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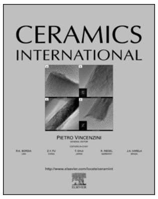

Thermodynamic evaluation and properties of refractory materials for steel ladle purging plugs in the system Al_2O_3-MgO-CaO

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ABSTRACT

The influence of iron oxide in the phase relationships of Al_2O_3-MgO-CaO and Al_2O_3-MgO purging plug refractory material has been studied by the thermodynamic analysis tool FactSage. Results showed that the system without CaO to be advantageous on the onset temperature of liquid phase, and on the liquid content at defined chemical composition and temperature. Therefore, CaO negatively influences the iron-rich slag resistance of the purging plug material. Analysis of used purging plugs proved the thermodynamic results. They showed that spinel solid solution and calcium hexaluminate as stable phases were formed in the reaction with iron oxide slag.

Corundum-spinel castables with and without calcium aluminate cement were investigated in the laboratory to compare the relevant technical properties. In the cement bonded castable, the curing and drying strength are increased by increasing the cement content. However high cement addition requires higher water demand, which results in higher open porosity and a lower hot modulus of rupture (HMoR). In the CaO-free, no-cement castable with hydratable alumina binder, the water demand is slightly higher when compared to the ultra-low cement castable. However, the curing and drying strength are still slightly higher for the no-cement castable. As there is no significant difference in HMoR with various hydratable alumina binder additions, low dosage of such binder in the range of two to four percent is normally recommended to avoid excessive water addition. Cement bonded castables (with CaO) show some advantages to the no-cement castable (non-CaO) regarding HMoR, however the no-cement castable could have advantages regarding the iron-rich slag resistance and thermal shock resistance.

1. Introduction

Alumina rich refractories in the Al_2O_3-MgO-CaO system are widely used in high temperature industries, especially in the severe working conditions of the iron and steel industry. Application areas include the working lining of steel ladles and in pre-cast shapes such as nozzles, well blocks and steel ladle purging plugs [1–5]. Purging plugs in the steel ladle bottom are used for stirring the steel in the ladle during metallurgical treatment. Their use is essential for the process (Fig. 1). Clogged purging plugs cannot perform their function and therefore the hot surface of the purging plug is examined after each heat to ensure the gas channels/slits are open. In the case of residual steel or slag being present on the surface, pure oxygen is blown through a lance onto the surface to melt and wash any residue. During that process an iron oxide slag is formed which attacks the refractories at temperature above 2000 °C. New developments in steel metallurgy involve clean steel, alloy steel, tool steel, and higher Manganese steel. This will make the working conditions for the purging plugs even more challenging.

Performance improvement of the purging plug and well block refractories is of high interest for both refractory producers and the steel industry. With regard to raw material, corundum is the first choice due to its high refractoriness and volume stability. The use of spinel in corundum castable refractories has become a standard over the past 15–20 years [1–5]. The addition of spinel significantly enhances the slag resistance and thermo-mechanical properties such as HMoR and Refractoriness under Load (RuL).

Over the past 20 years Al_2O_3-MgO-CaO low cement castables have become the standard solution for purging plug products [1–5]. However there is no systematic research on the influence of CaO (from the calcium aluminate binder) on the hot properties of such a system. The mineral phases in the Al_2O_3-MgO-CaO purging plug castable include corundum, spinel, calcium aluminate (CA), calcium dialuminate (CA_2), calcium hexaluminate (CA_6), and at

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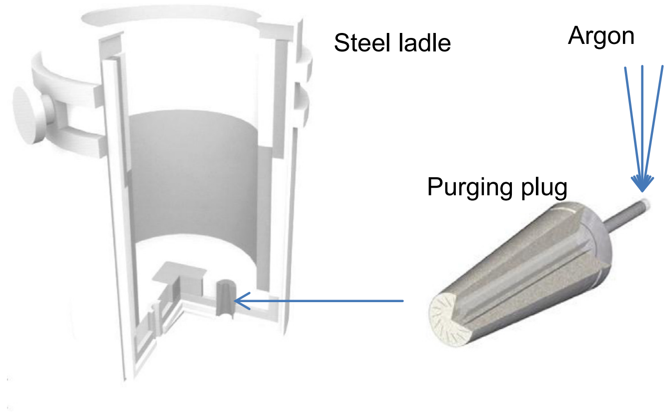

Fig. 1. Schematic picture of purging plug and steel ladle.

very high temperature, some metastable ternary phases such as CM_2A_8 and $C_2M_2A_{14}$ [6–10]. At high temperature, the content of calcium aluminate cement will influence the phase composition in the ternary system. The temperature at which melting starts and the liquid phase content during reaction with iron-rich slag at high temperature will also be affected. Corrosion of spinel containing corundum castables has been studied extensively [11–20], but research into the reaction between iron oxide-rich slag and the Al_2O_3-MgO-CaO refractory system has seldom been conducted. The previous studies have mostly focused on converter slag or steel ladle slag, while the present study is focusing on the chemical reactions between the iron oxide slag, which is created during oxygen lancing, and the refractory material, which accounts for one of the major reasons for excessive wear of the purging plug.

The present research evaluates the thermodynamic influence of iron oxide on purging plug refractories in the Al_2O_3-MgO-CaO and Al_2O_3-MgO systems, comparing the system with and without CaO with regard to onset temperature of liquid phase and the liquid phase content at high temperatures for different iron oxide contents. Some analysis was carried out on the used purging plug, to prove the results from the thermodynamic analysis. The mechanical properties of cement bonded castables and no-cement castables was checked through laboratory testing. To study the effect of the CaO percentage to the properties of castables, cement content was varied between 2% and 10%. Hydratable alumina Alphabond 300 was used as a binder for the no-cement castable with the content varying between 2% and 6%. An optimized addition of Alphabond 300 will be defined by the study on technical properties of the no-cement castables.

2. Experimental

Two types of castable Al_2O_3-MgO-CaO and Al_2O_3-MgO were produced using tabular alumina (T60/T64, Almatis), magnesium aluminate spinel (AR 78, Almatis), reactive alumina (CL 370, Almatis), and dispersing alumina (ADS 3, ADW 1, Almatis) as stated in Tables 1 and 2. For the Al_2O_3-MgO-CaO system, calcium aluminate cement (CA 14 M, Almatis) was used as binder. In order to study the calcia effect, the spinel content was fixed at 26%, while the cement content varied between 2% (C2S26), 5% (C5S26), 8% (C8S26) and 10% (C10S26). For the Al_2O_3-MgO castable, a hydratable alumina (Alphabond 300, Almatis) was used as the binder. The content of Alphabond 300 varied between 2% (A2S26), 4% (A4S26), and 6% (A6S26), keeping the spinel content fixed at 26%.

Raw materials were dry mixed in a Hobart mixer for 1 min and then wet mixed after adding sufficient water. The wet out time for the two types of mixes was different. For the cement bonded mix, the wet out time was around 40 s and wet mixing time a total of 4 min While for the Alphabond 300 mix, the wet out time was 2 min, resulting in a longer wet mixing time of a total of 6 min Longer mixing time for the hydratable alumina containing mix is important for both the laboratory test and in practical application. Insufficient mixing may, in practice, cause overdosing of water, which will significantly deteriorate the castable.

A vibration table (frequency 50 Hz, amplitude 0.5 mm) and a flow cone (top diameter 70 mm, bottom diameter 100 mm, height 50 mm, DIN EN ISO 1927-4) were used to check the vibration flow of the castables. Flow was tested at 10, 30, and 60 min after water addition. The flow cones for these tests were all filled immediately after wet mixing was completed. All castables were adjusted by appropriate water addition to achieve a vibration flow value of around 200 mm. This figure is that which is typically required for proper installation.

Mixes were casted into molds 40 × 40 × 160 mm for the testing of general physical properties. Smaller molds of 25 × 25 × 125 mm were used for casting sample bars for HMoR testing.

Sample bars were cured at room temperature for 24 h without covering the surface and then de-molded. The drying process was conducted in a drying oven at 110 °C for 24 h. The sample bars were then fired at 400 °C, 1000 °C, 1500 °C and 1650 °C respectively, with a holding time of 5 h. The cold modulus of rupture (CMoR), cold crushing strength (CCS), bulk density, open porosity and permanent linear change were then tested. The open porosity

Table 1
Composition of cement bonded Al_2O_3-MgO-CaO castables (additives on top of 100% sum).

Cement bond castable		**C2S26** %	**C5S26** %	**C8S26** %	**C10S26** %
Tabular alumina T60/T64					
	3–6 mm	25	25	25	25
	1–3 mm	18	18	18	18
	0.5–1 mm	6	6	6	6
	0–0.5 mm	10	7	4	2
Spinel (AR 78)					
	0.5–1 mm	7	7	7	7
	0–0.5 mm	10	10	10	10
	0–0.045 mm	9	9	9	9
Reactive Alumina					
	CL 370	13	13	13	13
Cement					
	CA-14 M	2	5	8	10
Additives					
	ADS 3/ADW 1	1	1	1	1

Table 2
Composition of Hydratable alumina Alphabond 300 bonded Al_2O_3-MgO castables (additives on top of 100% sum).

Non-cement castable		**A2S26** %	**A4S26** %	**A6S26** %
Tabular alumina T60/T64				
	3–6 mm	25	25	25
	1–3 mm	18	18	18
	0.5–1 mm	6	6	6
	0–0.5 mm	10	8	6
Spinel AR 78				
	0.5–1 mm	7	7	7
	0–0.5 mm	10	10	10
	0–0.045 mm	9	9	9
Alumina				
	CL 370	13	13	13
Binder				
	Alphabond300	**2**	**4**	**6**
Additives				
	ADS 3/ADW 1	1	1	1