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Microstructural transformations of two representative slags at high temperatures and effects on the viscosity

Yong Jiang [a,c], Xiongchao Lin [d], Keiko Ideta [a], Hiromichi Takebe [e], Jin Miyawaki [a], Seong-Ho Yoon [a,b,*], Isao Mochida [b]

[a] Institute for Materials Chemistry and Engineering, 6-1 Kasuga-Koen, Kasuga, Fukuoka 816-8580, Japan
[b] Research and Education Center of Carbon Resources, Kyushu University, 6-1 Kasuga-Koen, Kasuga, Fukuoka 816-8580, Japan
[c] School of Chemical Engineering and Pharmaceutics, Henan University of Science and Technology, Luoyang 471003, China
[d] School of Chemistry and Environmental Engineering, China University of Mining and Technology (Bejing), Bejing 100083, China
[e] Graduate School of Science and Engineering, Ehime University, Matsuyama, Ehime 790-8577, Japan

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ABSTRACT

The transformation of the Si-Al microstructures of slags, which have similar $SiO_2 + Al_2O_3$ and CaO contents but different SiO_2/Al_2O_3 ratios, was quantified using multinuclear SS-NMR. Three kinds of Si Q^n microstructures (Q^2, Q^3, and Q^4), where n denotes the number of bridging oxygen linked to other Si atoms for each Q (SiO_4) unit, and one Al structure (Al (IV)) were present in both slags. The Q^3 percentage in two slags was increased as increase of temperature from 1200 to 1600 °C. The transformation of Si-Al microstructures was interpreted by a hypothetic model of cristobalite cluster based on the crystal and Q^n structure.

1. Introduction

Coal remains one of the dominant fossil fuels used for power generation. Currently, more than 40% of the world's electricity is provided by coal-fired power plants [1]. The consumption of coal for this use is expected to increase. However, increasing the use of coal leads to serious problems such as increasing emissions of greenhouse gases, particulate matter, and trace elements. These problems may be solved by adopting integrated gasification combined-cycle (IGCC) technologies that use entrained-flow gasifiers. Because this type of gasifier generates lower NO_x, SO_x, and particulate matter emissions from pulverized coal-fired power stations [2,3].

In entrained-flow gasifiers, coal particles are combusted, gasified, and entrained. This generates fly ash and molten slag as by-products at high temperatures (>1200 °C) and pressures (20–30 atm) [1]. In the case of entrained-slagging gasifiers, the viscosity of the molten slag is a critical factor for the continuous operation since it affects slag formation, refractory attrition, and slag drainage along the gasification chamber walls. The viscosity of the coal slag as a function of temperature is strongly affected by the composition and microstructure of the melt [4]. To date, the viscosity–composition relationship has been studied using phase diagrams and empirical and modified models according to the bulk ash composition. Song et al. [5]. investigated the effect of compositon on the crystallization of coal slags at high temperatures using FactSage™ modeling, X-ray diffraction (XRD), and scanning electron microscopy (SEM). Acidic oxides such as SiO_2 and Al_2O_3 lead to high viscosities while basic oxides such as CaO, Fe_2O_3, K_2O, and Na_2O decrease the viscosity [6,7]. However, it is not very clear that the effect mechanism of acidic and basic oxides on the viscosity. The rheological properties of slag are thought to be strongly related to the microstructure of the melt, i.e., cluster structure, size, and intercluster connections [8]. Although the crystalline species in slag can be identified using FactSage™ and XRD, any amorphous content is ill-defined. Solid-state nuclear magnetic resonance (SS–NMR) spectroscopy can provide local information about a specific element in a slag even in the amorphous state; however, most of the traditional approaches fail to detect the local environments of each atomic species in sufficient detail. Shimoda et al. [9] investigated the local structures of an amorphous slag by multinuclear (^{29}Si, ^{27}Al, ^{17}O, ^{25}Mg, and ^{43}Ca) SS–NMR. They reported that the amorphous slag framework structure consisted of a depolymerized chain-like network of SiO_4

* Corresponding author. Tel.: +81 92 583 7959; fax: +81 92 583 7897.
E-mail address: yoon@cm.kyushu-u.ac.jp (S.-H. Yoon).

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tetrahedra connected with AlO_4 tetrahedra. ^{25}Mg and ^{43}Ca as a multi-site occupancy of the ions have coordination numbers about 6 to 7, respectively. Lin et al. [10] investigated three Asian coal ashes by SS–NMR and found a close relationship between the Si Q^n structure and viscosity: Q^2 and Q^3 having lower degrees of polymerization led to lower viscosity, while Q^4 with its high degree of polymerization resulted in high viscosity. The author also noted a large difference of viscosity between the ash and its quenched slag: the viscosities of the Datong ash and slag were 43.0 and 25.8 Pa·s at 1550 °C, respectively, because the losses of some elements in commercial gasifier are different from that in the laboratory furnace [10–12]. The apparent viscosity value, which was obtained from the ash using laboratory furnace, may make wrong prediction of operation temperature as a result of low thermal efficiency and short life of refractory wall. It is important that for the stable operation and smooth discharge to accurately know the real state of liquid slag in the gasifier and to understand the relationship between the viscosity and structure of slag [8,13–15].

Compared to the parent ash, slag has less oxide species so that the crystallization of slag is simple process relative to the ash sample. In the present work, we chose two representative coal slags having similar amounts of $SiO_2 + Al_2O_3$, CaO, and Fe_2O_3 contents but different Si/Al ratios. The quenched slags were obtained from a gasification pilot plant with a capacity of 3 t/d coal. The thermal transformations of the Si–Al microstructures of both slags upon heating at different temperatures were investigated. Measurements of the viscosities and thermodynamic properties provided indirect structural information concerning the aluminosilicate melts. XRD, Fourier transform infrared spectroscopy (FTIR), and SS–NMR were used to directly characterize the local structures. This study hypothesized that resolidified species maintained the structural features of the melts at the heat-treatment temperature. This work is expected to understand the thermal transformations of Si–Al slag microstructures and structure–property relationships between the microstructures and viscosities of molten slag.

2. Experimental

2.1. Samples

The glass-like coal slag samples, Coal Valley slag (denoted as CVS), and Tanito Harum slag (denoted as THS) were collected after rapid quenching with water of the molten slags flowing from the gasifier. The samples were provided by the Central Research Institute of Electric Power Industry (CRIEPI, Japan). The heat-treated slag samples were prepared by heating pulverized slag powders (less than 600 μm) at a rate of 2.9 °C/min to various temperatures, holding them there for preset periods, then allowing them to cool down to room temperature at the same rate in air. The detailed treatment conditions were as follows: soaking at 300 °C, 600 °C, 815 °C, and 900 °C for 2 h at each temperature; at 1000 °C, 1100 °C, 1200 °C, 1300 °C, 1400 °C, and 1500 °C for 30 min at each temperature; and at 1600 °C for 10 min because of the limitation of laboratory furnace. A sample that had been heated to 1700 °C at 5 °C/min for viscosity measurements was also investigated.

2.2. Characterization

The chemical compositions of the two coal slag samples were determined by X-ray fluorescence (XRF; Shimadzu, EDX800). XRD was used to identify the crystalline phases in the slag samples. The XRD pattern was recorded over 5–90° with a step of 0.01°/s using Cu Kα radiation at 40 kV and 30 mA at room temperature (Rigaku, RINT Ultima III). A differential scanning calorimeter (DSC; Seiko Instruments, EXSTAR DSC-6300) was used to investigate the endo- and exothermic changes in the slags during heating from room temperature to 1350 °C at a heating rate of 10 °C/min under 100 mL/min of N_2 flow. FTIR (JASCO, FT/IR-615) absorption spectra of KBr dispersions were recorded from 4000 to 400 cm^{-1}. The spectra were typically averages of 128 scans with 4 cm^{-1} resolution.

^{29}Si magic angle spinning (MAS) SS–NMR spectra were measured at a Larmor frequency of 79.43 MHz with a JEOL ECA-400 multinuclear spectrometer equipped with a magnetic field of 9.4 T at a 15 kHz MAS speed in zirconia rotors using a 3.2 mm CPMAS probe. ^{29}Si single-pulse spectra were obtained with π pulses having a length of 6.8 μs and a recycle time of 10 s, collecting up to 10,000 free induction decay (FID) signals. The ^{29}Si chemical shift scale was referenced to external polydimethylsiloxane (PDMS).

^{27}Al MAS SS–NMR spectra were measured at a frequency of 208.48 MHz with a JEOL ECA-800 spectrometer equipped with an 18.8 T standard bore magnet at a 20 kHz MAS speed. The ^{27}Al radio frequency (RF) field strength was 96 kHz, verified using a 1.0 M aqueous $AlCl_3$ solution. Chemical shifts were referenced to the $AlCl_3$ signal.

Slag viscosity was measured using a homemade rotary viscometer equipped with a high-purity alumina rotor and crucible in a N_2 atmosphere up to 1700 °C. Before viscosity measurement of slag, the viscometer was calibrated using a reference material (717a, borosilicate glass) certificated by the American National Institute of Standard and Technology. The measurement deviation was controlled to less than 5%. Details of the viscous instrument and viscosity measurement can be found elsewhere [10].

Table 1
Chemical compositions of the two slags.

	Weight percent (wt%)[a]		Mole fraction (%)	
	CVS	THS	CVS	THS
SiO_2	58.78	50.40	66.64	59.15
Al_2O_3	25.18	32.18	16.79	22.22
CaO	8.20	8.03	9.96	10.10
Fe_2O_3	3.84	4.03	1.63	1.77
TiO_2	0.47	0.95	0.40	0.84
MgO	2.07	3.00	3.52	5.28
K_2O	1.01	0.68	0.73	0.51
P_2O_5	ND[b]	0.41	0.00	0.20
BaO	0.22	ND	0.10	0.00
Cr_2O_3	0.12	ND	0.05	0.00
SrO	0.07	0.12	0.05	0.08
ZrO_2	0.05	0.04	0.03	0.02
Y_2O_3	0.01	ND	0.00	0.00
CuO	ND	0.04	0.00	0.04
MnO	ND	0.07	0.00	0.07
V_2O_5	ND	0.07	0.00	0.03
SiO_2/Al_2O_3	2.33	1.57	3.97	2.66
SiO_2–Al_2O–CaO system	Weight percent (wt%)		Mole fraction (%)	
	CVS	THS	CVS	THS
SiO_2	58.78	50.40	64.75	55.52
Al_2O_3	25.18	32.18	16.32	20.85
CaO[c]	16.04	17.42	18.93	20.56

[a] Dry free basis.
[b] ND: not detected.
[c] Other alkali and alkaline earth oxides were included with CaO.