Journal of Cleaner Production 149 (2017) 137–145

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Investigation of thermal properties of blast furnace slag to improve process energy efficiency

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ARTICLE INFO

Article history:
Received 21 September 2016
Received in revised form
7 February 2017
Accepted 7 February 2017
Available online 13 February 2017

Keywords:
Blast furnace slag
Slag viscosity
Slag heat exchange
Pig iron heating
Slag thermal behaviours
End use product value
High temperature hot stage SEM
In-situ SEM heating

ABSTRACT

Blast furnace slag (BFS) is the main by-product of iron making and is produced in large amounts worldwide. To improve energy use, it is necessary to understand the thermal behaviour of slags under differing compositions at varying temperatures. This study determines the thermal properties and behaviour of selected slag samples using several experimental techniques, including high temperature Hot Stage Scanning Electron Microscopy (HS-SEM), and Computer Aided Thermal Analysis (CATA). Further methods, such as Energy Dispersive Spectroscopy (EDS) and Fourier Transfer Infrared Spectroscopy (FTIR) were applied to determine the chemical content and nature of the studied BFS samples. Comparing the chemical composition of the slags and their thermal behaviour, the effect of magnesium oxide and aluminium oxide was evident on the crystallisation and fluidity of the molten slag. Additionally, the content of silicon dioxide had an effect on the crystallisation temperature and network strength.

1. Introduction

Iron is one of the most common metals used worldwide. The main raw materials required for production of iron are iron ore, coal, limestone and recycled steel. The amount of iron slag produced in 2012 was 270–320 Mt and this amount increases every year as the demand increases (Sadek, 2014). China is the largest producer of iron ore at 1.5 Gt per annum and Australia is the second largest with 660 Mt of iron ore produced per year (Iron Ore and Global market, 2015). Any improvement in the efficiency of energy recovery and recycling in the iron making process, including the recycling of the by-product slag, will have positive global implications, both economically and environmentally (Zhao et al., 2015).

The iron and steel making process generates significant amounts of waste materials, such as slags (Kan et al., 2015). Because of landfill restrictions and other environmental considerations, possible recycling of these materials or development of new by-products have become principal incentives for this industry (Francis, 2005), aiming to preserve the natural resources and, where possible, conserve energy where material properties and characteristics are suitable (Motz and Geiseler, 2001).

One of the steps in the iron making process is to heat the pig iron up to 1500 °C for the next phase of steel-making. In this process a significant amount of energy is transferred to the blast furnace slag (BFS), which reaches temperatures of around 1500 °C at the end of this process (Sadek, 2014). Utilising the waste heat energy from the slag to contribute to heating the pig iron would achieve better energy efficiency and sustainability of the blast furnace steel-making process. To improve energy use, it is necessary to understand behaviour of the slags with different compositions and at varying temperatures.

The properties of different blast furnace slags (BFS) vary and are determined by the ore type, ash of the coke and the process operating conditions. Slag can be considered as a resource not used before and, depending on its properties, its use is possible in another part of the industry (Dimitrova, 1995), which helps to reduce environmental contamination, energy use and production costs (Ozturk and Gultekin, 2015). The possible reuses of BFS depend on the slag properties and heat treatment of the molten slag. Accordingly, it is necessary to enhance the knowledge of the phase chemistry of slag to optimise the productivity and performance in recycling (Jak and Hayes, 2004).

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http://dx.doi.org/10.1016/j.jclepro.2017.02.052

In the blast furnace (BF) gangue and non-metallic impurities are separated from the iron ore with the final products being pig iron and slag (Dippenaar, 2005). Pig iron and molten slag accumulate at the hearth of the BF, and the slag is positioned above the pig iron, as its density is lower than iron (Ito et al., 2014). There are some difficulties associated with draining the slag from the BF as it has high viscosity while in the lower temperature zones of the furnace this viscosity increases (Ito et al., 2014).

When slag is tapped from the furnace it has high temperature and different methods of cooling will affect the slag composition (Dippenaar, 2005). Appropriate treatment of high-temperature slag with a suitable cooling process improves the slag properties and its applications for recycling (Liapis and Papayianni, 2015).

The molten slag has two separate final solid states; (i) crystalline phase, which comes from the slow cooling of the molten slag, and (ii) glassy, amorphous or vitreous phase, which is caused by quenching or rapid cooling of the slag (Kriskova et al., 2013). Table 1 demonstrates the most important type of slag as a by-product and the end use of these materials.

There have been many attempts to recover the energy from slag for use as heat, electricity generation or fuel, but none of them has been commercialised yet (Baati et al., 2011). The reason for this is that the industry is more focused on quenching the slag and promoting the formation of glassy phases for use in cement rather than recovering the energy. If energy recovery is the goal of slag quenching, then the slag will not be cooled fast enough to manufacture the preferred glassy and amorphous phase. The water quenching technique produces glassy BFS (Crossin, 2015). The air-cooling technique is applied for some lower value applications, such as the production of bitumen (Crossin, 2015).

During slag cooling, the solid phases appear and increase the viscosity (Kim et al., 2004). The composition of phases will change continually when the temperature is reduced from liquid to solid. The melting point is one of the critical properties of BFS related to the chemical content. The BFS melting point and liquid temperature increase by increasing the basicity ratio (Dai and Zhang, 2012), which is the ratio of CaO to SiO_2. The basicity is an important slag characteristic as this ratio affects crystallisation (Kuo et al., 2007).

High amounts of SiO_2 reduce the melting point and retard the formation of crystals in the slag, increasing the strength and water permeability. For this reason, engineering the slag cooling process so that energy is recovered, while producing the favourable slag properties for its further use or recycling, is an essential part in designing cleaner iron and steelmaking production.

The aim of this research is to determine how changes of chemical content during slag melting and solidification processes of different industrial BFS affect the underlying thermal properties and energy use. In this research, the thermal properties of BFS were determined and slag melting and solidification phenomena observed, such as crystal formation and glassy phase segregation. The changes of chemical content during melting and cooling process of different industrial BFS were additionally determined. The understanding and insights of the high temperature behaviour and properties of blast furnace slag assist improvement of the BF performance and optimisation of heat energy recovery of slags without detriment to the higher value use as an ingredient in the manufacture of cement or other applications.

Table 2
Chemical composition of the samples.

Slag	TFe	SiO_2	CaO	MgO	Al_2O_3	MnO	TiO_2	Basicity
Sample A	0.43	35.93	40.41	8.38	13.54	0.26	0.5	1.12
Sample B	0.35	33.31	40.94	8.46	14.99	0.26	0.57	1.22
Sample R	0.39	30.78	33.83	13.34	19.01	0.84	0.97	1.09

2. Materials and methods

2.1. Materials

The samples used in this study were BFS supplied from iron-making BF plants in China. For minimizing variability, each sample was ground into a fine powder and mixed to form homogeneous sub-sample. A standard ring mill batch pulverizer was used to grind the samples to fine powder. The particle size distribution for each sample after grinding was between 10 and 100 μm determined with SEM imaging. The standard chemical analysis of the samples determined with X-ray fluorescence spectroscopy is presented in Table 2.

2.2. Analytical methods

In this research a variety of instruments were used for studying the thermal properties of the BFS, which include Hot Stage Scanning Electron Microscope (HS-SEM), Energy Dispersive Spectroscopy (EDS), Computer Aided Thermal Analysis (CATA), and Fourier Transform Infrared (FTIR) Spectroscopy.

2.2.1. High temperature hot stage scanning electron microscopy (HS-SEM)

The SEM used in this study was a JEOL JXA-840 Scanning Microanalyzer, while stage modifications, high temperature furnace and appropriate detector system were custom built before the commencement of this work.

In this instrument, each sample was heated up to 1500 °C inside the microscope chamber, and the heating process was recorded to monitor the morphological changes of the sample during heating with magnifications from x 12 for panoramic viewing to x 10,000 for slow scanning high resolution images and up to x 5000 for TV filming. A molybdenum strip with dimple was used as sample holder for this study, as molybdenum is a comparatively stable material against molten slag erosion.

Working distance, which is the distance between the sample and the final lens and typically set to 12 mm, was increased to 25 mm in this study, because of the physical dimensions of the furnace used inside the microscope. The pressure inside the chamber was high vacuum. The appropriate voltage for the tungsten filament (heater) was rated nominally to 12 V for 100 W. The sample was then cooled down, and the formation of crystals that appeared on the molten surface during cooling was also recorded. The scintillator was modified for protection by covering with a

Table 1
Potential slag by-products and uses.

Slag By-Products	Slag Uses
Crystalline Phase (Slow Cooling)	Road base, ready-mix concrete, clinker manufacture, asphaltic concrete aggregate, fill, railroad ballast, hot mix asphalt, concrete pavement, concrete base, prevent erosion in the slope,
Amorphous Phase (Rapid Cooling)	Concrete, cementitious additive, can be mixed with Portland cement clinker to make a blended Type 1S cement, high fire-rated concrete base, lightweight fill applications over edgy soils,