CHARACTERISATION OF STEEL INDUSTRY SLAG SUITABILITY AS RAW MATERIAL FOR REFRACTORY CASTABLES

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Introduction

Refractories are inorganic non-metallic materials which are used at high temperatures usually exceeding 1000°C and they should remain chemically and physically stable at high temperatures. Castable refractory materials are needed in all thermal energy intensive industries for example in the construction of the furnaces, kilns, incinerators or reactors. Utilisation of industrial by-products together with innovative processing routes are seen to be key aspects for more sustainable refractories development. Production of high carbon ferrochrome (HCFeCr) produces by-product, ferrochrome (FeCr) slag[1]. The FeCr slag utilisation has been reported for example in road construction[2], brick manufacturing[3] and in cement industry[4] as a base layer material in road pavements. In the recent studies by Kumar *et al*. [5,6] the utilisation of FeCr slag as raw material for low cement refractory castables were reported. In study[5] refractory castables were prepared using FeCr slag, calcined bauxite, high alumina cement and microsilica as raw materials and in study[6] using FeCr slag, calcined bauxite, superfine calcined alumina and high alumina cement as a hydraulic binder. Particle size distribution, phase structure and phase characteristics of the castable mixture are one of the most important factors controlling the properties of the refractory castables. In the current work, the FeCr slag suitability as raw material for refractory castables was studied. FeCr slag sample was analysed by particle size analysis, microstructure and composition studies (SEM+EDS), X-ray-diffraction (XRD) analysis and thermal analysis (TGA/DSC) to find out characteristic properties. Experimental characterisation results were compared to thermodynamic FactSage software simulations of equilibrium phase structures and phase fractions. Presented study is a first part of the research work which eventually aims to the industrial pilot scale demonstration of processing route for refractory castables based on maximal utilisation of secondary raw materials.

Materials and Methods

FeCr slag fine aggregates (0-4 mm) was selected for characterisation. Particle size and its distribution was determined with laser diffractometry (Malvern Mastersizer). Microstructure and morphology was investigated using scanning electron microscopy

(SEM JEOL JSM-6360LV) equipped with energy dispersive spectroscopy (EDS). The identification of crystalline phases was done by using an X-ray diffractometer (XRD, Empyrean, PANanalytical B.V., ALMELO, Netherlands) with Cu-Kα radiation source, and analysed using HighScore Plus software. The thermal behaviour was studied using thermogravimetry (TGA, Netzsch STA 449 F1 Jupiter) giving a simultaneous Differential Scanning Calorimetry (DSC) signal. The measurements were made in air and in argon atmosphere with a heating rate of 10°C/min. Thermodynamic calculations were performed using FactSage 7.0 thermochemical software with FToxid database.

Results and Discussion

Approximately 40 wt% of the studied FeCr slag (0-4 mm) aggregates are above 2 mm. For under 2 mm sieved fraction Dv (10) value is 411 µm and Dv (50) value is 1230 µm. According to the resulting EDS spectrum and tabulated quantitative results the main elements in the slag are Al, Mg, Si and O. Fe, Cr, Ca and K were also identified. The typical chemical composition is 30% SiO_2, 26% Al_2O_3, 23% MgO, 8% Cr, 4% Fe and 2% CaO[1]. Figure 1 presents XRD patterns of FeCr slag at room temperature, at 800°C, at 1000°C and at 1500°C. The spinel phase appears as main crystalline peaks. Other phases identified are magnesium silicates: forsterite and enstatite. After heat-treatments some peaks are missing but spinel phase appears still as main crystalline peaks.

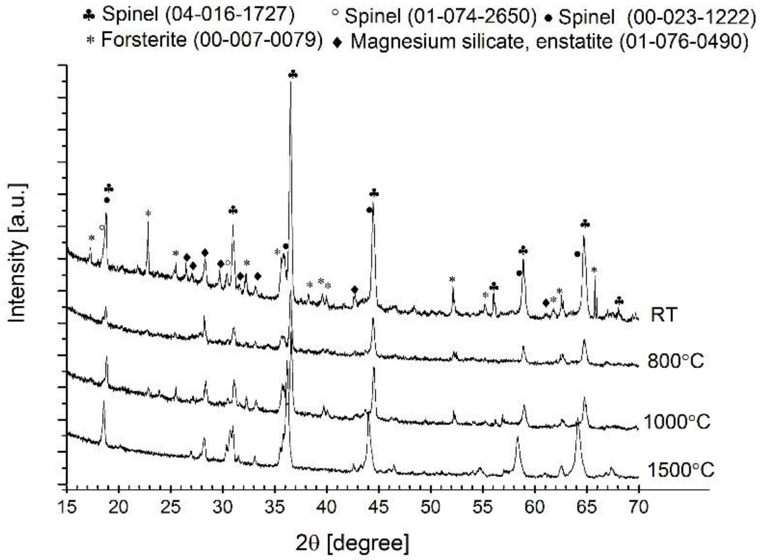
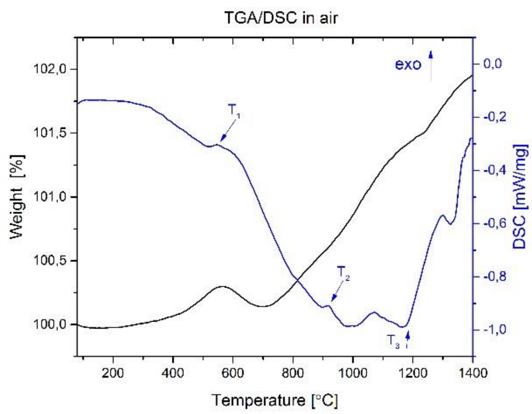


Figure 1: XRD patterns of FeCr slag

In the study by Makkonen and Tanskanen[7] the mineralogy of FeCr slag was detailed characterised showing also Fe-Mg-Cr-Al-spinels, forsterite (Mg_2SiO_4), Mg-Al-silicate and metal droplets as crystalline phases. With fast cooling rates, the slag is not totally crystalline and amorphous glass phase is solidifying between the grains. The amount of amorphous glass phase depends on the cooling rate being typically between 60-70% in FeCr slag.

The TGA/DSC results are shown in Figure 2. In air, the weight loss curve starts to increase after 400°C showing also a small exothermic peak in the DSC curve (T_1). Small amount of CO_2 release is also detected connected to this transformation which indicates carbon combustion in small quantities. In air, the weight curve continues to increase relating most probably to metal (Fe, Cr) oxidation. In both atmospheres, an exothermic peak is detected is DSC curve above 900°C (T_2) relating probably to crystallisation of amorphous glass phase. Above 1200°C (T_3) both in air atmosphere and in argon atmosphere shows transformation which relates probably to liquid phase formation.



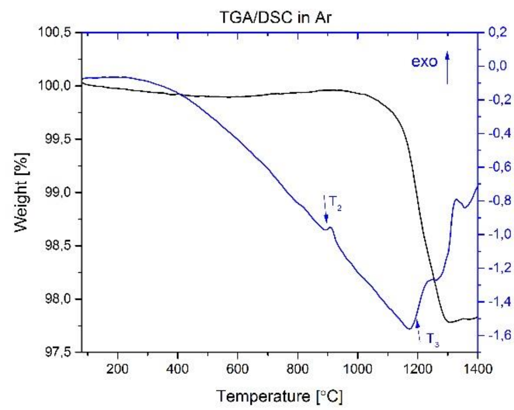


Figure 2: TGA/DSC result in air (left) and in argon (right)

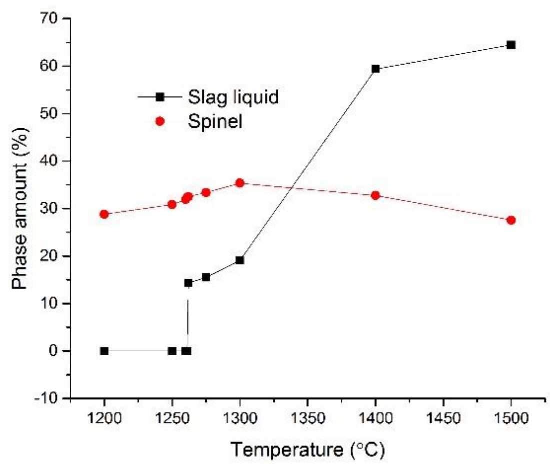


Figure 3: Simulated FeCr slag phase structure as function of temperature

Figure 3 shows FactSage simulations for main equilibrium phases and their amounts for FeCr slag. According to Figure 3 simulated results the spinel phase is the main crystalline phase and liquid slag phase is formed at a temperature between 1261-1262°C. Simulation results support the characterisation results presented previously. However, it must be noted that the non-equilibrium phase or metastable phase cannot be included to equilibrium calculations straightforward.

Conclusions

Steel industry by-product, ferrochrome slag, was analysed by laser diffractometer, SEM/EDS, XRD and thermal analysis to find out its characteristic properties in order to be utilised as raw material in the manufacturing of novel refractory castables. Characterisation and simulation results indicate that ferrochrome slag will be the potential option to achieve successful properties for refractories to withstand high temperatures up to 1200°C in gaseous atmosphere. Presented study is a first part of the research work which eventually aims to the industrial pilot scale demonstration of processing route for refractory castables based on maximal utilisation of secondary raw materials.

Acknowledgements

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