Probing Viscosity and Structural Variations in CaF$_2$-SiO$_2$-MnO Welding Fluxes

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ABSTRACT

Recent demand on welding fluxes for high-strength low-alloy steel grades has necessitated the development of CaF$_2$-free fluxes towards high heat input applications. To meet such requirements, a flux design strategy has been postulated by varying MnO/(CaF$_2$+MnO) mass ratio in the CaF$_2$-SiO$_2$-MnO flux system. The effect of MnO substitution for CaF$_2$ on the flux viscosity and structure has been investigated, and a quantitative relationship between viscosity and structural units has been put forward. In addition, it has been suggested that the degree of polymerization (DOP) of silicate network is reduced with increasing MnO/(CaF$_2$+MnO) mass ratio, indicating MnO plays the role of network-breaker. The spectra of F$_{1s}$ and ^{19}F prove that F$^-$ predominantly bonds with Ca^{2+} rather than Si^{4+}, revealing CaF$_2$ acts as a diluent and does not effectively depolymerize the silicate network. Linear correlations can be obtained between the logarithm viscosity and the average non-bridging

25   oxygen per silicon atom (NBO/Si), which can potentially be used as a DOP index to quantify the

26   impact of silicate structure on the viscosity of the flux.

27   **KEYWORDS**: Welding flux; Structure; Viscosity; MnO; CaF_2

28   **I. INTRODUCTION**

29   High heat input submerged arc welding (SAW) has been widely used for welding thick steel

30   plate products due to its high efficiency and low-cost.[1, 2] However, high heat input may cause

31   deteriorated mechanical properties of the welded products as a result of coarsened grains.[3] Recent

32   studies have demonstrated that welding fluxes play vital roles in such as improving alloying element

33   transfer, stabilizing the arc, and refining the weld pool, and could be utilized as a countermeasure to

34   offset adverse impact caused by high heat input welding.[4-6]

35   Physicochemical properties of the welding fluxes, including viscosity, softening temperature,

36   and crystallization behaviors are essential indicators for flux design.[4, 7] In particular, flux viscosity

37   directly affects weld formability, slag-metal reaction kinetics, alloying element transfer behaviors, and

38   slag detachability.[5, 8] It is widely acknowledged that flux viscosity is inherently rooted in the

39   structures of the fluxes.[9-11] Thus, it is essential to determine the flux viscosity and structural

40   characteristics quantitatively for designing fluxes with targeted properties.

41   CaF_2-SiO_2-MnO fused fluxes, owing to their satisfactory chemical homogeneity, fine anti-

42   porosity property, and excellent thermal crack resistance, have been employed for SAW construction

43   of high-strength low-alloy (HSLA) steel grades.[7] CaF_2 serves as a diluent to reduce the melting

44   temperature and viscosity during welding.[12] However, it is a growing recognition that the CaF_2

45   content shall be limited as it may pose environmental and ergonomic threats. To achieve the desired

2

46 low-fluoride fluxes, one major challenge is to elucidate the mechanism of CaF_2 in altering

47 physicochemical properties of pertinent fluxes. Nevertheless, studies undertaken so far provide

48 contradictory evidence concerning the roles of CaF_2 in flux/slag structure.[13-17] The addition of CaF_2

49 to silicate glasses is reported to lead to the depolymerization of silicate networks owing to the

50 abundant presence of Si-F bonds,[13, 14] while CaF_2 is also found to act as a diluent and not contribute

51 to the breakage of Si-O-Si bonds.[15, 16] On the other hand, it has been proven that MnO acts as a

52 network modifier and reduces fluxes viscosity,[11, 18] so that it can be used to replace CaF_2. Moreover,

53 MnO and SiO_2 are invariably decomposed into Mn, Si, and O under arc plasma, promoting Mn, Si, O

54 transfer from fluxes to weld metals.[7, 19, 20] Mn-containing and Si-containing inclusions could promote

55 the nucleation of acicular ferrites with interlocking structures, which could delay crack propagation in

56 the welded products.[21, 22] However, detailed studies on the effect of MnO on viscosity remain limited

57 for fluxes with relatively low MnO contents (< 10 mass pct).[11, 18, 23]

58   In the present study, a flux design strategy by replacing CaF_2 with MnO has been postulated.

59 The effect of MnO substitution for CaF_2 on viscosity and structures of CaF_2-SiO_2-MnO fluxes at high

60 temperatures has been thoroughly investigated by means of Raman spectra, X-ray photoelectron

61 spectroscopy (XPS), and magic angular spinning nuclear magnetic resonance (MAS-NMR).

62 Moreover, the structural roles of MnO and CaF_2 in CaF_2-SiO_2-MnO fluxes were elucidated. The

63 relationship between the viscosity and structure of the CaF_2-SiO_2-MnO fluxes has been quantitatively

64 established. This study aims to offer refreshed understanding with regard to the development of

65 fluorine-free welding fluxes.

66 **II. EXPERIMENTAL PROCEDURE AND METHODS**

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67   A. *Fluxes Preparation*

68   Fluxes were prepared from reagent-grade chemicals of CaF_2 (> 98.5 mass pct), SiO_2 (> 99.7

69   mass pct), and MnO (>99.0 mass pct). Chemical compositions of the fluxes with different

70    $MnO/(MnO+CaF_2)$ mass ratios are shown in Table I, in which the flux numbers represent

71   corresponding nominal MnO mass percentages. Totally 200 g reagents were fully mixed in a three-

72   dimensional mixing machine for 0.5 hours, then pressed to 4 cylinders (Φ50 mm×H20 mm) at 20

73   MPa pressure. The cylinders were placed in a molybdenum crucible (Φ60 mm×H120 mm) and

74   melted in a vertical tube furnace. The furnace temperature was raised to 1823 K and held for 1 hour to

75   ensure complete homogenization of flux under high purity Ar gas (99.999 vol pct). The premelted

76   fluxes were quenched in cold water (273 K), dried, and grounded into powders (< 74 μm) for

77   viscosity measurements and structural analysis.

78   Table I Chemical compositions of synthetic fluxes (mass pct).

Fluxes No.		CaF_2	SiO_2	MnO	$MnO/(CaF_2+MnO)$
F10	Designed	50.00	40.00	10.00	0.17
	After-quench	49.05(±1.30)	40.85(±0.23)	10.10(±0.20)	0.17
F20	Designed	40.00	40.00	20.00	0.33
	After-quench	39.25(±1.26)	40.76(±0.24)	20.19(±0.22)	0.34
F30	Designed	30.00	40.00	30.00	0.50
	After-quench	29.16(±1.28)	40.63(±0.25)	30.21(±0.26)	0.51
F40	Designed	20.00	40.00	40.00	0.67
	After-quench	19.02(±1.25)	40.53(±0.23)	40.45(±0.23)	0.68
F50	Designed	10.00	40.00	50.00	0.83
	After-quench	9.29(±1.21)	40.21(±0.21)	50.50(±0.25)	0.84

79   Chemical compositions of the after-quench fluxes were characterized using X-ray fluorescence

80   (XRF, ZSX Primus IV, Rigaku, Japan), as listed in Table I, which shows negligible differences as

81   compared to nominal compositions. The crystalline states of the fluxes were characterized by X-ray

82   powder diffraction (XRD, D8 Advance, Bruker, Germany), and corresponding XRD patterns over the

83   range of 10-90° were recorded by a Cu Kα radiation (λ=0.154 nm) at a scan rate of 4 °/min.

84   B. *Viscosity Measurement*

85   Viscosity measurements were performed by using a melt physical property comprehensive

86   testing instrument (VDR-16000, Chongqing University, China) with a Brookfield digital viscometer

87   (mold DV2T, Brookfield Engineering Laboratories, USA). The accuracy and the repeatability of the

88   viscometer according to the machine manufacturer were ± 1.0 pct and ± 0.2 pct, respectively. The

89   viscometer was calibrated by the standard silicone oils (0.5 Pa·s) at 298 K. High purity Ar flow (0.5

90   L/min) was injected from the bottom of the alumina tube to protect the Mo crucible and shaft from

91   oxidation. The molybdenum crucible (Φ50×H100 mm) containing 150 g of the quenched fluxes was

92   positioned in the uniform temperature zone of the tube furnace, which was calibrated by a reference

93   B-type thermocouple and controlled within ± 2 K using a proportional integral derivative controller.

94   The furnace was heated to 1773 K and maintained for 30 minutes to ensure the flux homogeneity.

95   Afterwards, a molybdenum spindle was slowly sunk into the liquid fluxes and kept at a distance of 20

96   mm above the crucible bottom. The flux viscosity in the temperature range of 1300 to 1773 K was

97   measured at the interval of 20 K after holding the sample at the measuring temperatures for 20

98   minutes to ensure thermal equilibrium. The final viscosity values at the target temperature were the

99   average results obtained at three rotation speeds (50, 75, and 100 r/min) and the deviation of all

100   measured experimental data from the average value is less than 3 pct.

101   C. *Spectral Measurements*

102   Structural analysis of the fluxes was performed using Raman spectra, XPS, and MAS-NMR

103   techniques. Raman spectra measurements were conducted using a laser confocal Raman spectrometer

104   (HR800, Horiba, France) with an excitation wavelength of 488 nm. The range of the measured

105 frequency band was from 400 to 1600 cm^{-1}, and the spectra resolution was in the order of 1 cm^{-1}. XPS

106 (EscaLab 250Xi, Thermo Fischer, USA) was employed to measure O_{1s} and F_{1s} binding energy of the

107 quenched fluxes. The XPS results were calibrated using C_{1s} binding energy at 284.8 eV. Detailed

108 fitting results of Raman and XPS spectra were provided in Appendix A. Solid-state ^{19}F NMR

109 measurements were recorded using a 400 MHz MAS-NMR (Avance III 400M, Bruker, Germany)

110 spectrometer at a resonance frequency of 376.7 MHz with a spinning rate of 8 kHz. The MAS-NMR

111 spectra of ^{19}F referenced to CaF_2 taken at -108 ppm,[24] and baseline correction was processed using

112 MestreNova 12.0.0 software.

113 **III. RESULTS AND DISCUSSIONS**

114 A. *Effect of MnO/(MnO+CaF$_2$) Mass Ratio on Flux Viscosity*

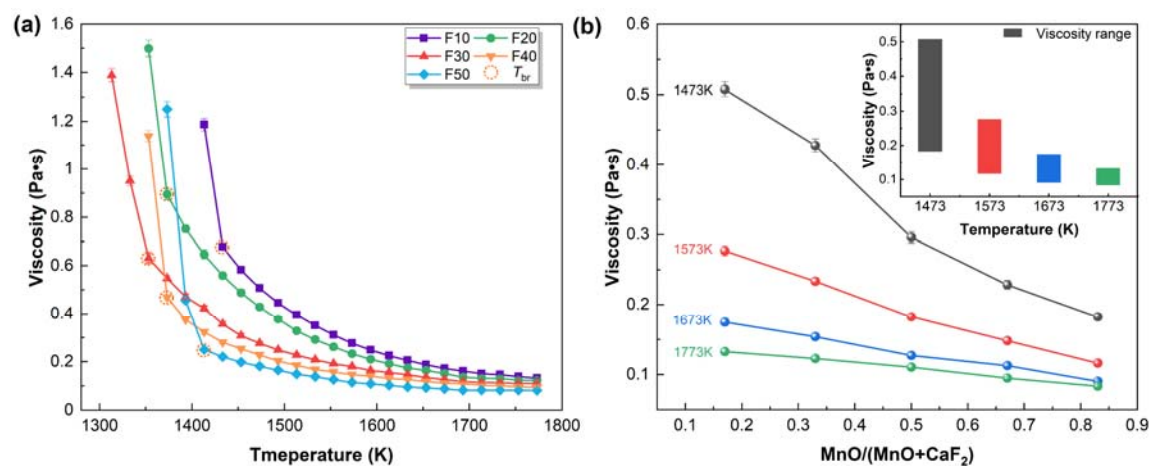116 Figure 1—Flux viscosity as a function of (a) temperature, and (b) MnO/(MnO+CaF$_2$) mass ratio.

117 Inset figure shows the viscosity range of flux with increasing MnO/(MnO+CaF$_2$) mass ratio from

118 0.17 to 0.84 at given temperatures.

119 Viscosity values of all the five fluxes measured at various temperatures are shown in Figure 1(a).

120 It can be observed that the viscosity increases smoothly with decreasing temperature until it reaches

121   the break temperature (T_{br}), which is a significant parameter indicating the precipitation of crystalline

122   phases in sizeable quantities and is generally employed to distinguish fully liquid region ($>T_{br}$) and

123   soild/liquid coexisting region ($<T_{br}$) in molten flux.[25-27] As shown in Figure 1(a), corresponding T_{br}

124   values for fluxes from F10 through F50 are 1433, 1373, 1353, 1373, 1413 K, respectively. T_{br} values

125   are obviously lower than the melting point of the weld metal, which could avoid pit formation on the

126   surface of the weld metal during solidification.[12] Figure 1(b) shows the effect of MnO/(MnO+CaF$_2$)

127   mass ratio on the viscosity at varied temperatures. As shown in Figure 1(b), at any given temperature,

128   viscosity continuously decreases with the substitution of CaF$_2$ by MnO. At 1473K, flux viscosity

129   substantially decreases from 0.51 to 0.18 Pa·s with increasing MnO/(MnO+CaF$_2$) mass ratio from

130   0.17 to 0.84. However, flux viscosity only slightly decreases from 0.13 to 0.08 Pa·s at 1773K. Thus,

131   the effect of the MnO/(MnO+CaF$_2$) mass ratio is more dominant at lower temperatures (1473 and

132   1573 K), as shown in the inset figure of Figure 1(b), which is consistent with the trend reported by

133   previous researchers.[28, 29] It is noted that viscosity values of all fluxes at 1673 K are ranging from

134   0.09 to 0.17 Pa·s, indicating excellent fluidity and mass transfer properties, which also fall nicely

135   within the requirements for SAW conditions.[12] Therefore, it is possible to design CaF$_2$-free fluxes

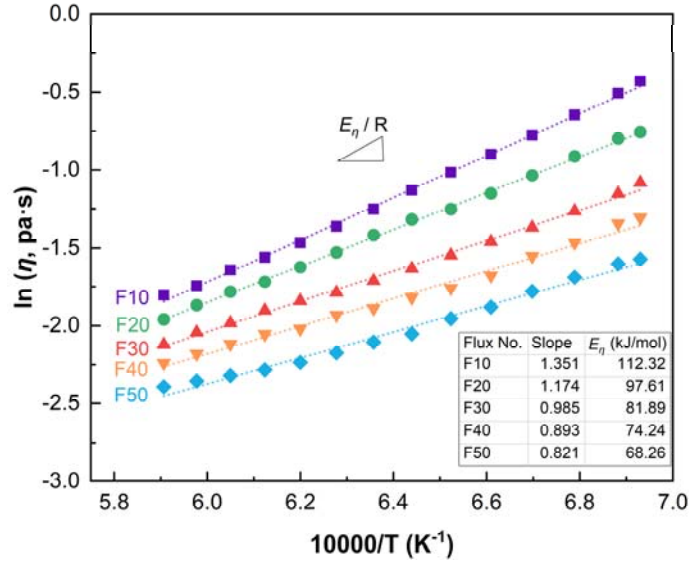136   with suitable viscosity for SAW applications.

Figure 2—Arrhenius plot for the fluxes in fully liquid regions.

To understand the mechanism of viscosity variations, the Arrhenius equation (Equation [1]) is employed to derive the relationship between viscosity and temperature.[30]

$$\ln\eta = \ln A_\eta + \frac{E_\eta}{R} \times \frac{1}{T} \qquad [1]$$

where η (Pa·s), A_η, E_η (J/mol), R ([J/(mol·K)]), and T (K) denote viscosity, pre-exponential factor, activation energy for the viscous flow, universal gas constant, and absolute temperature, respectively. In associated liquids featuring network structures, E_η means the energy barrier that cohesive flow units in slags have to overcome,[31] and the value of E_η is expected to be constant for a fully liquid flux.[32] Accordingly, $\ln\eta$ values have been plotted against reciprocal temperatures in Figure 2, which shows a linear relationship for the targeted fluxes in fully liquid regions, indicating viscosity variation is dictated by thermal activation energy. Furthermore, it is found that E_η values decrease from 112.32 to 68.26 kJ/mol with increasing MnO/(MnO+CaF$_2$) mass ratio from 0.17 to 0.84, indicating the reduction of liquid shearing resistance for viscous flow. From the ionic interaction of view,[33, 34] decreasing E_η is enabled by the flow unit change in the order of Si-O-Si and Si-O-Mn. In addition,

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152 relaxation effect of cationic species induced by the formation of Si-O-Mn could reduce E_η of the

153 viscous flow.[35, 36]

154 B. *Effect of MnO/(MnO+CaF₂) Mass Ratio on Flux Structure*
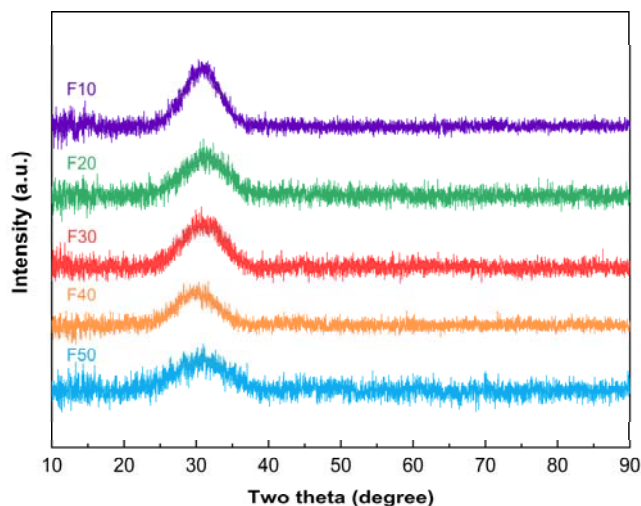

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156 Figure 3—XRD patterns of the quenched fluxes.

157   Figure 3 shows XRD patterns of the fluxes with different MnO/(MnO+CaF$_2$) mass ratios

158 quenched from 1823 K. It can be observed that all patterns unanimously show broad diffusive peaks

159 in the 2θ range of 20 to 40 deg, confirming the amorphous state of the quenched fluxes.

160 Homogeneous amorphous fluxes are considered to preserve the molten structure details, which could

161 be used for analyzing the fluxes structures at high temperatures.[31, 37] In addition, amorphous fluxes

162 are potentially beneficial for weldability as it could improve weld formability, slag detachability, and
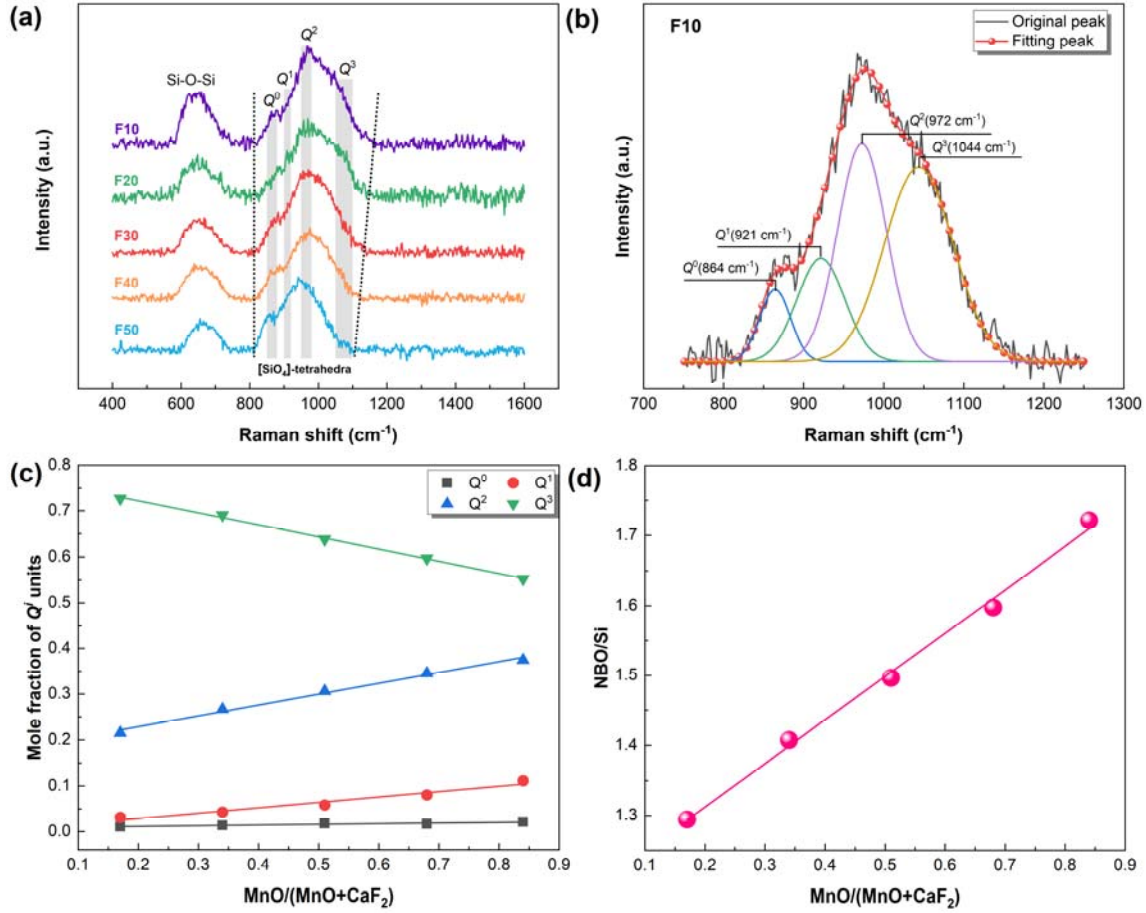
163 arc stability in SAW process.[38, 39]

Figure 4 —(a) Raman spectra of the fluxes, (b) typical Raman deconvolution results of F10, (c) mole fraction of different [SiO_4]-tetrahedra units as a function of $MnO/(MnO+CaF_2)$ mass ratio, and (d) degree of polymerization as a function of $MnO/(MnO+CaF_2)$ mass ratio.

Raman spectra of the fluxes tested as a function of Raman shift ranging from 400 to 1600 cm^{-1} are plotted in Figure 4(a). As can be seen, all spectra exhibit two bands: a higher frequency band (800-1160 cm^{-1}) and a lower frequency band (590-760 cm^{-1}). The lower frequency band is usually ascribed to symmetric stretching vibration of Si-O-Si, which shows no apparent shift with MnO substitution for CaF_2. The higher frequency band is related to the symmetric stretching vibration bands of Si-O in [SiO_4]-tetrahedra units.[10] In the frequency region of [SiO_4]-tetrahedra units, five types of [SiO_4]-tetrahedra units are defined as Q^i (i is the number of bridging oxygen in a [SiO_4]-

175   tetrahedra unit, and *i* ranges from 0 to 4), wherein five types of [SiO$_4$]-tetrahedra units are Q^0 ([SiO$_4$]$^{4-}$

176   , monomer), Q^1 ([Si$_2$O$_7$]$^{6-}$, dimmer), Q^2 ([Si$_2$O$_6$]$^{4-}$, chain), Q^3 ([Si$_4$O$_{11}$]$^{6-}$, sheet), and Q^4 (SiO$_2$, fully

177   polymerized),[10, 30] respectively. As marked in Figure 4(a), Q^0 to Q^3 bands are located at ranges of

178   850-880, 900-920, 950-980, 1050-1100 cm^{-1}, respectively. The band of [SiO$_4$]-tetrahedra (800-1160

179   cm^{-1}) moves to a lower frequency range (800-1100 cm^{-1}) with the increasing mass ratio of

180   MnO/(MnO+CaF$_2$) from 0.17 to 0.84, indicating that silicate networks are gradually depolymerized

181   with CaF$_2$ being substituted by MnO.

182   Various [SiO$_4$]-tetrahedra units overlap within higher frequency bands. Raman spectra have

183   been deconvoluted by the Gaussian fitting model.[31, 40]. Figure 4(b) shows typical Raman

184   deconvolution results of F10 (The rest of the devolution results are provided in Figure A1). According

185   to the areas of the obtained peaks (A_i) and the Raman scattering coefficient (S_i) of Q^i, mole fractions

186   (X_i) of various Q^i could be calculated by Equation [2],[41] and the values of S_0, S_1, S_2, and S_3 are 1,

187   0.514, 0.242, and 0.09,[40, 41] respectively.

$$X_i = \frac{A_i}{S_i} / (\sum_{i=0}^{3} \frac{A_i}{S_i}) \qquad\qquad [2]$$

189   Mole fractions of Q^i as a function of MnO/(MnO+CaF$_2$) mass ratios are plotted in Figure 4(c). As

190   observed, mole fractions of Q^2 and Q^1 increase with increasing MnO/(MnO+CaF$_2$) mass ratio. This

191   tendency demonstrates that silicate networks are depolymerized as MnO/(MnO+CaF$_2$) mass ratio

192   increases. Notably, silicate networks are predominantly constituted by Q^3 and Q^2, whereas Q^0 units

193   are negligible. Therefore, silicate networks are mainly transformed from highly polymerized Q^3 to

194   less polymerized Q^2 and Q^1 units as the MnO/(MnO+CaF$_2$) mass ratio increases. The network-

195   breaking role of MnO demonstrated in the present composition range can be explained as follows:

196   according to the analysis of McMillian,[42] double-charged Mn^{2+} with larger ionization potential than

197   Ca^{2+} may favor the higher charge concentration offered by the Q^2 (=Si-2O$^-$) sites. Moreover, Mn^{2+} ion

198   is balanced with two adjacent corner-shared O$^-$ ions due to its small $[MnO_6]$ cage. [36, 42] Therefore,

199   sheet-like silicate structures (Q^3) are mainly depolymerized into chain-like units (Q^2) by adding MnO,

200   as expressed in Equation [3].

$$[Si_2O_5]^{2-} + MnO = 2[SiO_3]^{2-} + Mn^{2+} \tag{3}$$
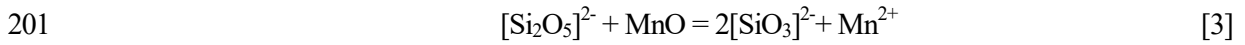
202   The average non-bridging oxygen number per silicon atom (NBO/Si) value measures the degree

203   of polymerization (DOP) of the melt, which can be calculated by Equation [4].[9] Figure 4(d) shows

204   NBO/Si values as a function of $MnO/(MnO+CaF_2)$ mass ratio. The NBO/Si value continuously

205   increases from 1.29 to 1.72 with higher $MnO/(CaF_2+MnO)$ mass ratio, indicating structural networks

206   are depolymerized. The NBO/Si value constantly increases with increasing $MnO/(MnO+CaF_2)$ mass

207   ratio because the added Mn-O bond incorporated the bridging oxygen (O^0) in Si-O-Si to form non-

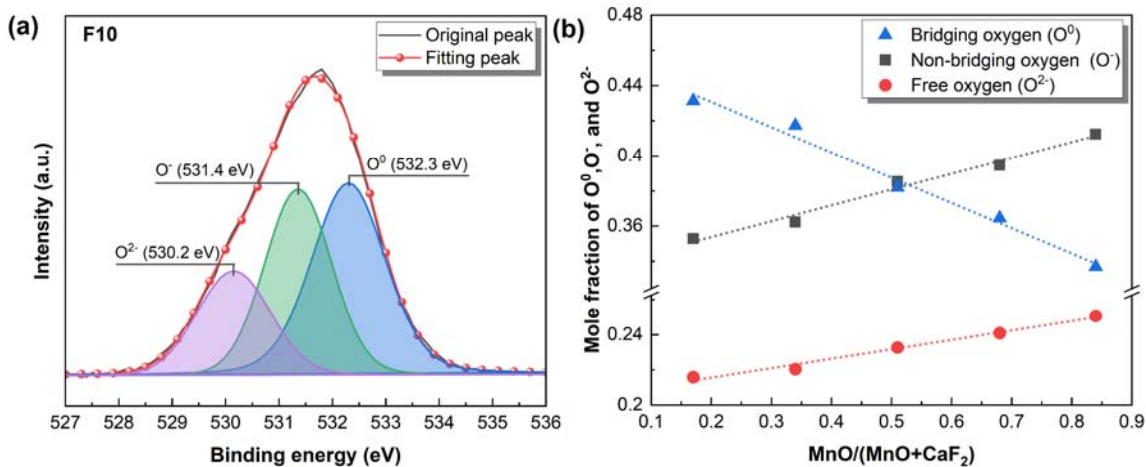208   bridging oxygen (O$^-$), as described by Equation [5].

$$NBO/Si = X_3 + 2X_2 + 3X_1 + 4X_0 \tag{4}$$

$$Si-O^0-Si + Mn-O = 2Si-O^- + Mn^{2+} \tag{5}$$
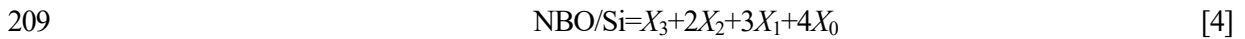
Figure 5—(a) Typical deconvolution results of O_{1s} for F10, and (b) mole fraction of different oxygen species as a function of $MnO/(MnO+CaF_2)$ mass ratio.

Figure 5(a) presents a typical deconvoluted peak from O_{1s} XPS analysis for F10 (The rest devolution results are shown in Figure A2). O_{1s} XPS spectra were deconvolved using the Gaussian method by assuming contributions from O^0 (532.4 eV), O^- (531.5 eV), and O^{2-} (530.4 eV). Moreover, mole fractions of each oxygen species are obtained from the integrated areas of corresponding deconvoluted spectra. Mole fractions of different oxygen species are shown in Figure 5(b). It can be observed that the mole fraction of O^0 significantly decreases, while that of O^- increases, with increasing $MnO/(MnO+CaF_2)$ mass ratio. The equilibrium relationship of O^0 and O^- in molten fluxes can be described as Equation [5].[43] O^{2-} is supplied as a result of MnO dissociation due to its higher ionization energy. Hence, increasing $MnO/(MnO+CaF_2)$ mass ratio may increase the concentration of O^{2-}, driving Equation [5] to the direction towards depolymerization. As a result, a more depolymerized structure is induced by higher $MnO/(MnO+CaF_2)$ mass ratio.

According to the above results, it can be summarized that flux viscosity decreases with higher MnO content due to the simplified network structure, although the details of structural roles of CaF_2

227 remain ambiguous. Thus, two hypotheses are proposed to reveal the structural roles of CaF_2: (a) CaF_2

228 acts predominantly as a diluent and does not depolymerize network units; (b) the depolymerization

229 ability of CaF_2 is weaker than that of MnO. These hypotheses can be further tested by investigating

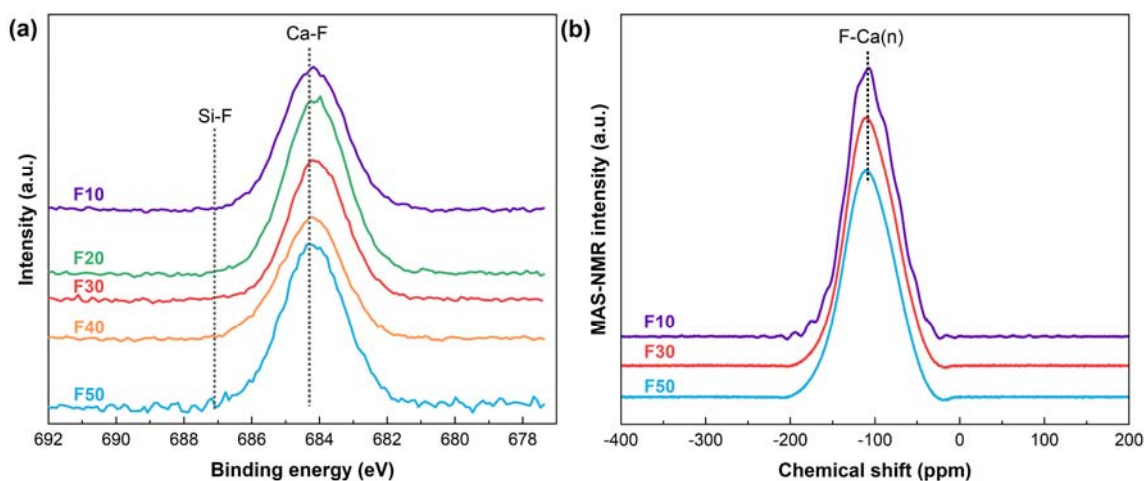230 F_{1s} XPS and ^{19}F MAS-NMR spectra.

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232   Figure 6—(a) F_{1s} XPS and (b) ^{19}F MAS-NMR spectra of the fluxes.

233   Figure 6(a) shows F_{1s} XPS spectra of the fluxes studied. Binding energies of pertinent

234 referencing F-containing glasses, such as Ca-F bond (684.3 eV[15, 44]) and Si-F bond (687.1 eV[44]), are

235 marked in Figure 6(a). The spectra of all fluxes share similar symmetrical peaks yet with an

236 unchanged center position (about 685.1 eV), which is close to that of the Ca-F bond rather than Si-F.

237 Therefore, it can be seen that F^- is pre-dominantly coordinated with Ca^{2+} for the entire composition

238 range of the targeted fluxes. Chemical shifts of ^{19}F MAS-NMR spectra can be used to measure the

239 structural information of F in the fluxes.[45] Typical ^{19}F MAS-NMR spectra of F10, F30, and F50 are

240 shown in Figure 6(b). Three centers of the ^{19}F MAS-NMR spectra are located at -109.2 ppm, which

241 can be assigned to F-Ca(n) species.[45] F-Ca(n) species contain F^- in close proximity to Ca^{2+} and are

242 charge-balanced by Ca^{2+}, which are not part of the silicate glass network.[24] In addition, no distinct

243   peak of oxyfluoride species can be observed in ^{19}F NMR spectra, *i.e.*, $Si(O^-)_xF_{4-x}$ at -123.4 to -134.5

244   ppm.[45] Structural studies carried out by Kiczenski *et al.*[46] showed that F^- preferentially bonds with

245   cations carrying highest field strength ($La^{3+} > Mg^{2+} > Ca^{2+} > Ba^{2+} > Na^+$). F_{1s} XPS and ^{19}F MAS-

246   NMR spectra results indicate that F^- predominantly bonds with Ca^{2+} rather than Si^{4+}, which proves the

247   first hypothesis, *i. e.* CaF_2 acts predominantly as a diluent and does not depolymerize network units.

248   C. *Relationship between Viscosity and Structure of the Flux*

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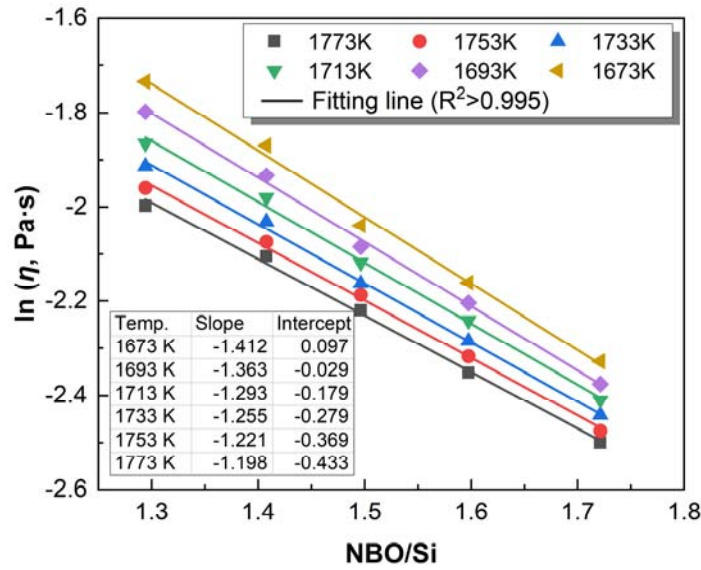
250   Figure 7—The relationship between logarithm viscosity and degree of polymerization of the fluxes.

251   The viscosity depends on DOP, which is ultimately dictated by the structure of the fluxes. The

252   logarithm viscosity as a function of the NBO/Si is shown in Figure 7 in the temperature range of 1673

253   to 1773 K. It can be seen that the viscosity decreases linearly with increasing NBO/Si of the fluxes. In

254   general, the logarithm viscosity and the NBO/Si can be described by the following Equation [6].

255 $$\ln \eta = a \times (NBO/Si) + b \qquad\qquad [6]$$

256   where *a* and *b* are the slope and intercept of fitting lines, respectively. These fitting results further

257   illustrate that NBO/Si can potentially be used as a DOP index to quantify the effect of silicate

258 structure on the viscosity of the flux.

IV. CONCLUSION

260 In this study, the effect of MnO substitution for CaF_2 on the viscosity and structure of molten

261 CaF_2-SiO_2-MnO welding fluxes has been investigated and the relationship between viscosity and

262 structure has been quantitatively identified. The main conclusions can be summarized as follows:

263 (1) With increasing MnO/(CaF_2+MnO) mass ratio in the CaF_2-SiO_2-MnO fluxes, viscosity and

264 activation energy of the fluxes continuously decrease, and silicate networks in the fluxes mainly

265 transform from highly polymerized Q^3 to depolymerized Q^2 and Q^1 units.

266 (2) F_{1s} XPS and ^{19}F MAS-NMR spectra prove that F^- predominantly bonds with Ca^{2+} rather than

267 Si^{4+}, indicating CaF_2 acts as a diluent and does not effectively depolymerize the silicate network.

268 (3) The NBO/Si value increases with increasing MnO/(MnO+CaF_2) mass ratio and NBO/Si can

269 potentially be used as a DOP index to quantify the influence of the silicate structure on flux viscosity.

CONFLICT OF INTEREST STATEMENT

277 On behalf of all authors, the corresponding author states that there is no conflict of interest.

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APPENDIX A: DECONVOLUTION RESULTS OF RAMAN AND XPS SPECTRA

332
333 Figure A1—Fitting results of Raman spectra of (a) F20, (b) F30, (c) F40, and (d) F50.

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335 Figure A2—Fitting results of XPS spectra of (a) F20, (b) F30, (c) F40, and (d) F50.
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