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The cause of surface tension increase with temperature in multicomponent aluminosilicates derived from coal-ash slags

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An explanation is proposed for the increase of surface tension with temperature in multicomponent aluminosilicate systems such as those derived from coal-ash slags. Two major factors are considered: (1) depolymerization of aluminosilicates caused by rearrangements of intermediate structures in the surface layers, and (2) the increase in surface entropy caused by evaporation of some ash slag components. Electron spectroscopy for chemical analysis spectra were recorded for oxygen 1s photoelectrons on quenched bulk slags and on sessile drops to gain insight into the depolymerization of coal-ash slags with temperature. The tests performed on quenched bulk slags indicated replacement of bridging oxygen [Si–O] with non-bridging oxygen atoms [Si–O$^-$] as a function of increasing temperature. Mössbauer spectra showed an increase in ferrous iron from 4% to 12% of total iron as temperature rose from 1400 °C to 1500 °C. The increase in non-bridging oxygens resulted from the reduction of tetrahedrally coordinated Fe^{3+} to octahedrally coordinated Fe^{2+}. Also, the intensity of the non-bridging oxygen 1s photoelectron peak was higher when detected on the surface of a sessile drop than when detected from the bulk of the drop.

1. Introduction

Generally, atoms/molecules which lie at a surface, experience an asymmetric force field from the atoms/molecules within the bulk of a liquid. As a result, the surface tends to contract in order to minimize the surface energy. Usually, surface tension decreases with increasing temperature (Eötvös or Guggenheim relations). For some materials, increase in surface tension with temperature is expected to occur if surface atoms/molecules are strained with respect to atoms/molecules in the bulk of the liquid. In silicate glasses, tetrahedra not fully bonded near the surface have geometric properties distinct from those in the bulk of the material [1]. The possible number of distinct rebondings is a measure of the sensitivity of the material to disordering. The geometric diversity of Si–O bonds in the surface layers may cause changes in bond lengths and angles between silicon and oxygen atoms. This effect may be favoured by the increased concentration of non-bridging oxygen in the surface layer and/or a preferential orientation of structural units because of their interaction with the atmosphere.

In silicate systems, the Si–O$^-$ bonds (where O$^-$ represents a non-bridging oxygen) are stronger and shorter, while Si–O bonds (where O represents a bridging oxygen) are weaker and longer [2, 3]. The shortening of Si–O bond length causes the increase in surface tension. Also, aluminium in a framework structure causes shortening of the Si–O bonds [4], and a corresponding increase in surface tension [5].

In our previous work, we have reported that in some coal-ash slags, the surface tension would either remain unchanged or increase with temperature above the temperature of critical viscosity, T_{cv} [6, 7]. The temperature of critical viscosity is roughly defined as the temperature at which the composition of slag is changed from a one-phase to a two- or more phase mixture, and this may correspond to flow changes from Newtonian (above T_{cv}) to non-Newtonian (below T_{cv}). The increase in surface tension was attributed to the possible depolymerization of aluminosilicate melts. In this paper, we provide evidence of depolymerization and its effect on surface tension in multicomponent aluminosilicates derived from coal ash. We also consider additional effects, such as vaporization, that may cause an increase in surface tension with temperature in coal-ash slags.

2. Experimental procedure

2.1. Viscosity and surface tension studies

The bulk viscosities of gehlenite aluminosilicate and multicomponent aluminosilicate from coal-ash slag were measured using a rotating bob viscometer described elsewhere [8]. The coal ash was produced from Beulah coal mine, North Dakota. Measurements were taken at 20 °C intervals after stabilization of the

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TABLE I Composition of starting materials (wt% expressed as equivalent oxide)

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5
Gehlenite	33.0	29.1	8.6	0.1	29.2	0.0	0.0	0.0	0.0
Beulah	38.0	15.3	10.9	1.6	22.4	5.1	5.8	0.7	0.0

viscosity (approximately 40 min). The viscometer was calibrated with the National Bureau of Standards lead silicate glass NBS 711. The accuracy of viscosity measurements was ± 15%. The slag and melt surface tensions were determined by the sessile drop technique [6]. Both experiments were performed in air. The bulk composition of both silicates is listed in Table 1.

2.2. Electron spectroscopy for chemical analysis (ESCA) tests

ESCA was used to analyse the bridging and non-bridging oxygen species by measuring the splitting of the oxygen 1s photoelectron spectrum. The experiment was carried out on fractured samples using a PHI 595 multiprobe with a 10 kV magnesium X-ray source and a double-pass cylindrical mirror electron analyser with a pass energy of 15 eV. Peak positions were corrected by assuming that the very weak carbon 1s photoelectron line present for each sample tested was at 284.6 eV. As discussed by Onorato *et al.* [9], it can be assumed for silicate systems that there are only two types of oxygen present, bridging and non-bridging, so the absolute binding energy of each peak is not significant. Thus, it is unnecessary to consider any charging effects which may change peak positions. A multicomponent silicate system derived from the ash of Beulah lignite coal was selected for the ESCA tests. The Beulah slag was the same as that used for viscosity and surface tension measurements. It was remelted at 1500, 1400, 1300, and 1200 °C, held for 0.5 h, and quenched in water. The bulk composition of the slag is listed in Table 1. Sessile drops of Beulah coal slag were also used for ESCA tests after surface tension was measured.

2.3. Mössbauer spectroscopy tests

Mössbauer spectroscopy was used to determine the oxidation state of iron ions in Beulah slags quenched from 1500 and 1400 °C. The ratio of Fe^{3+} to ΣFe was calculated as the ratio of the area of the Fe^{3+} doublet relative to the total absorption envelope. All measurements were made at room temperature. The measurements and the fitting procedure of the spectra were similar to those described by Mysen and Virgo [10].

3. Results and discussion

The viscosity and surface tension plots of the Beulah slag and gehlenite melts determined in air are illustrated in Figs 1 and 2, respectively. In general, viscosity increases gradually with decreasing temperature and then increases rapidly below T_{cv}. Below that temperature, crystalline phases may form as temperature on the liquidus is reached [11]. Surface tension, however, is unchanged or decreased at temperatures below T_{cv}. The significant decrease of surface tension at T_{cv} was attributed to a non-equilibrium state of surface tension caused by the random distribution of surface-active phases in the slag and higher polymerization of the silicate structure [6].

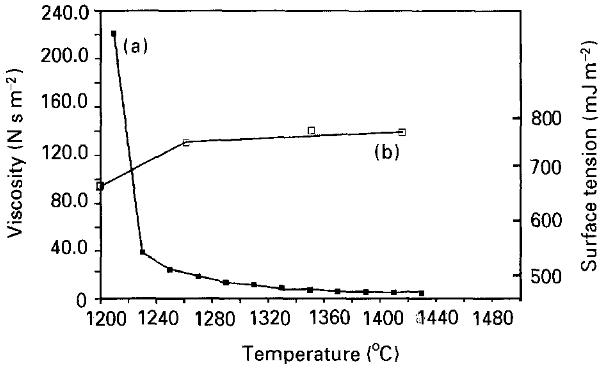

Figure 1 (a) Viscosity and (b) surface tension temperature relationship on the Beulah slag.

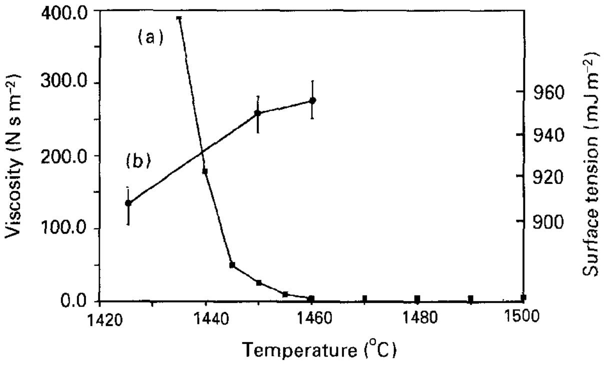

Figure 2 (a) Viscosity and (b) surface tension temperature relationship on the gehlenite melt.

Fig. 3 shows oxygen 1s photoelectron peaks detected on quenched Beulah slags between 530.5 and 532 eV. The peak widths measured as full width at half maximum (FWHM) are listed in Table II. The FWHM varied with annealing temperature and was large for a specimen quenched from 1500 °C. This is because of overlapping of the two oxygen 1s photoelectron lines with comparable intensities belonging to bridging oxygen atoms (higher value) and non-bridging oxygen atoms (lower value) [9, 12–14]. Below 1500 °C, FWHM decreased sharply because the $Si–O^-$ peak integral intensity diminished. In addition, the oxygen 1s peak detected in α-Al_2O_3, shown in Fig. 3, is a useful indicator of the position of the

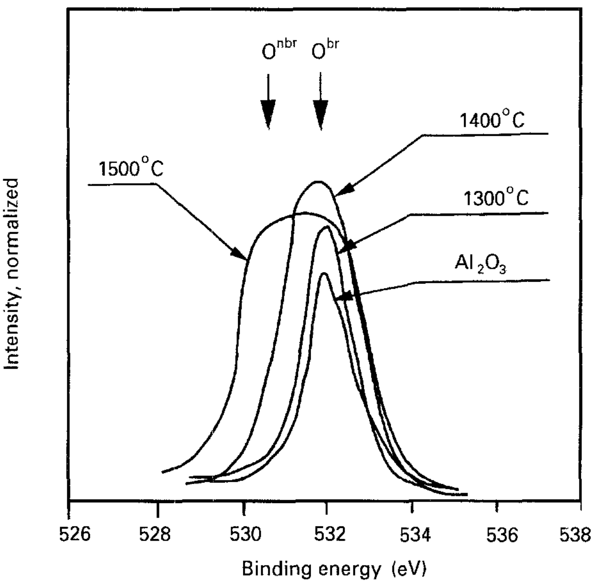

Figure 3 Oxygen 1s photoelectron spectra for Beulah slag quenched from various temperatures to room temperature.

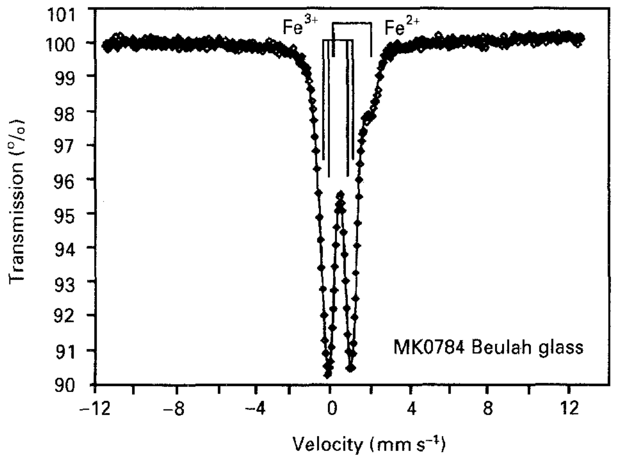

Figure 4 ^{57}Fe resonant-absorption Mössbauer spectral of Beulah slag quenched from 1500 °C to room temperature.

bridging oxygen photopeak. ESCA results show that the non-bridging oxygen content increases with temperature and is highest at 1500 °C. This may be caused by a partial change of iron oxidation state from Fe^{3+} to Fe^{2+} [10]. Kozakevitch [15] has found that an ionic double layer of adsorbed Fe^{2+}–SiO_4^{4-} is formed at the surface of the droplets.

It has been suggested that in an Na_2O–Al_2O_3–SiO_2–Fe–O system, the ferrous iron content increases with temperature and decreasing oxygen fugacity as a result of the reduction of tetrahedrally coordinated Fe^{3+} to octahedrally coordinated Fe^{2+} [10]. This should increase the depolymerization of slags. The ratios of Fe^{3+} to ΣFe, determined by Mössbauer spectroscopy on Beulah slag quenched from 1500 and 1400 °C, were 0.88 and 0.96, respectively. This implies that the ferrous iron formed at high temperatures may also cause the formation of non-bridging oxygen in coal slag. A representative iron absorption Mössbauer spectrum is shown in Fig. 4. Goldman [16] has indicated that the peak for oxygens associated with ferrous or ferric iron in the oxygen 1s spectrum is nearly coincident with the non-bridging peak and may thus make it impossible to distinguish between bridging and non-bridging oxygens in silicate glasses containing iron. Also, oxygens associated with aluminium, Si–O–Al, occur between the bridging Si–O–Si and non-bridging $Si–O^-$ peaks. Thus, detected bridging and non-bridging oxygen peaks on Beulah sessile drops should result from the variation of alkali content with depth.

Fig. 5 illustrates the bridging and non-bridging oxygen 1s photopeaks detected from both the surface layers and the bulk of sessile drops. The intensity of the non-bridging oxygen photopeak increases after the surface was sputtered with 2 keV Ar^+ ions for 40 s over a 6 mm × 6 mm raster. These data indicate that the top of the sessile drop is depleted in alkali ions because of vaporization.

Table II shows FWHM oxygen 1s photopeaks detected from the surface of the sessile drop and from its bulk. The larger FWHM values provide evidence that aluminosilicate surface layers are more depolymerized than those in the bulk of the sessile drop.

For the sake of clarity, we will discuss the variation of surface tension of soda–lime silicate melts with the change of sodium and calcium content expressed by NBO:Si (Fig. 6) [17]. Generally, surface tension increases with the number of non-bridging oxygens per

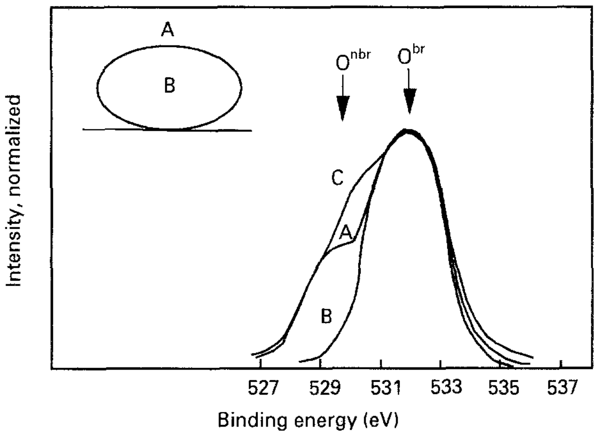

Figure 5 Oxygen 1s photoelectron spectra for quenched Beulah sessile drop, after surface tension was measured. A, surface layers; B, bulk of sessile drop; C, surface layers after sputterng.

TABLE II Half-band widths for O 1s photoelectron lines detected in quenched slags and sessile drops of Beulah ash

Material	Annealing temperature (°C)	FWHM (eV)
Beulah	1500	3.6
Beulah	1400	3.0
Beulah	1300	2.5
Beulah	1200	2.3
Gehlenite	1500	3.4
Al_2O_3	–	2.3
Gehlenite crystalline phase	–	2.4
Sessile drops		
Surface layers		4.3
Bulk drop		3.0

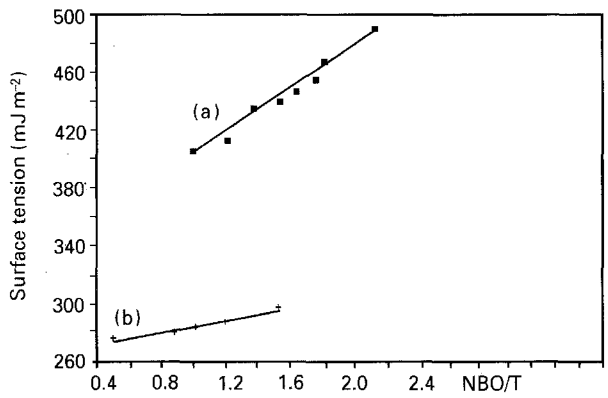

Figure 6 Surface tension as a function of NBO:T (T = Si) in two model glasses. (Surface tension for (a) $CaO-SiO_2$ and (b) Na_2O-SiO_2 glasses were determined at 1550 and 1300 °C, respectively [17].)

tetrahedrally coordinated silicon (NBO:Si) because of the depolymerization of silicate melts. Thus, the increase in surface tension with temperature in multicomponent silicate systems derived from coal ash may be primarily attributed to the depolymerization process in ash slags.

Another effect that may cause an increase in surface tension is the change of surface entropy because of the evaporation of some components. It is clear that the entropy per unit area at the surface, s_σ, is less than that of the bulk, s_β; in consequence, the excess entropy per unit area at the surface, $s_s = (s_\sigma - s_\beta)$, is negative [18]. The surface excess entropy is given by

$$-s_s = d\gamma\,(T)/dT \qquad (1)$$

The entropy deficiency due to evaporation yields to a positive gradient for $d\gamma/dT$. The surface will delocalize, and the excess entropy will pass through zero to positive values. Under progressive vapour transport across the liquid–vapour interface, the lowering of surface entropy will cause an increase in surface tension. This effect was well documented for liquid zinc [18]. Laboratory tests show that sodium and potassium may evaporate from ash above ~ 1400 °C [19]. There is also indication that sodium depletion causes calcium atoms to accumulate at the surface [20], which will either induce an increase or stabilize the degree of polymerization.

4. Conclusions

An explanation of the increase in surface tension with temperature in multicomponent aluminosilicate systems, such as those derived from coal-ash slags, was developed. The increase is the result of a depolymerization process in the surface layers of sessile drops and, to a lesser extent, of the increase in entropy.

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