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A SECONDARY ALUMINA SOURCE FOR THE STABILISATION OF CaO-SiO$_2$-MgO SLAGS

Remus Ion IACOBESCU[1,2], Yiannis PONTIKES[1,2*], Annelies MALFLIET[1], Lieven MACHIELS[1,2], Howard EPSTEIN[3*], Peter Tom JONES[1], Bart BLANPAIN[1]

[1] Department of Metallurgy and Materials Engineering, KU Leuven, 3001 Heverlee, Belgium
[2] Secondary Resources for Building Materials, Consortium in Sustainable Inorganic Materials Management, SIM[2], KU Leuven, Belgium
[3] RVA, La Vignette, 55120 Les Islettes, France

remusion.iacobescu@mtm.kuleuven.be, yiannis.pontikes@mtm.kuleuven.be, annelies.malfliet@mtm.kuleuven.be, lieven.machiels@mtm.kuleuven.be, hepstein@013net.net, peter.jones@mtm.kuleuven.be, bart.blanpain@mtm.kuleuven.be,

Abstract

This work aimed to assess the possibility of stabilising a CaO-SiO$_2$-MgO (CSM) rich slag by adding 15 wt% of the secondary alumina source Valoxy. A modified slag was also synthesised adding an equal weight fraction of analytical grade Al$_2$O$_3$. The CSM slag was successfully stabilised by both methods. In terms of mineralogy, the use of Valoxy promoted the formation of merwinite and bredigite, instead of gehlenite in view of its MgO content. In both cases the chromium in the CSM based slag was found entrapped in a spinel phase, whereas the γ-C$_2$S level was <2 wt%.

Introduction

Stainless steel slags are generated in the Electric Arc Furnace (EAF) operation as well as in the Argon Oxygen Decarburisation (AOD) and Ladle Metallurgy (LM) processes. These slags are CaO-SiO$_2$-MgO rich with Cr$_2$O$_3$, Al$_2$O$_3$ and F$^-$ in minor quantities. The major issue arising upon slag cooling is disintegration of the slag due to the high C$_2$S content which undergoes the β to γ phase transformation. This is accompanied by a volume increase and unless dopants like boron are used, the slag disintegrates into a fine powder. Because of the latter, slag handling, storage and use are problematic. To avoid C$_2$S precipitation, one method proved to be efficient is moving from the ternary CaO-SiO$_2$-MgO system to the quaternary system with Al$_2$O$_3$[1]. The Cr content in the slag is also a point of attention due to the tight legislation regarding Cr leaching. In the work of Mudersbach *et al.*[2], additions of bauxite, Al$_2$O$_3$ containing residues and aluminium metal have been suggested as a method to increase the stability of stainless steel EAF slags and also to stabilise Cr. The aim of the additions is to decrease the basicity of the slags and favour the formation of spinel type phases. In this study, the influence of introducing Valoxy, an alumina rich material, in CaO-SiO$_2$-MgO rich slags was investigated. A slag

sample with 15 wt% analytical grade Al_2O_3 was also produced for the sake of comparison.

Materials and methods

The raw materials used in this study were a secondary alumina namely Valoxy, received from RVA Company, France, and an industrially produced CaO-SiO_2-MgO (CSM)-rich slag. Chemical analysis was performed by XRF. For XRD/QXRD analysis, the materials were milled with 10 wt% ZnO as internal standard. The analysis was performed between 2θ range of 10° to 70°, CuKα radiation under 45 kV and 35 mA. Quantitative (QXRD) determination was done based on the normalised Rietveld method, normalised. For the design of the experiments, thermodynamic FactSage calculations were performed and the addition of 15 wt% Valoxy appeared as promising. Experimentally, two mixtures of (in wt%) 85 CSM-15 Valoxy and 85 CSM-15 Al_2O_3 (analytical grade) were prepared for comparison. The mixtures were heated in a bottom loading furnace in a platinum crucible. Each sample was heated up to 1640°C at 5°C/min, equilibrated for 1 h, followed by slow cooling at 5°C/min to room temperature, under static air. The samples were subsequently analysed with an electron probe micro-analyser (EPMA) on carbon coated polished sections and with XRD/QXRD analysis.

Results and discussion

Characterisation of raw materials

The XRF analysis of the raw materials is presented in Table 1, whereas the QXRD is shown in Table 2. Based on the bulk chemical analysis and assuming all Ca to be CaO, the CSM slag used has a CaO/SiO_2 of ~ 1.6. Valoxy is rich in Al_2O_3 (75 wt%), with also contains substantial levels of MgO (9 wt%) and SiO_2 (7 wt%).

Table 1: XRF analysis of CSM slag and Valoxy raw materials, in wt%

Raw materials	CaO	SiO_2	MgO	Al_2O_3	Na_2O	Others
CSM	55.7	33.0	7.6	1.3	n.d.	2.4
Valoxy	1.9	7.2	9.2	75.8	0.5	5.5
n.d. – not determined						

The mineralogical composition of CSM slag revealed merwinite, cuspidine, γ-C_2S and bredigite as the main crystalline phases, whereas for Valoxy, spinel and corundum were minor constituents and approximately 70 wt% were amorphous phases.

Table 2: QXRD characterisation: a) CSM slag and b) Valoxy, in wt%

a)
Identified phases	CSM
Merwinite ($Ca_3Mg(SiO_4)_2$)	22.4
Cuspidine ($Ca_4Si_2O_7F_2$)	21.2
γ-C2S (γ-Ca_2SiO_4)	20.3
Bredigite($Ca_7Mg(SiO_4)_4$)	18
Periclase(MgO)	8.1
β-C2S (β-Ca_2SiO_4)	7.5
Wollastonite ($CaSiO_3$)	2.1
Fluorite(CaF_2)	0.4

b)
Identified phases	Valoxy
Spinel ($MgAl_2O_4$)	12.2
Corundum (Al_2O_3)	8.6
Quartz (SiO_2)	0.8
Fluorite (CaF_2)	0.4
Others	8.5
Amorphous or unidentified	69.5

Mineralogical analysis of the stabilised CSM slag

The quantitative mineralogical analysis is presented in Table 3. It was found that for the Valoxy addition the main phases present were merwinite, bredigite, gehlenite and spinel. In the case of the Al_2O_3 addition, the sample was mainly composed of gehlenite, merwinite, spinel and cuspidine. Comparing the mineralogy of the slags, it is obvious that the (Mg,Ca)-silicates, like merwinite and bredigite, are enhanced in the sample with Valoxy, whereas gehlenite is higher in the sample with Al_2O_3. This was to some extent expected in view of the different starting composition, in particular the MgO/Al_2O_3 ratio, of the two additives.

Table 3: Quantitative analysis of the samples with Valoxy and Al_2O_3 addition, in wt%

Identified phases	CSM + 15 wt% Valoxy	CSM + 15 wt% Al_2O_3
Gehlenite ($Ca_2Al(AlSi)O_7$)	14.1	31.6
Merwinite ($Ca_3Mg(SiO_4)_2$)	45.7	38.4
Spinel ($MgAl_2O_4$)	12.2	9.1
Cuspidine ($Ca_4Si_2O_7F_2$)	4.4	9.3
Bredigite ($Ca_7Mg(SiO_4)_4$)	14.4	6.8
Periclase (MgO)	2.6	3
Fluorite (CaF_2)	0.5	0.8
γ-C2S (Ca_2SiO_4)	1.9	0.5
Lime (CaO)	0.3	0.4
Calcite ($CaCO_3$)	0.3	-
Wollastonite ($CaSiO_3$)	0.7	-
β-C2S (Ca_2SiO_4)	2.8	-

Other smaller differences relate to the content of cuspidine, γ- and β-C_2S and spinel. The higher spinel level in the sample with Valoxy is attributed mainly to its MgO and spinel content.
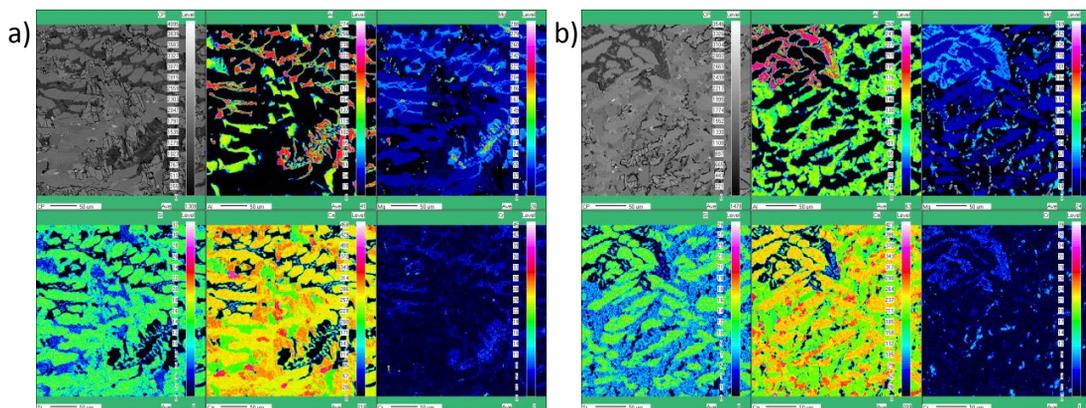
Figure 1: EPMA-WDS elemental maps of sample with 15 wt%: a) Valoxy and b) Al_2O_3

Microchemical analysis of the stabilised CSM slag

The microchemical analysis based on elemental maps is presented in Figure 1 (CP - Backscattered electron image of analysed area). Both samples are dense with gehlenite and merwinite as dominant phases. Spinel and bredigite are also distinguished. An important part of Cr, originating from the CSM-rich slag, appears to be incorporated in the spinel phase, therefore leaching is expected to be minimised.

Conclusion

Volumetric stabilisation of CSM slag was possible by addition of either 15 wt% Valoxy or Al_2O_3. Both Al-bearing materials changed the slag mineralogy considerably and C_2S formation was prevented. In samples with Valoxy, spinel formation was favoured instead of gehlenite as Valoxy serves as an extra source of MgO. In both samples elemental maps indicate that Cr is entrapped in a spinel phase.

Acknowledgments

References

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