Effect of SiO₂/Al₂O₃ and TiO₂/SiO₂ Ratios on the Viscosity and Structure of the TiO₂–MnO–SiO₂–Al₂O₃ Welding Flux System

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The effect of SiO₂/Al₂O₃ and TiO₂/SiO₂ ratios on the viscosity of the TiO₂–MnO–SiO₂–Al₂O₃ welding flux system was studied using the rotational spindle method. The viscosity was measured at the fully liquid region of the melt from 1 773 K to the break temperature at approximately 1 623 K. Higher TiO₂/SiO₂ ratio resulted in lower viscosity in the temperature range of interest. The SiO₂ dominant slag system showed higher viscosity values than the Al₂O₃ dominant slag in the present TiO₂ based system until a SiO₂/Al₂O₃ ratio of 1.61. Fourier transform infrared (FTIR) results revealed the [SiO₄]⁴⁻-tetrahedral symmetric stretching vibrations and the [AlO₄]⁵⁻-tetrahedral asymmetric stretching vibration became weaker with higher TiO₂/SiO₂, which was also apparent with the increase in the extended basicity ((TiO₂+MnO)/(SiO2+Al₂O3)). The Al–O–Si bending vibration and [SiO₄]⁴⁻-tetrahedral symmetric stretching vibrations were also pronounced with higher SiO₂/Al₂O₃ ratio. From the X-ray photoelectron spectroscopy (XPS) results, the bridged oxygen (O0) slightly decreased with higher TiO₂/SiO₂ and increased with higher SiO₂/Al₂O₃.

KEY WORDS: viscosity; welding flux; FTIR; XPS; slag structure.

1. Introduction

As the global community continues to test the limits of materials applications in high rise constructions, ultra-large ships, ultra-long suspension bridges and other superstructures requiring both high strength and formability, the development of new and improved steels such as transformation-induced plasticity (TRIP) and twinning-induced plasticity (TWIP) has been the focus of much research.¹–⁴) In particular, the stringent safety requirements for welded structures and the control of various impurities in the weld zone of these newer grades of steel is essential to obtain consistent and reliable mechanical properties at this dissimilar weld interface.⁵) The contamination of the weld zone can seriously affect the mechanical properties of the aforementioned high strength steels⁶–⁸) and elements transfer ⁹,¹⁰) between the metal and slag can also be a critical factor that affects the physical and chemical property of the weld zone. Thus, controlling the flux viscosity is important during flux cored arc welding of advanced high strength steels.¹¹–¹³)

To design welding fluxes, a fundamental understanding of the relationship between viscosity and molten oxide structure is required. The viscosity can also affect the wettability¹⁴) and crystallization¹⁵) of the welding flux, which in turn can impact the microstructure. But, only limited studies have been reported on the TiO₂–MnO based SiO₂ and Al₂O₃ containing flux systems. TiO₂ and MnO content have been described as a basic oxide under certain conditions, which can depolymerize the network structure of the acidic oxides by supplying free oxygen ions (O²⁻)¹⁶,¹⁷) and also as an acidic oxide,¹⁸,¹⁹) which polymerize the network structure. Thus, conflicting views on TiO₂ is apparent and further studies with the TiO₂ containing slag systems is needed. According to Bockris and Lowe,¹⁰) acidic oxides such as SiO₂ can increase the degree of polymerization and form complex silicate networks resulting in higher viscosity. The effect of the network forming acidic oxide SiO₂¹⁸,²¹) and the amphoteric oxide Al₂O₃¹²,²³) have been discussed separately, but lacks a comprehensive study on the combined effect of SiO₂/Al₂O₃ ratio and basicity for the TiO₂–MnO dominant slag systems. In addition, the presence of both SiO₂ and Al₂O₃ in the slag can affect the existence of the dominant structural units of complex silicate and alumino-silicate structures, which directly influences the thermophysical properties of slags such as viscosity and the spreading ability of the flux to protect the weld zone from atmospheric contamination and re-oxidation. Furthermore, in TRIP and TWIP steels, where significant concentrations of Al exist, the flux is typically designed with Al₂O₃ to lower the thermodynamic driving force to inhibit the reduction of SiO₂ in the flux by Al in the weld zone. However, the combined and substitutitional effects of SiO₂ and Al₂O₃ in the flux have yet to be fully understood.

Thus, in this study, the substitutional effect of SiO₂ and Al₂O₃ contents on TiO₂–MnO based slag systems at various basicities and temperature has been investigated. Structural analysis of the as-quenched slag was done using the Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). All compositions in the present study are reported as wt.% unless stated otherwise.
2. Experimental Procedure and Methods

2.1. Sample Preparation

All samples were prepared with reagent grade chemicals of TiO₂, MnO, SiO₂ and Al₂O₃. The sample was well mixed and pre-melted at 1 773 K (1 500°C) for 3 hours under 2 L/min of UHP Ar (99.9999 vol%) gas. The master slag was prepared through the pre-melting process for each compositional sample in a Kanthal® resistance box furnace. After measuring the viscosity, post-experimental chemical compositions of the present flux was analyzed by the X-ray fluorescence (XRF, S4 Explorer; Bruker AXS GmbH Karlsruhe, Germany) and is presented in Table 1. The liquidus temperature calculated by FactSage® is also presented in Table 1. It provides an approximate range for the experimental temperatures and the compositional boundaries, where viscosity measurements may be possible. The calculated values are not precise as was confirmed from preliminary DTA experiments and should not be assumed to be the actual liquidus temperature of the melt. Negligible change was detected during the pre- and post-experimental process. The experimental compositions at 1 673 K (1 400°C) are over-layed on the TiO₂–Al₂O₃–SiO₂–30MnO quaternary phase diagram in Fig. 1 calculated with Factsage®, Which also show the probable primary phase in equilibrium for the present slag composition. The expected primary phase precipitated at lower temperatures was identified to be the TiO₂ (rutile) phase except for the composition of the 30TiO₂–30MnO–15SiO₂–25Al₂O₃ composition, where the primary crystalline phase was estimated to be the Al₂TiO₅ phase.

| Table 1. Weighed sample mass and post-experimental results from the XRF for TiO₂–MnO–SiO₂–Al₂O₃ system. |
|---|
| Pre-experimental (weighed composition) | Post-experimental (XRF analysis) | FactSage® Liquidus Temp. (Tliq.: K) |
| TiO₂ | MnO | SiO₂ | Al₂O₃ | TiO₂ | MnO | SiO₂ | Al₂O₃ | TiO₂/SiO₂ | SiO₂/Al₂O₃ | TiO₂/SiO₂ | SiO₂/Al₂O₃ |
| 1 | 40 | 30 | 15 | 15 | 2.33 | 39.4 | 29.7 | 15.7 | 14.9 | 2.26 | 2.50 | 1.05 | 1 720.1 |
| 2 | 35 | 30 | 20 | 15 | 1.86 | 34 | 29.3 | 20.5 | 16 | 1.73 | 1.65 | 1.28 | 1 735.9 |
| 3 | 30 | 30 | 25 | 15 | 1.50 | 29.9 | 29.4 | 25.2 | 15.4 | 1.46 | 1.19 | 1.64 | 1 745.6 |
| 4 | 30 | 30 | 20 | 20 | 1.50 | 30.6 | 29.4 | 20.1 | 19.8 | 1.50 | 1.53 | 1.02 | 1 690.7 |
| 5 | 30 | 30 | 15 | 25 | 1.50 | 31 | 30.6 | 15.2 | 23 | 1.61 | 2.03 | 0.66 | 1 719.2 |
| 6 | 30 | 30 | 30 | 10 | 1.50 | 27.8 | 32 | 29.6 | 10.5 | 1.49 | 0.94 | 2.82 | 1 707.5 |

Fig. 1. The experimental composition of the present study overlaid on the TiO₂–30MnO–SiO₂–Al₂O₃ phase diagram calculated by FactSage®.
2.2. Viscosity Measurements

The schematic of the experimental apparatus is described in Fig. 2. A total of 120 g of sample was filled into a beaker type Rh-10Rh crucible and placed within the hot zone of the vertical resistance furnace held at 1 273 K (1 000 °C). An Ar atmosphere of 0.4 L/min was passed into the reaction chamber. The gas was purified with columns of CaSO₄ and soda lime to eliminate excess moisture and CO₂ gas. The temperature was then increased to 1 773 K (1 500 °C) and held for 1 hour to obtain a sufficient thermal equilibrium of the molten slag with the atmosphere and a fully liquid phase. The length of the hot zone in the vertical resistance furnace was approximately 5 cm and calibrated with a B-type reference thermocouple, which is long enough for the entire molten slag to be within the hot zone of the furnace. The target temperature was within ±3 K error using a proportional-integral-derivative controller (PID). The viscosity was measured by using a Brookfield digital rheometer (LVDV-II+; Brookfield Engineering Laboratories, Middleboro, MA), which was connected with a Pt-10Rh spindle and bob (total weight; 80 g). The viscosity was measured during the cooling period at 25 K intervals until the break temperature (Tₜₐₙ) was reached. Each temperature step was held for 15 min prior to the actual measurements to ensure thermal equilibrium and the measured viscosity values were chosen using the average value acquired for approximately 5 min at 1 Hz. The break temperature signifies the transition temperature, where a sudden increase in the viscosity is observed during the cooling cycle and a typical measurement up to the Tₜₐₙ is depicted in Fig. 3. The break temperature is different from the fully crystallized temperature provided in the DTA exothermic curve measurements, where the slag is fully solidified and crystallized. Thus, the break temperature lies within the solid-liquid coexisting region and the fully crystallized temperature of the DTA measurements would lie below the break temperature, as was verified from the DTA analysis provided in Fig. 3. The viscosity measurements for the present work were done in the fully liquid melt phase, which would be the temperatures above the Tₜₐₙ.

2.3. Flux Structure Analysis Using FTIR and XPS

The complex network structure of the welding fluxes at high temperature was analyzed with FTIR (Spectra100; Perkin-Elmer, Shelton CT, USA) and XPS (K-Alpha; Thermo Scientific Instrument, XPS mono, model: K-alpha by Thermo U. K.). High concentration of TiO₂ and MnO contents promotes crystallization and thus accelerates the formation of primary and secondary crystalline phases that make it extremely difficult to obtain an amorphous phase for structural analysis of the molten state. Thus, to ensure a high heat transfer rate of the molten melt, a copper plate is cooled by placing it on top of a pool of liquid N₂. When the molten slag contacts the surface of the liquid N₂ cooled copper plate a thin amorphous layer can be obtained absent of crystal phases. The amorphous layer was verified through back-scattered cross-sectional SEM micrograph (JSM-6700F; JEOL, Japan) analysis. A clear distinguishable interface between the non-crystalline and crystalline phase could be identified at low magnifications of 500 and 1 000 times, as
shown in Fig. 4. The average thickness of the non-crystalline amorphous phase was approximately 600 μm, which is sufficient thickness for the FTIR and XPS analysis. The as-is SEM images are unpolished to ensure the original morphology. The present sample shows needle-like crystals in the crystalline phase and entrapped bubbles in the non-crystalline phase. The needle-like crystals were revealed to be pyrophanite (MnTiO₃) mixed with individual Ti₆O₁₁, SiO₂, AlO phases according to the X-ray diffraction (XRD) analysis. From the as-quenched samples, the individual crystalline and amorphous phases could be physically separated for FTIR and XRD analysis. The depth of the amorphous phase at approximately 600 μm is sufficient since the XPS penetration depth is typically reported to be within a few nm.²⁵)

The O₁s XPS spectrum was measured using a monochromatic Al Kα source. The individual oxygen peaks were calibrated with the C₁s core level standard at 285 eV. The Shirley’s method²⁶) was selected as the background subtraction method and the peaks were fitted with a mixed Gaussian-Lorentz function. The commercial software SDP v4.11 (XPS International, LLC software, USA) was used for to deconvolute the spectra. All peaks were calculated within an r² value over 0.99.

3. Results

3.1. Effect of TiO₂/SiO₂ and SiO₂/Al₂O₃ Ratio on the Viscous Behavior in the TiO₂–MnO–SiO₂–Al₂O₃ System

Figures 5(a) and 5(b) show the effect of TiO₂/SiO₂ ratio on the viscosity in the TiO₂–MnO–SiO₂ and TiO₂–MnO–SiO₂–Al₂O₃ system at various temperatures, respectively. The viscosity values of the ternary system published in a previous publication¹¹) is provided as a comparison. Both graphs show similar trend regarding the effect of TiO₂/SiO₂. Higher TiO₂/SiO₂ lowers the viscosity. The amphoteric oxide Al₂O₃ in the TiO₂–MnO–SiO₂ system is likely an acidic oxide, that promote the formation of more complex network structures, since the total sum of the basic oxides of TiO₂ and MnO significantly exceeds the amount of SiO₂ present in the system. The viscosity measurements in the present quaternary TiO₂–MnO–SiO₂–Al₂O₃ slag system at high temperatures between 1 773 K (1 500°C) and 1 673 K (1 400°C) were comparably higher than the ternary TiO₂–MnO–SiO₂ slag system below a TiO₂/SiO₂ ratio of approximately 2.0. At TiO₂/SiO₂ ratios above 2.0, the viscosity values were similar between the quaternary and ternary slag systems. From the variation of the viscosity with TiO₂/SiO₂, the Al₂O₃ containing quaternary system seems to be more affected than the Al₂O₃ free ternary TiO₂–MnO–SiO₂ slag system. Figure 6(a) shows the re-plotted viscosity values according to the extended basicity ((TiO₂+MnO)/(SiO₂+Al₂O₃)). The viscosity at comparatively high temperatures decreased almost linearly before 1 673 K (1 400°C), but as the temperature nears the Tₓ of 1 648 K (1 375°C), the viscosity did not follow a linear trend. Thus, at the fully liquid region, a linear dependency with the extended basicity is observed, but as the melt nears the solid-liquid two phase region it may experience significant deviations from a Newtonian fluid. Figure 6(a) also includes the partial results by Saito et al.²⁷) and described slag system was also a quaternary system with the MnO replaced with CaO. Thus the extended basicity of the TiO₂–CaO–SiO₂–Al₂O₃ slag system was defined as (TiO₂+CaO)/(SiO₂+Al₂O₃). The viscosity values by Saito et al.²⁷) were within the acidic region of the extended basicity to the far left of the figure and it seems that viscosity values decrease with increasing extended basicity. This trend was also found in the higher extended basicity region for the present slag system. It should be noted that the slope of the work by Saito et al.²⁷) is steeper than the present work. This is speculated to be the presence of significantly more network breaking oxides in the present

Fig. 4. Cross-sectional image of the SEM micrograph of as-quenched flux samples on liquid N₂ cooled copper plates from 1 773 K. Note the presence of an amorphous layer for structural analysis.
slag system compared to the slag composition of Saito et al.\textsuperscript{27} and the absence of large complex network structures within the slag. When the TiO\textsubscript{2} content increases, the temperature dependence of the viscosity is observed to decrease similar to the TiO\textsubscript{2}–MnO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} system. Figure 6(b) described the viscosity values as a function of reciprocal temperature (1/T) in the fully liquid region of the flux. It shows the viscosity to be relatively temperature independent resulting in a low apparent activation energy of viscous flow.

The effect of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} or the substitutional effect of SiO\textsubscript{2} with Al\textsubscript{2}O\textsubscript{3} on the viscous property of the present flux system is depicted in Fig. 7(a). The overall trend indicated that higher SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} increases the viscosity and seems to level out beyond SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} of unit ratio. The viscosity at SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} of 0.6 is significantly lower compared to other SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios. This apparent uniqueness compared to the samples of other compositional regions is speculated to coincide with the difference in the primary phase of Al\textsubscript{2}TiO\textsubscript{5} compared with the primary phase of TiO\textsubscript{2} for other compositions. FactSage\textsuperscript{®} calculations indicate that most of the slag compositions have the rutile (TiO\textsubscript{2}) phase as the primary phase during equilibrium cooling, but the TiO\textsubscript{2}–30MnO–15SiO\textsubscript{2}–25Al\textsubscript{2}O\textsubscript{3} slag system with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} of 0.6 has the Al\textsubscript{2}TiO\textsubscript{5} primary phase during similar cooling conditions. The effect of the primary and secondary phases will be discussed specifically in the discussion section.

Similar to Figs. 6 (b), 7(b) also shows the overall viscosity slightly increased with higher temperatures and having only a slight temperature dependency. The flux with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} of 0.6 and 1.0 showed a comparable temperature dependency with the flux at SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} of 0.6 to be slightly
steeper in slope. The flux with SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} of 3.0 had a slightly lower temperature dependency than the aforementioned fluxes corresponding to a lower apparent activation energy described later in a separate section. The relatively low temperature dependency of the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} at 1.67 is within the transition region of the flux structure, where a change in the primary phase is observed. These changes in the primary phase and the dominant network structure of the flux are speculated to influence the temperature dependency of the flux.

3.2. Effect of TiO\textsubscript{2}/SiO\textsubscript{2} and SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} Ratio on the Flux Structure Using FTIR Analysis

Figure 8 provides the structural analysis of the bonding characteristics of the molten flux to identify the polymerization degree, which comprises the network structure of the present slag system. The vibration region between approximately 850 cm\textsuperscript{-1} to 1200 cm\textsuperscript{-1} is identified as the [SiO\textsubscript{4}]\textsuperscript{4–}tetrahedral symmetric stretching vibration.\textsuperscript{28–30} The vibration from 600 cm\textsuperscript{-1} to 800 cm\textsuperscript{-1} is identified as the [AlO\textsubscript{4}]\textsuperscript{5–}tetrahedral asymmetric stretching vibration.\textsuperscript{31,32} According to Huang \textit{et al}.\textsuperscript{33} the characteristic vibration around 450 cm\textsuperscript{-1} corresponds to the Al–O–Si bending vibration. The [SiO\textsubscript{4}]\textsuperscript{4–}tetrahedral symmetric stretching vibration becomes less pronounced with higher TiO\textsubscript{2}/SiO\textsubscript{2} as expected due to the lower absolute concentration of SiO\textsubscript{2}. At fixed Al\textsubscript{2}O\textsubscript{3} of 15 wt\%, the [AlO\textsubscript{4}]\textsuperscript{5–}tetrahedral asymmetric stretching vibration troughs are relatively unaffected with TiO\textsubscript{2}/SiO\textsubscript{2} ratios, but the Al–O–Si bending vibration peaks seems to become slightly weaker due to the lower content of SiO\textsubscript{2}. Mysen has described the existence of the Ti–O–Ti stretching vibration existing through Raman analysis for high TiO\textsubscript{2} melts near 830 cm\textsuperscript{-1}, but the present work could not find the specific band using FTIR analysis.\textsuperscript{34}

Figure 9 shows the effect of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio on the slag structure ascertained from the FTIR analysis of as-quenched slags. The slag structure seems to consist of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} based structural units, where the [SiO\textsubscript{4}]\textsuperscript{4–}tetrahedral symmetric stretching vibrations and the [AlO\textsubscript{4}]\textsuperscript{5–}tetrahedral asymmetric stretching vibration are more pronounced with higher SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}. In addition, the trough of the Al–O–Si bending vibration became more pronounced with higher SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} at 1.67. Thus, at high SiO\textsubscript{2} the silicate structures dominate and the Al–O–Si interactions can become obscured. At low SiO\textsubscript{2}, there may be insufficient SiO\textsubscript{2} to form Al–O–Si bonds and inferiority of the [AlO\textsubscript{4}]\textsuperscript{5–}tetrahedral asymmetric stretching bands also was identified at Al\textsubscript{2}O\textsubscript{3} dominant slag system.

3.3. Effect of TiO\textsubscript{2}/SiO\textsubscript{2} and SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} Ratio on the Flux Structure Using XPS Analysis

Figure 10 is a typical example of the deconvoluted peaks of the O\textsubscript{1s} binding energy (eV) from the XPS spectra for the 35TiO\textsubscript{2}-30MnO-20SiO\textsubscript{2}-15Al\textsubscript{2}O\textsubscript{3} flux as-quenched from 1773 K (1500°C). Three oxygen ion species can be deconvoluted, which include the bridged oxygen (O\textsuperscript{0}), non-bridged oxygen (O\textsuperscript{–}), and free oxygen (O\textsuperscript{2–}) ions. The semi-quantitative ratio of the individual oxygen constituents were obtained by integrating the area of the individual deconvoluted peaks as a function of binding energy. All peaks were fitted with a full-width half maximum (FWHM) of less than 2.0 eV to ensure reliable deconvolution. The respective
binding energies are provided in Table 2.

Figures 11 and 12 describe the percent of the bridged oxygen (O$^0$), non-bridged oxygen (O$^-$), and free oxygen (O$^{2-}$) as a function of TiO$_2$/SiO$_2$ and SiO$_2$/Al$_2$O$_3$ ratio, respectively. When TiO$_2$/SiO$_2$ ratio is increased, the fraction of non-bridged oxygen (O$^-$) slightly increases and the bridged oxygen (O$^0$), free oxygen (O$^{2-}$) slightly decreases, resulting in slightly simpler network structures. The opposite could be observed for higher SiO$_2$/Al$_2$O$_3$ ratio, where the O$^-$ slightly decreases and the O$^0$ and O$^{2-}$ increase resulting in more complex network structures. However, the change in the relative oxygen species with SiO$_2$ additions was not significant above SiO$_2$/Al$_2$O$_3$ ratio of unity.

3.4. Temperature Dependency of the Viscosity with TiO$_2$/SiO$_2$ and SiO$_2$/Al$_2$O$_3$ Ratio

The temperature dependence of the viscosity for the TiO$_2$–MnO–SiO$_2$–Al$_2$O$_3$ slag system was already depicted in Figs. 6(b) and 7(b). Lower temperatures result in higher viscosity as expected, but overall the temperature dependency is not highly pronounced. This low temperature dependency in the TiO$_2$-containing flux system at low SiO$_2$ and Al$_2$O$_3$ content is typical, since there is a significant absence of large oligomer structures within the melt. The temperature dependency of the viscosity at various fixed TiO$_2$/SiO$_2$ ratio is weaker than the dependency observed at various fixed SiO$_2$/Al$_2$O$_3$ ratio and an extended basicity of 1.5. The absence of complex structure and in particular SiO$_2$ content, which can form complex Si–O network structures seems to be an important factor in determining the temperature dependency of the melt. The apparent activation energy calculated from the slope of the natural logarithm of the viscosity (ln η) with reciprocal temperature (1/T)$^{21}$ assuming an Arrhenius type relationship is shown in Figs. 13(a) and 13(b).

![Fig. 11. Effect of TiO$_2$/SiO$_2$ ratio on the slag structure at fixed 30MnO-15Al$_2$O$_3$ using XPS of as-quenched flux sample.](image)

![Fig. 12. Effect of SiO$_2$/Al$_2$O$_3$ ratio on the slag structure @ 30TiO$_2$&30MnO using XPS of as-quenched flux sample.](image)

![Fig. 13. Calculated activation energy by using Arrhenius type relationship in present slag system.](image)

### Table 2. O$_1$s deconvoluted peaks with binding energy and FWHM.

| No. | (T+M)/(S+A) | SiO$_2$/Al$_2$O$_3$ | O$^{2-}$ (eV) | FWHM (eV) | O$^-$ (eV) | FWHM (eV) | O$^0$ (eV) | FWHM (eV) |
|-----|-------------|-------------------|--------------|-----------|------------|-----------|------------|-----------|
| 1   | 2.33        | 1.00              | 530.25       | 1.74      | 531.33     | 1.33      | 532.15     | 1.54      |
| 2   | 1.86        | 1.33              | 530.45       | 1.79      | 531.34     | 1.26      | 532.24     | 1.36      |
| 3   | 1.50        | 1.67              | 530.52       | 1.68      | 531.34     | 1.08      | 532.01     | 1.17      |
| 4   | 1.50        | 1.00              | 530.47       | 1.62      | 531.52     | 1.33      | 532.47     | 1.38      |
| 5   | 1.50        | 0.60              | 530.48       | 1.97      | 531.49     | 1.42      | 532.06     | 1.40      |
| 6   | 1.50        | 3.00              | 530.65       | 1.75      | 531.37     | 1.31      | 532.05     | 1.45      |
Contrary to the temperature dependency of the viscosity at fixed TiO$_2$SiO$_2$, the temperature dependency of the viscosity at various fixed SiO$_2$/Al$_2$O$_3$ and an extended basicity of 1.5 was comparatively more pronounced. The apparent activation energy at various fixed TiO$_2$/SiO$_2$ ratio was between 6.41 and 30.48 kJ/mol and the apparent activation energy at various fixed SiO$_2$/Al$_2$O$_3$ ratio was between 30.48 and 128.03 kJ/mol with the highest apparent activation energy for higher SiO$_2$ substitution with Al$_2$O$_3$. The direct cause of the higher temperature dependency with the Al$_2$O$_3$ rich melt has yet be fully understood, but it could be related to the Ti–O–Al vibration. The activation energy after SiO$_2$/Al$_2$O$_3$ ratio of 1.67 increased and is anticipated to be correlated to the complex Si–O structure. When the TiO$_2$/SiO$_2$ ratio increases, the apparent activation energy slightly decreases, which is speculated to be the effect of the lower SiO$_2$ content and subsequent substitution of complex Si–O structures with less complex Ti–O structures. From the aforementioned FTIR and XPS analysis, the [SiO$_4$]$^{4-}$-tetrahedral symmetric stretching bands decreased with higher TiO$_2$/SiO$_2$, which correlates with the trend of the apparent activation energy.

4. Discussion

The viscosity decreased with higher TiO$_2$/SiO$_2$ ratio in the TiO$_2$–MnO–SiO$_2$ and TiO$_2$–MnO–SiO$_2$–Al$_2$O$_3$ system, as shown in Fig. 5. According to past work by the present authors, the basic oxide MnO provides free oxygen ions, which interact with the available bridged oxygen, depolymerizing the network structure and subsequently lowering the viscosity, but was unclear of the possible network forming ability of TiO$_2$ content in TiO$_2$–MnO–SiO$_2$ slag system of past publication. However, it was noted that the absolute amount of SiO$_2$ was perhaps too low to form large and complex oligomers that can significantly affect the viscosity. The function of TiO$_2$ and MnO content was also examined by Yagi et al. in Fig. 5(a). Both components were characterized to be a strong basic oxide decreasing the viscosity. The TiO$_2$ dilution effect of SiO$_2$ and the subsequent decrease in the complex silicate structure could also be implied above a certain critical amount of TiO$_2$. From the FTIR analysis appropriate amounts of SiO$_2$ and Al$_2$O$_3$ within the melt could result in the formation of complex alumino-silicate structures in the TiO$_2$–MnO–SiO$_2$–Al$_2$O$_3$ slag system.

Although the presence of Si–O, Al–O, and Al–O–Si network structures were verified from the spectroscopic analysis, 30MnO present in the slag creates an environment in the melt for network structures to be significantly depolymerized and if melt network structures are present, there would be dominance in the simple oligomers. Furthermore, according to Mysen and Richet, Ti–O stretching and Ti–O–Al vibrations can create short range ordered simple network structures, which result in lower viscosity in the SiO$_2$ based slag system. In other words, the substitution of SiO$_2$ with TiO$_2$ decrease the viscosity by not only lowering the absolute amount of SiO$_2$, but also consumes the bridged oxygen (O$^-$) of the silicate structures forming short range simple [TiO$_4$]$^{4-}$-tetrahedral networks. Thus, only a slight viscosity change can be observed at high temperatures, but when sufficient Al$_2$O$_3$ is present, the melt may form less complex titania-aluminum oxide structures and change the viscous behavior, as was observed in Fig. 7(b). With higher SiO$_2$/Al$_2$O$_3$, the viscosity seems to increase and level out above 1.0. The FactSage estimation predicts that the primary phase of Al$_2$TiO$_5$ is prevalent for SiO$_2$/Al$_2$O$_3$ of 0.6, which is unique from other melt compositions of the present study and more temperature dependent. For all other melt compositions beyond SiO$_2$/Al$_2$O$_3$ of 0.6, the primary phase of the melt was predicted to be TiO$_2$ and there was less temperature dependent. Figure 7(a) also shows the primary and secondary phase predicted from the FactSage calculations during cooling. It is expected that the high temperature melt viscosity is highly dependent upon the initial solid phase from which was originally derived, particularly if the working temperature of the liquid flux is not significantly above the T$_{\text{Br}}$. With changes in the content of Al$_2$O$_3$ to the system, the viscosity can slightly increase as [SiO$_4$]$^{4-}$-tetrahedral structures and alumino-silicate Al–O–Si bonds form, polymerizing the existing structure with SiO$_2$/Al$_2$O$_3$ ratio increase.

The FTIR analysis showed the [SiO$_4$]$^{4-}$-tetrahedral symmetric stretching vibration to become less pronounced with higher TiO$_2$/SiO$_2$ ratio, but the [AlO$_4$]$^{5-}$-tetrahedral asymmetric stretching vibration and the characteristic Al–O–Si bending vibration were insignificantly changed. For the flux composition at 15Al$_2$O$_3$ and 30MnO, it could be postulated that the amount of SiO$_2$ is sufficient for the silicate structures to be dominant and a subsequent increase in the TiO$_2$/SiO$_2$ results in lower viscosity through both the substitutional depolymerization of Si–O with Ti–O structures and the decrease in the absolute amount of SiO$_2$, which decreases the silicate complex structures. The depolymerization of the Al–O and Al–O–Si structures through the spectroscopic analysis was not apparent but the viscosity is observed to decrease. Thus, the change in viscosity is likely due to the effect on the [SiO$_4$]$^{4-}$-tetrahedral symmetric stretching vibration and possible the Ti–O–Ti stretching vibrations, which could not be verified through FTIR.

The substitutional effect of SiO$_2$ with Al$_2$O$_3$ showed FTIR spectra having pronounced [SiO$_4$]$^{4-}$-tetrahedral stretching bonds for higher SiO$_2$/Al$_2$O$_3$ with the Al–O–Si bond becoming evident for SiO$_2$/Al$_2$O$_3$ at 1.67, but absent for SiO$_2$/Al$_2$O$_3$ at lower ratios. This Al–O–Si bending vibration became weaker with SiO$_2$/Al$_2$O$_3$ above 0.6. It is likely that due to the lower overall amount of SiO$_2$ present and forming the Ti–O–Al vibration, the Ti–O–Al short range ordered structures is unlikely to play the major role in dominating the viscous behavior for the present flux compositions with lower SiO$_2$/Al$_2$O$_3$ ratios. Because, for the SiO$_2$/Al$_2$O$_3$ of 0.6, the Si–O tetrahedral stretching bonds of the silicate network structures does not seem to be dominant and the [AlO$_4$]$^{5-}$-tetrahedral network structures also seem to be absent. Thus, it may be possible at high Al$_2$O$_3$ and TiO$_2$ content, that the Ti–O–Al simple structures are formed providing some viscosity to the system. According to Saito et al., Ti–O–Al vibration was found to exist near approximately 583 and 439 cm$^{-1}$ with very low intensity, but this could not be observed in the FTIR of the TiO$_2$–MnO–SiO$_2$–Al$_2$O$_3$ slag system depicted in Fig. 9.

The XPS analysis correlate well with the FTIR results and
the trend related to the structural changes with melt composition. According to Toop and Samis, there is a thermodynamic relationship correlating the various oxygen species in equilibrium at high temperatures, as expressed as reaction (2), which depicts the depolymerization of molten oxides.

\[
O^0 + O^2- \rightarrow 2O^- \quad \text{----------------} \quad (2)
\]

The bridged oxygen \((O^0)\) and free oxygen \((O^2-)\) react to form two non-bridged oxygen \((O^-)\) in the depolymerization process, but the effect of TiO2/SiO2 on the network structure was not pronounced since the variation in the bridged oxygen \((O^0)\) and non-bridged oxygen \((O^-)\) was not significant. The complex network structures formed by the \([\text{SiO}_4]^{4-}\)-tetrahedral structure can be simplified to possibly the Ti–O–Ti and Ti–O–Al simple network structures decreasing the viscosity.

According to the XPS deconvolution, the non-bridged oxygen \((O^-)\) slightly decreased and the bridged oxygen \((O^3)\) slightly increased at unit SiO2/Al2O3 ratio without significant change in the free oxygen \((O^2-)\) in Fig. 12. The corresponding decrease in the viscosity was found to correlate to a polymerization of the Ti–O–Al simple structures becoming dominant in the quaternary TiO2–MnO–SiO2–Al2O3 flux system during an increase in the SiO2/Al2O3 ratio.

5. Conclusion

The lower viscosity values were observed with higher TiO2/SiO2. When the SiO2/Al2O3 ratio is increased at a fixed extended basicity of 1.5, the viscosity increases and reaches a steady value beyond SiO2/Al2O3 ratio above 1.0. FTIR analysis showed the \([\text{SiO}_4]^{4-}\)-tetrahedral symmetric stretching band becoming weaker with higher TiO2/SiO2, but the \([\text{AlO}_4]^{5-}\)-tetrahedral asymmetry stretching vibration and Al–O–Si bending vibration were comparatively unchanged. XPS analysis indicated that the bridged oxygen \((O^0)\), free oxygen \((O^2-)\) and non-bridged oxygen \((O^-)\) was slightly changed with the TiO2/SiO2 and the SiO2/Al2O3 variation. It can be inferred from XPS analysis that Ti–O stretching and Ti–O–Al vibration likely exists due to the insignificant change in the oxygen ion species with compositional variation. The apparent activation energy for viscous flow was calculated to be between 19.29 and 128.03 kJ/mol from the slope of the temperature dependency. Higher apparent activation energies were found to be prevalent for Al2O3 content above 20% and SiO2 of at least 15%.

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