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Evaluation of the protective C_2S layer in the corrosion process of doloma-C refractories

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Abstract

The performance of doloma-C refractory bricks during the steel refining step is essential for a cost effective production of steel and should be well understood. Occasionally, in special runs, the industrial practice requires a fast adjust of slag composition to fulfill the metallurgical requirements. This procedure can lead to active corrosion of the refractories, which decrease dramatically their overall life. This work aims to investigate the phenomena involving the protective layer of dicalcium silicate (C_2S), which is formed through the reaction between silica slag and dolomitic refractories. C_2S layer samples were characterized by analyzing their chemical composition, phase formation and microstructure. C_2S was observed as the main phase, but the presence of cuspidine, a silicate-based phase with low melting point, promoted the mechanism of C_2S layer dissolution by a slag with a high content of fluorspar. This work was completed with a case study in which C_2S/slag samples were taken from different points of the ladle in order to evaluate the effect of fluorspar on C_2S layer dissolution. Post mortem doloma-C refractory brick samples were also analyzed to verify the influence of fluorspar on the corrosion process.

Keywords: Doloma-C refractories; C_2S layer; Corrosion

1. Introduction

Doloma carbon refractories are widely used as ladle lining for the steelmaking process. The understanding about the behavior of the refractory lining during the secondary steel refining and the resistance to slag corrosion is critical to ensure high refractory performance. The refractory consumption is a significant part of the cost of steel production. The steel mills consume on average between 5 and 15 kg of refractory per ton of steel produced, with significant consumption in refractories of the ladles [1].

Doloma-C bricks are used in the production of steels, due to their excellent refractoriness in service conditions, especially in plants that make silicon killed steel (effervescing steel). The wide use of this refractory is due to a natural formation of the C_2S phase (melting temperature of 2154 °C [2]) in the refractory/slag interface. This phase protects the refractory from slag penetration, and it is an example of passive corrosion [3]. MgO-C lining behaves differently: a molten slag layer may adhere and penetrate into the pores, forming a layer referred to as ladle glaze, or ‘penetrated slag layer’ [4,5].

The corrosion process on doloma-C refractories is complex and requires a good comprehension, especially in atypical runs, which sulfur in the steel is very high. In that case, desulphurization must be intense, and this procedure can lead to a strong damage of the refractories. According to industrial practice, whenever the level of sulfur in the steel becomes too high, it becomes necessary to supply considerable amounts of fluorspar (calcium fluoride), to increase both the CaO and liquid content in the slag. The higher the amount of fluorspar, the higher is the liquid area in the SiO_2-CaF_2-MgO-CaO diagram [6].

The good resistance to slag corrosion presented by the doloma-C refractories is a result of the presence of free CaO in its composition, which is not found in other refractory materials. When in contact with basic slags that are not saturated with CaO, the slag begins to dissolve the CaO of

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the brick, forming a liquid of high basicity and viscosity, until the formation of a dense layer of dicalcium silicate (C_2S) on the brick surface [7,8].

The great advantage of the C_2S layer is that it is formed by a chemical reaction that is thermodynamically favorable, with strong adhesion on the brick surface. This means that only a passive or indirect corrosion of the refractory with a slower corrosion rate can be expected. After the C_2S layer is formed, the presence of oxides such as Al_2O_3, FeO and CaF_2 (fluorite) can dissolve the passive layer, forming fluxing phases such as aluminates and calcium silicates. The breakup of the C_2S layer means that refractory dissolution may be accelerated by direct corrosion [7].

Some studies have also showed the importance of improving hydration resistance [9,10]; however, chemical corrosion itself can be considered the most important cause of refractory wearing [11]. Jansson et al. [12] studied the dissolution of three doloma based refractories in liquid slag (CaO-Al_2O_3-SiO_2-MgO). Their results indicated that the overall corrosion process took place due to the dissolution of refractory material into the slag, slag penetration into the pores and grain boundaries, to end with pull out of the grains.

Dicalcium silicate (Ca_2SiO_4) and its polymorphism have been widely studied because of the considerable importance of this compound in the refractory and cement industry [13]. The most accepted sequence of C_2S transformations has five polymorphs that can exist at atmospheric pressure: α, α'$_H$, α'$_L$, β, γ [14,15]. The sequence of phase transformations and the respective temperatures is illustrated in Fig. 1.

α-C_2S polymorph cooling from 1425 °C to 675 °C changes to β-C_2S (metastable) which is not formed during heating. γ–C_2S is formed by temperature decreases to <490 °C by reconstructive transformation.

The β-C_2S polymorph has a monoclinic structure and can only be stabilized by rapid cooling and by the incorporation of minor elements in the solid solution. The change from β-C_2S to γ–C_2S is a slow kinetics reaction, according to Amoros [17].

Understanding the sequence of phase transformations during heating and cooling cycles is of great importance for ceramic technology in general. The dusting phenomenon (C_2S solid phase becomes dust) occurs due to the transformation from β-C_2S to γ–C_2S during slow cooling between 500 and 400 °C, which causes a volume increase of ~12% [16]. This phenomenon can be observed when the steel ladle with doloma-C lining is cooled for refractory maintenance.

Nettleship et al. [16] carried out studies with dicalcium silicate. The C_2S powders were prepared by a modified Pechini method. Phase transformations of C_2S were studied with XRD and TEM.

The present work aims to investigate the chemical factors and thermal stresses that can lead to the break up or dissolution of the C_2S layer formed on doloma-C brick surfaces. The technical characterization of the C_2S layer was realized in order to generate information to improve the life of the C_2S layer and, subsequently, to decrease refractory corrosion.

2. Experimental methods

Dicalcium silicate (C_2S layer) samples from a ladle in normal process conditions after a significant number of runs (so-called STD samples) were used in this work. The samples were obtained from a steelmaking machine: a mini-mill that produces long carbon steels mainly for civil construction and uses a doloma-C ladle lining (the composition of the slag before and after deoxidation with calcium carbide is shown in 'Results and Discussion', Table 1).

The samples were characterized by X-ray diffraction-XRD (Philips X'Pert), X-ray fluorescence-XRF (spectrometer Shimadzu - 1800), scanning electron microscopy-SEM (Hitachi TM3000 with EDS Swift ED 3000), and laser particle size analyzer (CILAS model 1180).

C_2S samples were heated in an electric furnace in order to evaluate the thermal stress generated during cooling. These samples were heated to 1400 °C with 30 min of dwell, and allowed to cool inside the furnace until the temperature reached 600 °C. At this moment the samples were taken out of the furnace and allowed to cool naturally. They were photographed with a digital camera with time control.

Mixtures of C_2S samples with increase content of fluorspar (0, 5, 10 and 20 wt%) were heated to 1400 °C with 30 min of dwell. The influence of fluorspar content on the melting/dissolution of C_2S was then evaluated.

The last part of this work is a case study. C_2S/slag samples from a doloma-C lining ladle, which was removed from operation early because of its high rate of refractory dissolution, were studied. This was believed to be caused by an increase in slag attack, as a consequence of the amount of fluorspar (an increase of 3x compared to standard slag) used to improve the steel desulphurization rate. Samples were taken from different points of the ladle in order to evaluate the effect of fluorspar on C_2S layer dissolution. These samples were taken from the slag line area and from different regions of freeboard. We also aimed to analyze the heterogeneity of slag composition during this peculiar run. Tests were performed in an electric furnace to analyze the melting behavior of samples with increasing content of fluorspar.

Post mortem refractory brick samples were also analyzed to verify the influence of fluorspar on brick wearing. XRD and SEM/EDS analysis were used to analyze the corrosion process.

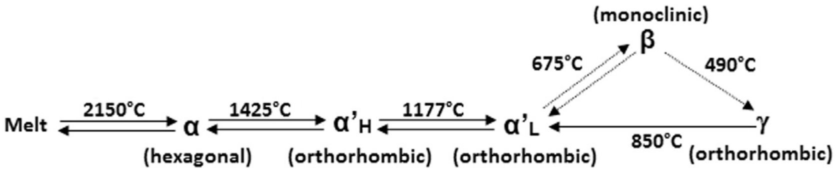

Fig. 1. Polymorphism of Ca_2SiO_4 [16].