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Influence of TiO₂ on the Viscous Behavior of Calcium Silicate Melts Containing 17 mass% Al₂O₃ and 10 mass% MgO

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1. Introduction

Iron ores consisting of significant TiO₂ such as ilmenite are low cost ores, but due to the high TiO₂ content its use may result in significant issues within the blast furnaces such as lower reduction degree,^{1–4)} changes in the liquidus temperature in slag,^{5–7)} lower residual removal by the slag,^{8–10)} and viscosity changes within the bosch and hearth.^{11–15)}

However, potential benefits of TiO₂ in the blast furnace slags have also been known by forming a protective layer of titanium carbo-nitride on the refractory brick and inhibiting the premature failure and erosion of the hearth.^{9,15–18)}

Ohno and Ross¹³⁾ found TiO₂ additions increase the slag viscosity in the CaO–SiO₂–Al₂O₃–TiO₂ slags under reducing atmospheres of C/CO equilibrium. Shankar *et al.*¹⁹⁾ revealed the effect of TiO₂ in the CaO–SiO₂–MgO–Al₂O₃ slag system, where the viscosity decreased with TiO₂ up to 2 mass%. Saito *et al.*¹⁴⁾ found TiO₂ lowered the viscosity in the CaO–SiO₂–MgO–Al₂O₃ slag system at 10 mass% and 20 mass% TiO₂. However, the viscosity data between 0 to 10 mass% TiO₂ is still ill-defined. In this study, the influence of TiO₂ from 0 to 10 mass% on the viscous behavior of CaO–SiO₂–17 mass%Al₂O₃–10 mass%MgO slags have been

Table 1. Chemical composition and measured viscosities of CaO–SiO₂–Al₂O₃–MgO–TiO₂ slags.

No.	C/S	Composition (mass%)					Viscosity (Pa·s)		
		CaO	SiO ₂	Al ₂ O ₃	MgO	TiO ₂	1400°C	1450°C	1500°C
1	0.8	33.2	39.8	17	10	0	0.76	0.51	0.34
2	0.8	30.9	37.1	17	10	5	0.56	0.37	0.25
3	0.8	28.6	34.4	17	10	10	0.48	0.33	0.24
4	1.0	36.5	36.5	17	10	0	0.69	0.43	0.28
5	1.0	34.0	34.0	17	10	5	0.52	0.32	0.23
6	1.0	31.5	31.5	17	10	10	0.48	0.28	0.21
7	1.2	40.6	32.4	17	10	0	0.56	0.33	0.22
8	1.2	37.8	30.2	17	10	5	0.46	0.28	0.17
9	1.2	35.0	28.0	17	10	10	0.42	0.24	0.14

investigated and correlated to the slag structure using XPS (X-Ray Photoelectron Spectroscopy).

2. Experimental Methods

Samples were synthesized using reagent grade chemicals of CaO, SiO₂, MgO, Al₂O₃, and TiO₂. The samples were premelted at 1773 K under 0.4 L/min of Ar in a Pt crucible to obtain a homogeneous slag sample. Post-experimental chemical composition using X-Ray Fluorescence (XRF) spectroscopy (S4 Explorer; Bruker AXS GmbH, Karlsruhe, Germany) showed and no apparent change and is given in **Table 1**.

The viscosity of 120 g of slag placed in a Pt crucible was measured using a rotating spindle connected to a calibrated Brookfield digital rheometer (model LVDV-II+; Brookfield Engineering Laboratories, Middleboro, MA) details of which have been given elsewhere.^{20–22)} Measurements were taken at each target temperature during a 5°C/min cooling cycle after 30 minutes of soaking and in the fully liquid region of the slag system well above the break temperature (T_{Br}) of each slag composition.^{20,21)} After completing the viscosity measurements, slag samples were reheated to 1773 K and quenched on a water-cooled copper plate to confirm the slag structure using XPS (VG Scientific Instrument, ESCALAB 220i-XL).

3. Results and Discussion

3.1. Effect of TiO₂ on the Viscosity

Figure 1 shows the viscosity of the CaO–SiO₂–17 mass% Al₂O₃–10 mass% MgO based slag with TiO₂ additions and a constant CaO/SiO₂ of 0.8 at various temperatures. TiO₂ additions at 5 and 10 mass% decreased the viscosity and the effect of TiO₂ is more pronounced at lower temperatures. At higher temperatures of 1723 K and above, TiO₂ additions above 5 mass% has only a slight effect in lowering the viscosity. The present study seems to show that TiO₂ additions decrease the viscosity and since the viscous behavior of molten slags is closely related to the slag structure, the decrease in the viscosity with TiO₂ additions seems to suggest that TiO₂ behaves as a basic oxide and modification of the network structure is likely.

Effect of TiO₂ at constant temperature of 1773 K at various CaO/SiO₂ ratio is provided in **Fig. 2**. The addition of

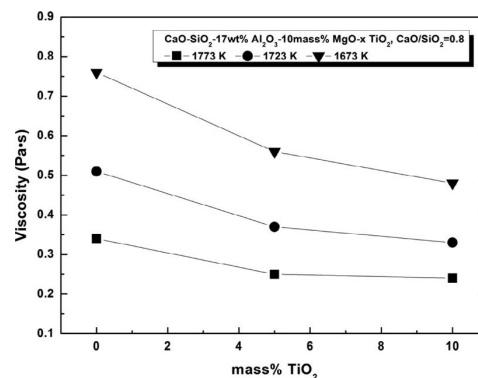


Fig. 1. Effect of TiO₂ additions on the viscosity in the CaO–SiO₂–17 mass% Al₂O₃–10 mass% MgO–x TiO₂ slag system at constant CaO/SiO₂ of 0.8 and various temperatures.

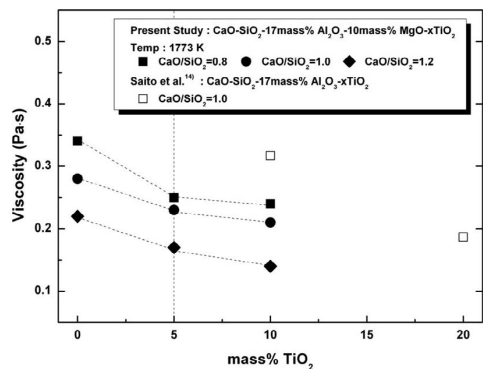


Fig. 2. Effect of TiO₂ additions on the viscosity in the CaO–SiO₂–17 mass% Al₂O₃–10 mass% MgO–x TiO₂ slag system at various CaO/SiO₂ ratio.

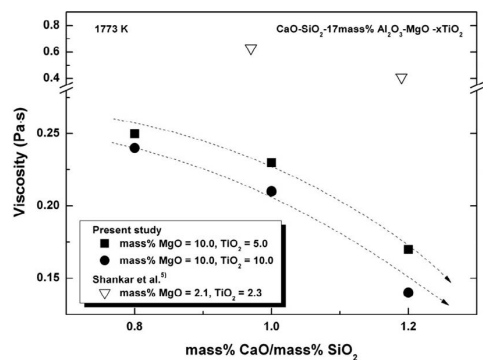


Fig. 3. Effect of CaO/SiO₂ on the viscosity of the CaO–SiO₂–17 mass% Al₂O₃–MgO–TiO₂ slags at 1773 K.

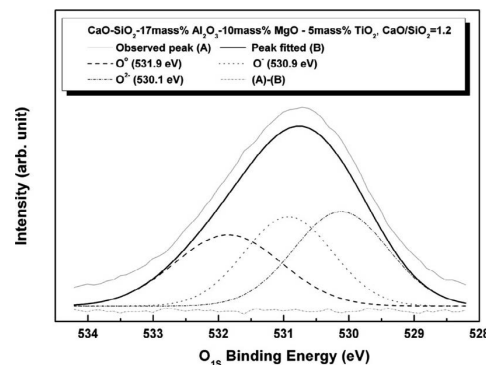


Fig. 4. Deconvoluted XPS O_{1s} binding energy of CaO–SiO₂–17 mass% Al₂O₃–10 mass% MgO–5 mass% TiO₂ slags at constant CaO/SiO₂ of 1.2 quenched from 1773 K.

Table 2. Peak analysis of the O_{1s} in the CaO–SiO₂–17 mass% Al₂O₃–10 mass% MgO–x mass% TiO₂ slag system quenched from 1773 K.

CaO/SiO ₂	'x' TiO ₂	Item analysis	Bridged oxygen (O [°])	Non-bridged oxygen (O ⁻)	Free oxygen (O ²⁻)
0	0	Maximum amplitude	532.09	531.28	530.39
		FWHM	1.99	1.60	1.71
0.8	5	Maximum amplitude	531.97	531.04	530.28
		FWHM	1.96	1.74	1.99
0.8	10	Maximum amplitude	531.92	531.00	530.14
		FWHM	1.86	1.47	1.69
1.2	0	Maximum amplitude	531.86	530.95	530.14
		FWHM	1.81	1.63	1.55
1.2	5	Maximum amplitude	531.91	530.94	530.16
		FWHM	1.91	1.66	1.75
1.2	10	Maximum amplitude	532.0	531.08	530.14
		FWHM	1.76	1.50	1.70

TiO₂ lowers the viscosity in the CaO/SiO₂ of 0.8 to 1.2 range. From comparison of the initial slope of 5 mass% TiO₂ additions and the slope between 5 mass% and 10 mass% TiO₂ additions, it can be inferred that the effect of TiO₂ additions becomes less pronounced at higher TiO₂ concentrations. The results of Saito *et al.*¹⁴⁾ seems to show a similar decreasing trend. Saito *et al.*'s¹⁴⁾ viscosity measurements were slightly higher, which is likely due to the absence of MgO and a higher Ar flowrate.

3.2. Effect of CaO/SiO₂ on the Viscosity

Figure 3 shows the effect of CaO/SiO₂ at constant TiO₂ content of 5 and 10 mass% at 1773 K. In both cases, higher CaO/SiO₂ or higher apparent basicity (*a_o²⁻*) lowers the viscosity of the present slag system. This has been typically observed in other slag systems due to the supply of free oxygen ions (O²⁻) with increased CaO/SiO₂ and the subsequent modification of the large silicate network. Comparison of the 5 and 10 mass% TiO₂ at constant basicity seems to also indicate that the effect of basicity is more significant in modifying the slag viscosity.

3.3. Effect of TiO₂ on the Slag Structure Using XPS

Figure 4 shows an example of the deconvoluted peaks of O[°], O⁻, and O²⁻ as a function of O_{1s} binding energy (eV) for the CaO/SiO₂ of 1.2. Peak fitting resulted in an optimum full width half maximum (FWHM) of less than 2.0 and the subsequent peak binding energies for the various oxygen ion species after background removal and C_{1s} calibration are given in Table 2. These binding energies of O[°] between

531.86 to 532.00 eV agree well with Park *et al.*²³⁾ at 532.12 eV and previously published work of the authors.²¹⁾

The resulting fraction of oxygen ion species with TiO₂ additions at CaO/SiO₂ of 0.8 and 1.2 is shown in Figs. 5(a) and 5(b), respectively. The fraction of bridged oxygen (O[°]) and the non-bridged oxygen (O⁻) decreased with TiO₂ additions, but the free oxygen (O²⁻) increased with TiO₂ additions. Thus, higher TiO₂ content seems to provide a higher potential to depolymerize the slags network structure. Similar trends were observed for constant CaO/SiO₂ of 1.2. It should be noted that the additions of TiO₂ above 5 mass% at constant CaO/SiO₂ of 0.8 had comparatively less effect on changing the fraction of O[°], O⁻, and O²⁻, which seems to correlate well with the viscosity measurements in Fig. 2. Similar correlations can be made from the results of CaO/SiO₂ at 1.2 in Figs. 5(b) and 2.

3.4. Temperature Dependence and Activation Energy

The temperature dependence of the viscosity at CaO/SiO₂ of 0.8 and various TiO₂ content is shown in Fig. 6. As expected, the viscosity decreases with increasing temperatures. Although not shown, similar trends were obtained for CaO/SiO₂ of 1.0 and 1.2. In order to calculate the activation energy for viscous flow (*E_η*), the Arrhenius type relationship of Eq. (1) was used and the slope from the plot of the natural logarithm of the viscosity (*ln η*) with reciprocal temperature (*1/T*) provided *E_η*.

$$\eta = \eta_0 \exp(E_{\eta}/RT) \dots\dots\dots (1)$$

Table 3 shows the calculated activation energies for the

various slag compositions, where values between 195 kJ/mol to 262 kJ/mol were calculated depending on the various slag compositions. These values are comparable to the results

obtained by Saito *et al.*¹⁴⁾ between 150 to 210 kJ/mol for CaO–SiO₂–20 mass% Al₂O₃ slags at constant CaO/SiO₂ of unity and containing either MgO or TiO₂. Kim *et al.*²⁰⁾ has also published activation energy values of viscous flow from 200 to 240 kJ/mol for the CaO–SiO₂–20 mass% Al₂O₃–10 mass% MgO slags at CaO/SiO₂ from 0.8 to 1.2, which is also comparable to the present study.

4. Conclusion

TiO₂ additions lowered the viscosity by depolymerizing the slag network structure. The XPS results showed the fraction of bridged oxygen (O[°]) decreased with TiO₂ additions and free oxygen (O²⁻) increased. The additions of TiO₂ above 5 mass% at constant CaO/SiO₂ of 0.8 had comparatively less effect on changing the fraction of O[°], O⁻, and O²⁻, which seems to correlate well with the viscosity measurements. Increasing basicity seems to be more effective in decreasing the viscosity compared to TiO₂ additions. From the temperature dependence, the activation energy of viscous flow was calculated between 195 kJ/mol to 262 kJ/mol depending on the slag composition.

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REFERENCES

- 1) T. Paananen and K. Kinnunen: *Steel Res. Int.*, **80** (2009), 408.
- 2) M. V. C. Sastri, R. P. Viswanath and B. Viswanathan: *Int. J. Hydrog. Energy*, **7** (1982), 951.
- 3) G. Li, J. Ma, H. Ni, Q. Shen and F. Tsukihashi: *ISIJ Int.*, **46** (2006), 981.
- 4) T. Nagasaka, M. Hino and S. Ban-ya: *Metall. Trans. B*, **31B** (2000), 945.
- 5) A. Shankar, M. Görnerup, A. K. Lahiri and S. Seetharaman: *Metall. Trans. B*, **37B** (2006), 941.
- 6) L. B. McRae, E. Pothast, P. R. Jochenst and D. D. Howat: *J. SAImm*, (1969), 577.
- 7) K. Nomura, B. Ozturk and R. J. Fruehan: *Metall. Trans. B*, **37B** (1991), 783.
- 8) J. Tanabe and H. Suito: *Steel Res. Int.*, **63** (1992), 515.
- 9) Y. Morizane, B. Ozturk and R. J. Fruehan: *Metall. Trans. B*, **30B** (1999), 29.
- 10) M. Chapman, O. Ostrovski, G. Tranell and S. Jahanshahi: *Elektrometall.*, **3** (2000), 34.
- 11) M. Kato and S. Minowa: *Trans. Iron Steel Inst. Jpn.*, **9** (1969), 31.
- 12) G. Handfield and G. G. Charette: *Can. Metall. Q.*, **10** (1971), 235.
- 13) A. Ohno and H. U. Ross: *Can. Metall. Q.*, **2** (1963), 259.
- 14) N. Saito, N. Hori, K. Nakashima and K. Mori: *Metall. Trans. B*, **34B** (2003), 509.
- 15) K. Datta, P. K. Sen, S. S. Gupta and A. Chatterjee: *Steel Res. Int.*, **64** (1993), 232.
- 16) R. Yamamoto, R. Nakajima, Y. Koyama and K. Niiya: *Ironmaking Conf. Proc., ISS-AIME, Detroit, MI*, **44** (1985), 149.
- 17) M. Higuchi: *Trans. ISS, I&SM*, (1978), 33.
- 18) L. Zhang, L. Zhang, M. Wang, G. Li and Z. Sui: *ISIJ Int.*, **46** (2006), 458.
- 19) A. Shankar, M. Görnerup, A. K. Lahiri and S. Seetharaman: *Metall. Trans. B*, **37B** (2007), 911.
- 20) H. Kim, W. H. Kim, I. Sohn and D. J. Min: *Steel Res. Int.*, **81** (2010), 261.
- 21) H. Kim and I. Sohn: *ISIJ Int.*, **51** (2011), 1.
- 22) S. Sridhar, K. C. Mills, O. D. C. Afrange, H. P. Lorz and R. Carli: *Ironmaking Steelmaking*, **27** (2000), 238.
- 23) J. H. Park and P. C.-H. Lee: *J. Non-Cryst. Solids*, **282** (2001), 7.

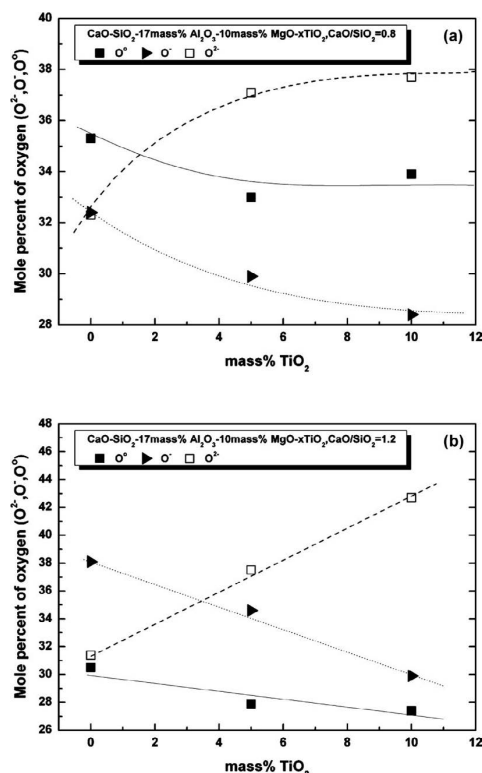


Fig. 5. XPS result of as-quenched samples with varying TiO₂ concentration in the CaO–SiO₂–17 mass% Al₂O₃–10 mass% MgO–TiO₂ slags at (a) CaO/SiO₂=0.8 and (b) CaO/SiO₂=1.2 quenched from 1 773 K.

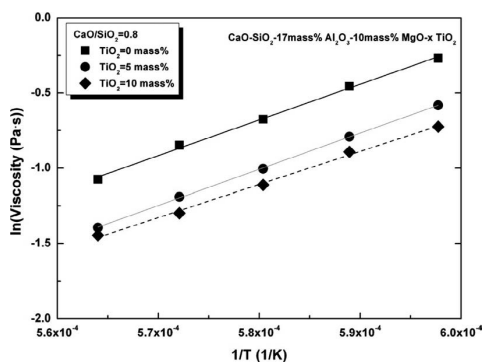


Fig. 6. Temperature dependence for the CaO–SiO₂–17 mass% Al₂O₃–10 mass% MgO–TiO₂ slag system at various TiO₂ content and CaO/SiO₂=0.8.

Table 3. Calculated activation energy (kJ/mol) using an Arrhenius type relationship for the CaO–SiO₂–17 mass% Al₂O₃–10 mass% MgO–TiO₂ slag system at various CaO/SiO₂ ratio and TiO₂ content.

CaO/SiO ₂	TiO ₂		
	0 mass%	5 mass%	10 mass%
0.8	206 ± 3	221 ± 7	195 ± 4
1.0	220 ± 7	199 ± 12	209 ± 18
1.2	225 ± 9	246 ± 1	262 ± 4