Inorganic materials

Replacement of fluorine in mould powders: influence on the crystallization kinetics

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Mould fluxes (mould powders or casting powders) are used in the continuous casting process of steel. These powders melt when are poured onto the liquid steel, and then penetrate between the steel shell and the mould wall. In this stage, the heat transfer must be controlled to prevent several problems because it is responsible to bring an adequate heat extraction from the steel solidified shell to the copper mould [1]. In order to control the heat extraction, the formation of crystals at temperatures between 500–900°C must be taken into account. For this reason, it is important to know the kinetics of crystallization of these fluxes in such temperature range. At present, commercial mould powders contain fluorine (F) in their chemical composition. However, the presence of F produces gas emissions that can cause corrosion problems in the plant, water acidification in refrigeration circuits and damage to personnel health. Therefore, the replacement of fluorine by less harmful constituents such as B_2O_3, Na_2O, TiO_2 and Li_2O [2-4] is a research topic of industrial interest.

In the present work mould powders were prepared using different raw materials. One powder was fluorine-containing and the others were free-F. The total fluorine content (approx. 10 wt%) was replaced by different percentages of boron, sodium and lithium oxides. Fluorspar (CaF_2), borax anhydrous ($Na_2B_4O_7$), and lithium carbonate (Li_2CO_3) were employed as source of fluorine, boron, and lithium, respectively. These powders were milling during 2 hours, then were melted at 1300°C and finally fast cooled onto a stainless steel plate. The amorphous solid layers as obtained were milling to produce glass powders which were tested by DTA at different heating rates: 5, 10, and 15°C/min. Several non-isothermal methods (Kissinger, Augis-Bennet, Ozawa, Cheng) were applied to study their kinetics of crystallization. From these models, different parameters associated to crystal growth, such as the activation energy (Ec), the frequency factor (ν) and the nucleation rate (kc), were determined. Crystallographic phases and crystal size distribution were determined by X-ray diffraction and microscopic observation techniques.

Regardless of the models used, it is observed that the replacement of F by B_2O_3 increases the values of the activation energy Ec and decreases the reaction rate kc. The sample containing B_2O_3 and Li_2O showed the lowest crystallization peak (between 585°C and 625°C). This flux also presented the lowest values of Ec (≈ 180 kJ/mol), νc (≈ 4x109 s-1) and kc (between 0.06 s-1 and 0.18 s-1). It is noted that the fluorine-containing powder presented a higher crystallization rate kc (between 0.15 and 0.43 s-1) than the free-fluorine powders.

References

1. Brandaleze E, Di Gresia G, Santini L, Martín A, Benavidez E. Mould fluxes in the steel continuous casting process. In: Srinivasan M, editor. Science and Technology of Casting Processes. Rijeka, Croatia: InTech; 2012. pp. 205–233.
2. Fox AB, Mills KC, Lever D, Bezerra C, Vadalares C, Unamuno I, Laraudogoitia J J, Gisby J. Development of fluoride-free fluxes for billet casting. ISIJ Intern. 2005;45:1051–8.
3. Wen G, Sridhar S, Tang P, Qi X, Liu Y. Development of fluoride-free mold powders for peritectic steel slab casting. ISIJ Intern. 2007;47:1117–25.
4. He S, Wang Q, Xie D, Xu C, Li ZS, Mills KC. Solidification and crystallization properties of CaO-SiO_2-Na_2O based mold fluxes. Intern. J. Min. Metall. Mater. 2009;16:261–4.