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INFLUENCE OF HIGHER MANGANESE CONTENT IN HOT METAL ON LINING

VPLIV VEČJE VSEBNOSTI MANGANA V GRODLJU NA OBLOGO

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Metallic charging materials, with higher manganese content (up to 4%) show a deleterious influence on the lining of the melting shop equipment. Manganese from hot metal or manganese oxide from slag reacts with CaO and MgO from dolomite refractory lining forming different oxide compounds. MnO acts as solutant and catalizator of some processes. In this way dolomite lining or bricks are destroyed.

Key words: hot metal, manganese, charging materials, steelmaking

Tekoči grodelj z zvišanim manganom (do 4%) negativno vpliva na ognjevzdržno obzidavo talilnih agregatov za izdelavo jekla in zmanjšuje življensko dobo teh agregatov. Mangan ali oksid mangana v žlindri reagira s CaO in MgO iz dolomitne obloge. MnO deluje kot topilo in katalizator različnih procesov. Na ta način se ognjevzdržna obloga in opeka razkrajata in razpadata. Razpad ognjevzdržnega materiala je predvsem posledica kemičnih reakcij med MnO in ognjevzdržnim materialom. Zaradi tega so nujni ukrepi za pripravo tekočega grodlja.

Ključne besede: grodelj, mangan, vložek, izdelava jekla

1 INTRODUCTION

The influence of high manganese content in hot metal and high manganese oxide content in slag on refractory materials was discussed in several experimental and theoretical papers[1,2,3,4]. Inspite of the great significance in steelmaking practice and the extent of research studies of reactions occurring at slag (melt)- refractory interface, some of the basic problems have not been yet explained and the mechanisms of the chemical processes, which occur during the manganese oxidation, is not completely understood. Experimental and theoretical attempts have only shown the resultant reactions taking place in this system[1-4]. The reason is in the fact that the handling of melts necessary for the investigation of the metal behavior under experimental conditions is both problematical and costly.

To determine changes observed on the phase interface slag (melt) - refractory, it is necessary to examine many aspects of the process. The thermodynamic analysis provides a criterion defining the probability of occurrence of a selected reaction, since changes in free enthalpy (ΔG) for individual stages under constant conditions of temperature and pressure are calculated. Another important problem encountered in the investigation of processes which occur at the phase slag (melt) - refractory boundary, is to determine quantitatively the changes in chemical composition which take place on the surface layer and depend on parameters such as: contacting time, slag type, melt type, etc.

If the primary interest in a as longer as possible refractory life, the processes occurring at the slag (melt) - refractory interface are of primary importance, such is e.g. the system characterized by 3-4% of manganese in hot metal and slag with 20-40% MnO. Examinations carried out on the laboratory, pilot and industrial scale have proved that in this case a large quantity of manganese is transferred from the hot metal in converter to the slag and same parallel by also to the refractory material[1-7]. This caused a considerable drop in manganese concentration in (the surface layer of) melt. At the same time, a phase with high manganese content started to form in the refractory, where the presence of MnO and FeO leads to the formation of liquid oxides or silicates, which destroy CaO, a base of the dolomite material. It is not yet clear how can manganese penetrate from slag (melt) into the refractory material[1-5], although some explanations were proposed. The depth of manganese penetration inside the refractory material sometimes extends from a few to a few tens of millimeters. By prolonged contact between the examined phases a new phase containing iron beside manganese was not observed.

The evidence discussed in this paper is based mostly on industrial scale experiments[4-7] and the penetration in liquid or vapour state, as well as penetration related with chemical reactions are discussed[1-5].

An argument supporting the thesis of an important role of the vapour penetration is the high partial pressure of manganese $p_{1900°K}$ = 963 mbar. By a melt at the temperature of 1900°K. The evaporation occurs the most probably by lower oxides. Also other slag components could evaporate as f.i. MgO and SiO_2. The rate of evaporation increases by rising the slag temperature[2,3]. The rate and quantity of vaporizing slag components depend on their content in the slag[3].

2 PROCESS CHARACTERISTICS

A few process possibilities have been taken into account. One possibility is that manganese and other elements from the hot metal and the gaseous oxygen react directly with dolomite. A second assumption is that the reaction of FeO and other oxides forming the slag with dolomite is preceeded by the diffusion of gaseous manganese, oxygen, or/and MnO into dolomite.

If the first assumption is correct, than the reactions occur mainly in the layer of dolomite located near melt (slag) - gaseous oxygen interface. In the second case the reactions would occur mainly in the dolomite layer lying higher in slag area, deeper in dolomite and at greater distance from the slag (melt) - dolomite interface.

The free energy change for the transfer from slag (melt solution) to dolomite and for the manganese oxidation by reduction of some oxides is positive ($\Delta G^\circ > 0$). Inspite of that the diffusion of manganese or MnO (solid or vaporous) in bulk of (slag) dolomite (and subsequently their reactions with components of (slag) refractory materials) shifts the equilibrium of mentioned reactions to the right side[2-5].

In the first possibility the same temperature is assumed for the refractory materials and the liquid slag (melt). This situation is examined in this paper since it is met in practice of hot metal treatment, where the penetration occurs in the layer of refractory material close to the melt and slag. It is assumed that the entire process takes place at a steelmaking temperature of about 1900°K.

MnO can react with SiO_2 and form liquid oxide mixtures of $MnSiO_3$ and Mn_2SiO_4. The corresponding changes of free energy are ΔG°_{1573} = -26.7 kJ/mol[7] and ΔG°_{1573} = -187.68 kJ[2].

Rhodonite and tephroite are not formed at constant temperature but at cooling, and are neglected.

The formed MnO can react with SiO_2 in dolomite to form manganese metasilicate $MnSiO_3$ with ΔG°_{1517} = -5,73 kJ or manganese ortosilicate Mn_2SiO_4 with ΔG°_{1517} = -398,63 kJ.

3 RESULTS

The dolomite[6-8] lining life in steelworks Zenica is significantly lower then in the European steelmaking practice. It is supposed that the reason is in the strong influence high manganese and MnO contents. The average content of MnO in the slag is 23.4 ± 5% for the processing without tapping of slag in the middle. By tapping after 11 ± 3 minutes, the manganese content is 31.6 ± 5%, and at the end of the processing is 18.5 ± 3%. The drop of MnO content in slag does not result from MnO reduction, but mainly from the continuously CaO addition in the slag. The average slag composition is CaO 43 ± 2%, MnO 22.5 ± 5%, FeO 15.2 ± 1% and MgO 2.5 ± 1.4% with basicity 4.5 ± 0.3.

The reactions between slag and dolomite were investigated on samples taken from the converter neck area and the slag level, where the lining wearing was of 90.7%.

Bricks on the slag level were covered by a continuous layer of slag. Three samples of layers of dolomite bricks were investigated by optical microscopy and by EPMA: the slag layer of thickness 10 - 15 mm, the penetrated layer of thickness 20 - 25 mm and the intact dolomite brick of thickness of 40 mm.

The microstructure of the slag layer consists of a CaO matrix with a significant share of MnO and FeO, and some SiO_2. Phosphor and aluminium oxides as well as oxides of some minor elements are dispersed in MgO (**Figure 1**). Then slag layer consists of components with a low melting point near 1473°K and with a structure of olivine type (MnO, FeO)-CaO-SiO_2. This slag attacks dolomite very aggressively and penetrates deeply. At the interface between the slag layer and the penetrated dolomite brick zone grains are found consisting of CaO and SiO_2, which form compounds of the types 2CaO-SiO_2 and 3CaO-SiO_2.

Liquid manganese-ferrous silicate type slag and manganese-ferrous-aluminium silicate type slag penetrate into dolomite bricks deeply up to 20 - 25 mm. By the penetration process a matrix is produced consisting of CaO and MgO with inserts of MnO, FeO and SiO_2. MnO and FeO react with CaO from dolomite and form a complex compound. Also, in the penetrated brick zone grains of periclas (MgO) are conserved. EPMA examination shows a significant solubility of CaO from dolomite brick into the slag, which becomes a complex compound of the type MnO-FeO-Fe_2O_3-CaO. In the penetration process the periclas barrier impairs the deeper manganese (vapour or liquid slag component) penetration into brick. Behind the periclas barrier MnO and FeO are not detected. By the interface MnO and FeO diffuse into periclas grains and form a magnesium wustite. By sufficient oxygen also the oxide type MgO-Fe_2O_3 is formed.

Figure 1: Structure of dolomite used in converter lining. Sample from penetrated zone with phases: 1 - periclas, 2 - pores

Slika 1: Struktura dolomita iz obzidave konvertorja. Vzorec iz zone penetracije s fazami: 1 - periklas, 2 - pore

The microstructure of dolomite consists of CaO and MgO with inserts of small grains of silicon and aluminium oxide and without ferrous oxide.

4 DISCUSSION AND CONCLUSIONS

A high share of manganese transferred into the slag reacts with dolomite. It is possible that the presence of manganese compounds deeply in dolomite does not result from the manganese oxidation with oxygen from dolomite, but from manganese oxidation with penetrated oxygen. It is possible also that MnO is transported in slag by diffusion. In both cases MnO reacts in solid state with CaO. Also the harmful effect of vapour transportation of manganese and oxygen, and MnO cannot be neglected, while the evaporation of CaO and Al_2O_3 is negligible and both oxides react with liquid slag. The composition of slag layer on dolomite proves that it results from reactions with slag components such as MnO, SiO_2, FeO, CaO with MgO and also Al_2O_3 and P_2O_5.

The possibility for manganese penetration into brick is so large becausein all phases in front of dolomite surface the content of manganese is high. Therefore, manganese has to penetrate the dolomite brick.

Slag of the system FeO-CaO-SiO_2 can penetrate in dolomite bricks forming an interface layer consisting of compounds of the types 2CaO-SiO_2 and 3CaO-SiO_2. Manganese or MnO have to penetrate through this layer from the slag. MnO (and FeO) as vapour or in liquid phase enhance the penetrate into dolomite. Complex compounds of the type MnO-FeO-Fe_2O_3-CaO(-Al_2O_3) are formed. Also some SiO_2 dissolves in the periclas. The examination by EPMA shows that Al_2O_3 is found in solution in periclas together with MnO.

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