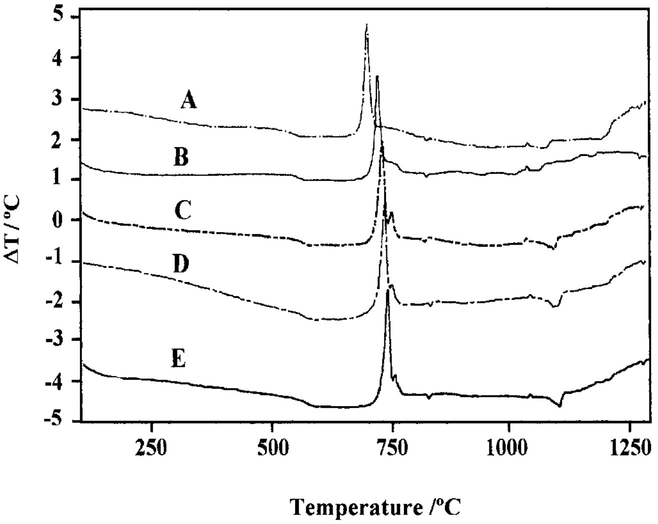

Fig. 2. DTA curves of the vitreous original mold powder and of the samples collected after the casting start up. (A) original mold powder; the same at (B) 15 min; (C) 50 min; (D) 120 min; and (E) 140 min.

Table 1
Main structural transition temperatures of original mold powder (time=0 s) and its slag of top mold, obtained by DTA.

Time/s	T_g [a]/°C	T_{c1}/°C [b]	T_{c2} [c]/°C	T_m [d]/°C
0	541	700	—	1070
15	546	723	747	1065
50	554	731	749	1091
120	562	739	752	1096
140	564	741	757	1101

[a] Glass-transition temperature.
[b] First crystallization temperature.
[c] Second crystallization temperature.
[d] Melting temperature.

transition temperature is shifted by ca. 25°C, but the melting temperature is increased by 41°C as was the first crystallization peak. This indicates that the alumina, which was an impurity of the steel, interacts with the original mold powder during the casting, changing the composition of the resulting slag and, consequently, its crystallization and melting temperatures as shown in Fig. 2.

The change in glass-transition temperature from 541° to 546°C shows that the lubricant action of the slag is also modified due to a change in softening points, and this can harm the surface quality of the steel slab.

Figs. 3 and 4 show the X-ray diffraction patterns of the slag sample collected at 140 min and that of original mold powder, respectively. Both of them were analyzed before and after a heat treatment at 760°C to induce their crystallization. The peaks are more intense in the slag, showing the influence of the non-metallic contaminant in promoting further crystallization. Although only one crystallization peak has been observed in the DTA curves of pure mold powder, both samples (pure mold powder and its slag) show the development of two crystal phases: cuspidine ($Ca_4Si_2O_7F_2$) and nepheline ($NaAlSiO_4$).

The analyses by EDX of the original and contaminated samples, in Figs. 5 and 6, respectively, show the presence of Si, Ca, K, Na, F and oxygen, besides the carbon from sample coating for analysis. Manganese and magnesium were also detected and they probably come from the refractory material of the machinery. The most relevant fact is a small increase of the intensity of the aluminum peak in the slag sample, as shown in Fig. 6. This indicates that the higher crystallization temperature (T_c) of the slag samples, as shown in Fig. 3, is very probably due to the higher alumina content of the slag compared with the original mold powder. Soares [7] has already observed that the T_c of the same original mold powder is increased by 21°C when it is contaminated with 2% by mass of Al_2O_3.

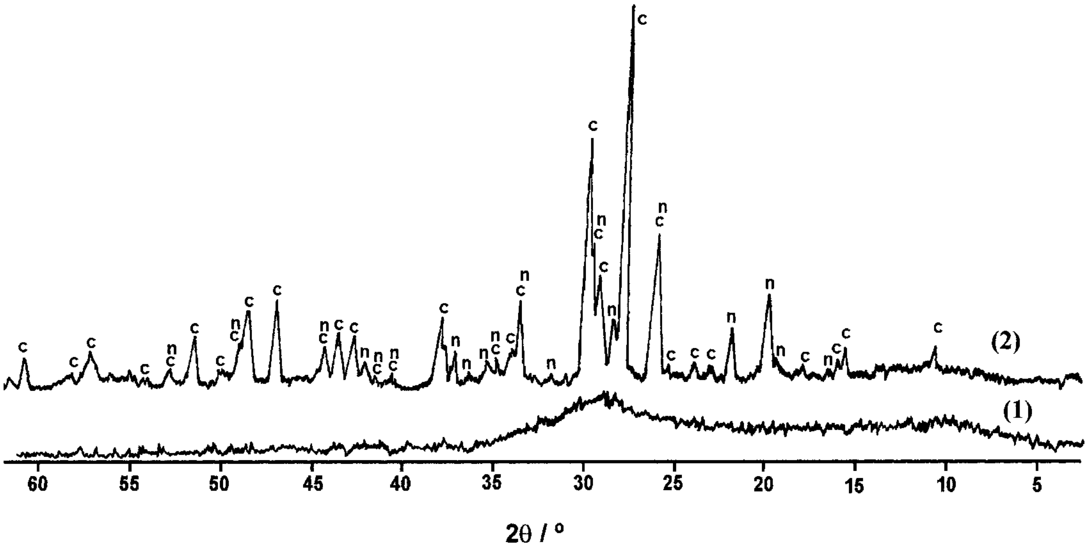

Fig. 3. XRD of the mold powder collected from the top of the mold at 140 min of casting (1) before and (2) after the thermal treatment at 760°C. [c], Cuspidine; and [n], nepheline.

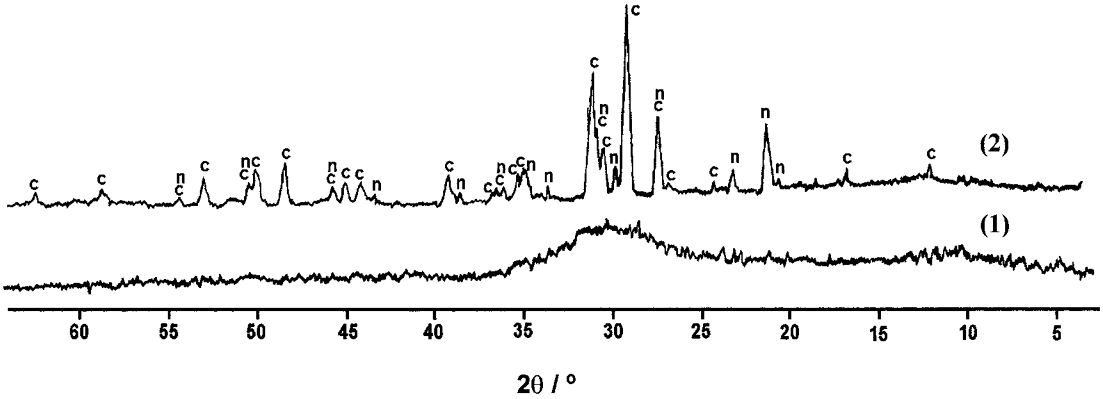

Fig. 4. XRD of the original mold powder sample (1) before and (2) after the thermal treatment at 760°C. [c], Cuspidine; and [n], nepheline.

4. Conclusions

The changes in thermal properties of mold powder contaminated during continuous casting can be measured by using DTA, thus providing better planning of the operating conditions.

The change in mold powder characteristics during continuous casting of steel, brought about by the incorporation of steel inclusions, can endanger the surface quality of the slabs produced. This is due to the change in heat-exchange conditions, as a consequence of the ΔT_c observed between the mold powder and its top mold slag, together with a change in viscosity, due to the change in softening temperature.

The greater potential for crystallization of the top mold slag, compared with the original mold powder, and its possible viscosity change during continuous casting, suggest the necessity of studying the nature of inclusions found in steel and a judicious choice of mold powder that should be used, because of the

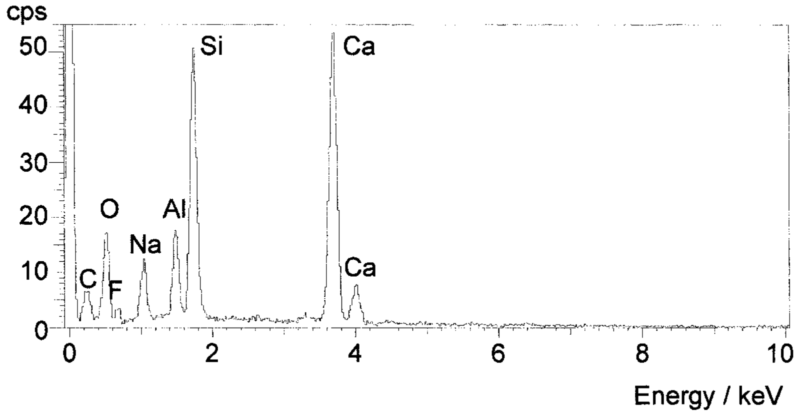

Fig. 5. EDX analysis of the original mold powder sample after its crystallization.

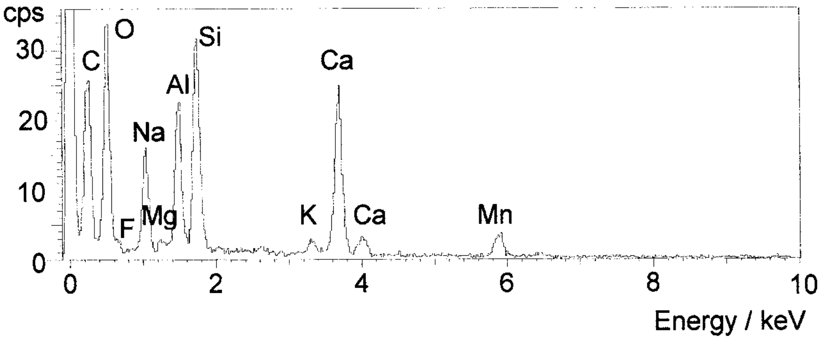

Fig. 6. EDX analysis of the mold powder collected after 140 min of casting, after its crystallization.

importance of its functions to ensure homogeneous heat transfer between the slab and the mold and suitable lubrication throughout the mold.

Acknowledgements

The authors would like to thank the Fundação de Amparo à Pesquisa do Rio de Janeiro Estado do Rio de Janeiro (FAPERJ and FIWEP/P Ronẽx) for financial support to carry out the research.

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