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INFLUENCES OF DIFFERENT COMPONENTS ON VISCOSITIES OF CaO-MgO-Al$_2$O$_3$-SiO$_2$ MELTS

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Abstract

The present study is aimed to distinguish the different influences of CaO and MgO, as well as Al$_2$O$_3$ and SiO$_2$ on viscosity of CaO-MgO-Al$_2$O$_3$-SiO$_2$ melts. It is found that for melt without Al$_2$O$_3$, viscosity increases monotonously as CaO is gradually replaced by MgO. The addition of Al$_2$O$_3$ leads to a complex variation of viscosity. In different composition ranges, viscosity may exhibit different variation tendencies as changing the relative contents of CaO and MgO while keeping contents of other components constant. It is also found that when replacing SiO$_2$ by equivalent mole of Al$_2$O$_3$, (i) in CaO-Al$_2$O$_3$-SiO$_2$ system, viscosity increases when Al$_2$O$_3$ content is small relative to CaO content (there are enough Ca^{2+} ions to charge compensate Al^{3+} ions), but decreases when CaO content is inadequate for charge compensation; (ii) in MgO-Al$_2$O$_3$-SiO$_2$ system, viscosity always decreases as substituting Al$_2$O$_3$ for SiO$_2$. The reason for this difference for two systems may be resulted from the weak charge compensation ability of Mg^{2+} ion for Al^{3+} ion relative to Ca^{2+} ion. All the viscosity variations can be interpreted well by our new proposed viscosity model.

Keywords: Viscosity; CaO-MgO-Al$_2$O$_3$-SiO$_2$; Bridging oxygen; Non-bridging oxygen

1. Introduction

The viscosities of aluminosilicate melts are important because of their dramatic effects on pyrometallurgical processes. For instance, reliable viscosities are needed (*i*) to guarantee smooth operation of the blast furnace, (*ii*) for foaming processing, (*iii*) for the successful separation of metal and slag during the basic oxygen steelmaking process and (*iv*) in the continuous casting process where the slag acts as a lubricant. Therefore, accurate viscosity values are essential for the optimization and improvement of metallurgical processes. CaO-MgO-Al$_2$O$_3$-SiO$_2$ slag system is a fundamental system in the pyrometallurgical processes. Up to now, many experimental [1-19] and theoretical [20-24] researches have been done for this system. Lots of viscosities data for CaO-MgO-Al$_2$O$_3$-SiO$_2$ system [12, 14-17, 19] and its sub-binary systems [1-8] (*e.g.* CaO-SiO$_2$ system, MgO-SiO$_2$ system, *etc.*) and sub-ternary systems [2, 7-13, 18] (*e.g.* CaO-Al$_2$O$_3$-SiO$_2$ system, MgO-Al$_2$O$_3$-SiO$_2$ system *etc.*) have been measured. However, deep analyses about the influences of different components on viscosities are lacking. In CaO-MgO-Al$_2$O$_3$-SiO$_2$ system, there are mainly three questions involved: viscosity variation in the cases of (*i*) substituting CaO by MgO, or vice versa (*ii*) substituting Al$_2$O$_3$ by SiO$_2$, or vice versa, and (*iii*) substituting MO (M=Mg or Ca) by Al$_2$O$_3$, or vice versa, while keeping contents of the other components constant. Among these three cases, the third one has received much attention [3, 20, 23-24]. It was found that there was a maximum viscosity along the constant SiO$_2$ content line in CaO-Al$_2$O$_3$-SiO$_2$ system and MgO-Al$_2$O$_3$-SiO$_2$ system. In other words, viscosity first increases and then decreases when gradually replacing MO by Al$_2$O$_3$. The present study mainly deals with the viscosity variation law of the first and second cases based on the measured viscosity data in the literature to distinguish the different influences of CaO and MgO, as well as Al$_2$O$_3$ and SiO$_2$.

2. Theoretical basis

In the following sections, when analyzing the viscosity variation behavior, our new proposed viscosity model [24-29] will be utilized. This structurally based viscosity model can well describe the viscosity variation of aluminosilicate melts

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involving MgO, CaO, SrO, BaO, FeO, MnO, Li_2O, Na_2O, K_2O, Al_2O_3, SiO_2, CaF_2, TiO_2, Fe_2O_3 and P_2O_5 components. The temperature dependence of viscosity is calculated by Arrhenius equation,

$$\ln\eta = \ln A + E / RT \qquad [1]$$

where η is the viscosity, Poise; A is the pre-exponent factor, Poise; R is the gas constant, 8.314 J/(molK); T is the absolute temperature, K; E is the activation energy, J/mol, while is calculated as follows,

$$E = 572516 \times 2 \bigg/ \left(\begin{array}{l} n_{O_{Si}} + \alpha_{Al} n_{O_{Al}} + \sum \alpha_i n_{O_i} + \sum \alpha_{Al,\,i} n_{O_{Al,\,i}} + \\ + \sum \alpha^i_{Si} n_{O^i_{Si}} + \sum \alpha^j_{Al,\,i} n_{O^j_{Al,\,i}} \end{array} \right) \qquad [2]$$

where $n_{O'}$ are the mole numbers of different types of oxygen ions; parameter α describes the deforming ability of bond around the corresponding unit, which is optimized from the viscosity data of simple system. The deforming abilities of chemical bonds around different types of oxygen ions are shown in Table I. The higher the value in Table I is, the weaker the chemical bond around this type of oxygen ion will be. In the denominator of Eq. [4], the first, second, third, fourth, fifth and sixth terms represent the contributions of bridging oxygen bonded with Si^{4+} ion; oxygen bonded with Al^{3+} ion not being charge compensated; free oxygen bonded with metal cation i; bridging oxygen bonded with compensated Al^{3+} ion by cation i; non-bridging oxygen bonded with Si^{4+} ion, and non-bridging oxygen bonded with cation j and Al^{3+} ion charge balanced by cation i. The numbers of different types of oxygen ions are related to composition and can be calculated by following the following assumption [28].

Assumption I: Ca^{2+} ion has a higher priority than Mg^{2+} ion to charge compensate Al^{3+} ion. Only when the Ca^{2+} ion is exhausted, Mg^{2+} ion could be used to charge compensate Al^{3+} ion.

Assumption II: The equilibrium constant for the charge compensation reaction of MO with Al_2O_3 to generate $M_{1/2}AlO_2$ unit (oxygen ion in this unit is bridging oxygen $O_{Al,\,i}$) is infinite. Following this rule, in the case of $x_{MO} / x_{Al_2O_3} > 1$, all MO act as charge balancers, whereas in the case of $x_{MO} / x_{Al_2O_3} > 1$, all Al^{3+} ions form the AlO_4^{5-} tetrahedrons, and any excess $MO \cdot (= x_{MO} - x_{Al_2O_3})$ acts as a network modifier.

Assumption III: When the free oxygen (in excess MO) react with bridging oxygen (in $M_{1/2}AlO_2$ or SiO_2) to generate non-bridging oxygen, it is assumed that the bridging oxygen for AlO_4^{5-} and SiO_4^{4-} tetrahedra are equivalent, and the numbers of non-bridging oxygen bonded to Al^{3+} ion and Si^{4+} ion are proportional to the numbers of AlO_4^{5-} and SiO_4^{4-} tetrahedral present.

Assumption IV: The equilibrium constant for the reaction of a free oxygen (in excess MO) with a bridging oxygen (in $M_{1/2}AlO_2$ or SiO_2) to generate non-bridging oxygen is infinite. Therefore, for a $MO\text{-}\sum_i M_{1/2}AlO_2\text{-}SiO_2$ system, when the mole fraction of the excess basic oxide MO exceeds 2/3, it is assumed that there are no bridging oxygens present in melt.

Assumption V: For systems $\sum (MO)_i\text{-}\sum_i M_{1/2}AlO_2\text{-}SiO_2$ containing both excess CaO and MgO, the numbers of different types of oxygen ions can be calculated by the random mixing rule. In practice, the calculation makes use of firstly, *Assumption IV by* considering all the excess basic oxides to be one basic oxide; then multiply each term by the re-normalized mole fractions of the excess basic oxides $(MO)_i / \sum (MO)_i$, or $M_{1/2}AlO_2$ $\left(or\ SiO_2\right) / \left(1 -\right) . \sum (MO)_i$

3. Different influences of CaO and MgO on viscosity

In order to distinguish the different influences of CaO and MgO on viscosity, viscosities of compositions with the same contents of Al_2O_3 and SiO_2 should be known. The measured compositions in the literature fulfilling this condition are summarized in Table II.

3.1. CS-MS group

The comparisons of viscosities for $CaO\text{-}SiO_2$ and $MgO\text{-}SiO_2$ melts with the same content of SiO_2 are shown in Figure 1, from which it can be seen that $MgO\text{-}SiO_2$ melt possesses a higher viscosity value than $CaO\text{-}SiO_2$ melt. This phenomenon is also found by many researchers [22, 23, 25].

Viscosity is related to the bond strength. Melt with a strong bond strength means a large resistance to viscous flow under the external force, so a high viscosity will be. For a ionic bond, the bond strength can be approximately evaluated by the coloumbic force I between cation M and O ($I = \frac{2Q}{(r_{M^{Z+}} + r_{O^{2-}})^2}$, where Q is the covalence of M ion; $r_{M^{Z+}}$ and $r_{O^{2-}}$ are the radii of M^{z+} and oxygen ions, respectively). According to the Pauling's method [30], the ionic bond percentage for Ca-O and Mg-O bonds are 77.4% and 67.8% [25]. Thereby, Ca-O and Mg-O bonds are mainly composed of ionic bond. From the magnitude of $I_{Mg\text{-}O}$=1.956 and $I_{Ca\text{-}O}$=0.907, it could be concluded that the Mg-O bond is stronger than Ca-O bond. From Table I, the deforming ability of chemical bond around O_{Si}^{Mg} is weaker than that around O_{Si}^{Ca} , so, a stronger non-bridging bond is formed in $MgO\text{-}SiO_2$ melt relative to $CaO\text{-}SiO_2$ melt, which means a higher viscosity.

Table 1. *Deforming abilities of chemical bonds around different type of oxygen ions*

O_{Si}	O_{Ca}	O_{Mg}	O_{Al}	O_{Si}^{Mg}	O_{Si}^{Ca}	$O_{Al,Mg}^{Mg}$	$O_{Al,Ca}^{Mg}$	$O_{Al,Ca}^{Ca}$	$O_{Al,Mg}$	$O_{Al,Ca}$
1	17.34	15.54	5.671	6.908	7.422	3.975	8.334	7.115	4.996	5.606

Table 2. *Compositions for studying different influences of CaO and MgO on viscosity*

Group	No.	Composition				Refs.
		CaO	MgO	Al_2O_3	SiO_2	
CS-MS	CS-MS-1	0.417			0.583	1,2,3
	CS-MS-2		0.414		0.586	4,5
	CS-MS-3	0.5			0.5	1,4,5,6,7,8
	CS-MS-4		0.5		0.5	4,5,8
CS-MS-CMS	CS-MS-CMS-1	0.5			0.5	5,8
	CS-MS-CMS-2	0.333	0.165		0.5	7
	CS-MS-CMS-3	0.278	0.222		0.5	7
	CS-MS-CMS-4	0.25	0.25		0.5	9
	CS-MS-CMS-5		0.5		0.5	5,8
CAS-MAS	CAS-MAS-1	0.125		0.125	0.75	8,10
	CAS-MAS-2		0.125	0.125	0.75	8,11
	CAS-MAS-3	0.165		0.168	0.667	11
	CAS-MAS-4		0.165	0.167	0.667	11
	CAS-MAS-5	0.25		0.25	0.5	8,10,11
	CAS-MAS-6		0.25	0.25	0.5	8
	CAS-MAS-7	0.28		0.092	0.627	2,12
	CAS-MAS-8		0.281	0.092	0.627	12
	CAS-MAS-9	0.199		0.11	0.691	12
	CAS-MAS-10		0.2	0.11	0.69	12
MAS-CMAS	MAS-CMAS-1		0.281	0.092	0.627	12
	MAS-CMAS-2	0.139	0.14	0.092	0.629	12
	MAS-CMAS-3		0.446	0.206	0.349	13
	MAS-CMAS-4	0.376	0.065	0.207	0.351	14
CAS-CMAS	CAS-CMAS-1	0.199		0.11	0.691	12
	CAS-CMAS-2	0.1	0.099	0.109	0.692	12
	CAS-CMAS-3	0.28		0.092	0.627	2,12
	CAS-CMAS-4	0.139	0.14	0.092	0.629	12
	CAS-CMAS-5	0.381		0.06	0.559	2
	CAS-CMAS-6	0.101	0.28	0.055	0.564	15
CMAS_1	CMAS_1-1	0.423	0.073	0.119	0.385	16
	CMAS_1-2	0.208	0.289	0.114	0.388	17

3.2. CS-MS-CMS group

The viscosity of CaO-SiO_2, MgO-SiO_2 and CaO-MgO-SiO_2 melts with the same content of SiO_2 are shown in Figure 2. With the gradual increase of MgO content, viscosity increases, which agrees with the conclusion obtained in CS-MS group. Therefore, in melt without Al_2O_3, viscosity increases monotonously as substituting MgO for CaO.

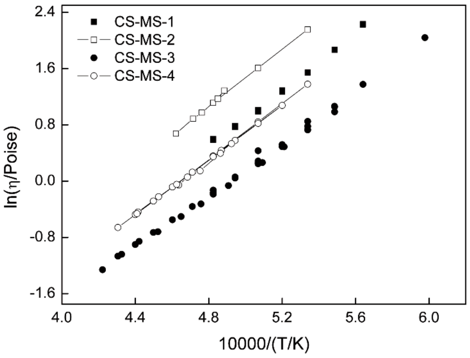

***Figure 1.** Variation of viscosity for CS-MS group*

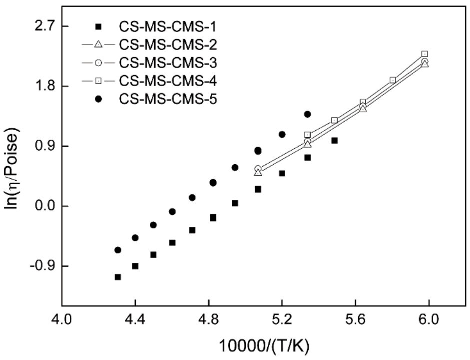

***Figure 2.** Variation of viscosity for CS-MS-CMS group*

3.3. CAS-MAS group

Al_2O_3 is an amphoteric oxide, and it can form AlO_4^{5-} tetrahedron, and be incorporated into the SiO_2 network provided there are enough metal cations present to charge balance the Al^{3+} ions. When Al_2O_3 is absent, basic oxides CaO and MgO mainly act as network modifiers and participate in forming non-bridging oxygen which decreases the viscosity; while when Al_2O_3 is added, some parts of basic oxide will charge compensate Al^{3+} ion to form more bridging oxygen which increases viscosity. So, the viscosity variation will exhibit complex behavior when Al_2O_3 is present. Variations of viscosity with temperature for compositions in CAS-MAS group are shown in Figure 3. By comparing the viscosities of compositions CAS-MAS-1 and CAS-MAS-2, CAS-MAS-3 and CAS-MAS-4, as well as CAS-MAS-5 and CAS-MAS-6 for which the mole fraction of MO is lower than that of Al_2O_3, it can be seen that MgO-Al_2O_3-SiO_2 melt has a lower viscosity than CaO-Al_2O_3-SiO_2 melt (with the same contents of Al_2O_3 and SiO_2). However, by comparing viscosities of compositions CAS-MAS-7 and CAS-MAS-8, as well as CAS-MAS-9 and CAS-MAS-10, MgO-Al_2O_3-SiO_2 melt for which the mole fraction of MO is higher than that of Al_2O_3 has a higher viscosity than CaO-Al_2O_3-SiO_2 melt.

The content of CaO (or MgO) is less or equal to the content of Al_2O_3 for compositions CAS-MAS-1～CAS-MAS-6, so almost all the CaO and MgO will participate in charge compensating Al^{3+} ion but not forming non-bridging oxygen. In this case, content of non-bridging and free oxygen can be neglected. The melt is mainly composed of bridging oxygen O_{Si} and $O_{Al,Ca}$ for CaO-Al_2O_3-SiO_2 system (or O_{Si} and $O_{Al,Mg}$ for MgO-Al_2O_3-SiO_2 system). For CaO-Al_2O_3-SiO_2 and MgO-Al_2O_3-SiO_2 melts with the same contents of Al_2O_3 and SiO_2, concentration of O_{Si} is the same. Therefore, the viscosity difference is mainly determined by the difference between the deforming abilities of chemical bond around bridging oxygen $O_{Al,Ca}$ and $O_{Al,Mg}$. From Table I, it can be seen that the deforming ability of chemical bond around $O_{Al,Ca}$ is lower than that around $O_{Al,Mg}$. Therefore, a higher viscosity will be anticipated for CaO-Al_2O_3-SiO_2 melt than MgO-Al_2O_3-SiO_2 melt when the content of MO is less than that of Al_2O_3.

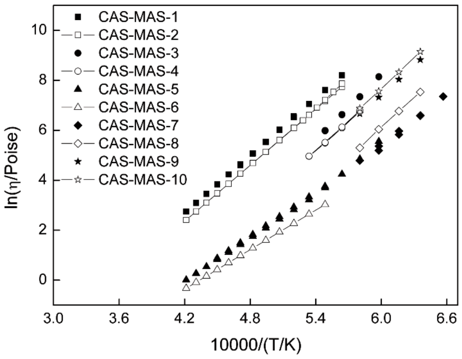

***Figure 3.** Variation of viscosity for CAS-MAS group*

The contents of MO is higher than that of Al_2O_3 for compositions CAS-MAS-7～CAS-MAS-10. In this case, part of CaO or MgO ($=x_{Al_2O_3}$) charge compensate Al^{3+} ion to form bridging oxygen, while the other part ($=x_{MO}-x_{Al_2O_3}$) form non-bridging oxygen O_{Si}^{i} and $O_{Al,i}^{i}$ (i=Mg, Ca). The values in Table I show that deforming abilities around O_{Si}^{Mg} and $O_{Al,Mg}^{Mg}$ are weaker than O_{Si}^{Ca} and, $O_{Al,Ca}^{Ca}$ while it is stronger for bridging oxygen $O_{Al,Mg}$ than $O_{Al,Ca}$ since the AlO_4^{5-} tetrahedron charge balanced by Ca^{2+} ion is much more stable than that balanced by Mg^{2+} ion [11]. So, from CaO-Al_2O_3-SiO_2 melt to MgO-Al_2O_3-SiO_2 melt with the same contents of Al_2O_3 and SiO_2, there will be two changes: bridging oxygen $O_{Al,Ca}$ transforms to; $O_{Al,Mg}$ non-bridging oxygen O_{Si}^{Ca} and $O_{Al,Ca}^{Ca}$ transforms to O_{Si}^{Mg} and $O_{Al,Mg}^{Mg}$. The first change decreases viscosity, while the later one increases viscosity. The viscosity increment will exceed the decrement when there is enough extra basic oxide $x_{MO}-x_{Al_2O_3}$ to generate enough non-bridging oxygen. So, MgO-Al_2O_3-SiO_2 melt has a higher viscosity than CaO-Al_2O_3-SiO_2 melt when content of MO is higher than that of Al_2O_3. Furthermore, the larger the $x_{MO} - x_{Al_2O_3}$ is, the larger the viscosity increment will be for MgO-Al_2O_3-SiO_2 melt relative to CaO-Al_2O_3-SiO_2 melt. The $x_{MO} - x_{Al_2O_3}$ value is higher for compositions CAS-MAS-7 and CAS-MAS-8 than compositions CAS-MAS-9 and CAS-MAS-10, so in Figure 3, the viscosity increment is higher for the former group.

3.4. MAS-CMAS group

Figure 4 shows that viscosity decreases when partly replacing MgO in MgO-Al_2O_3-SiO_2 ternary system by CaO to form a quaternary system CaO-MgO-Al_2O_3-SiO_2 ($x_{CaO} > x_{Al_2O_3}$). The reason for the phenomenon is that CaO content is higher than Al_2O_3 content, so after substitution, all Al^{3+} ions originally compensated by Mg^{2+} ions will be compensated by Ca^{2+} ions for the higher priority of Ca^{2+} ion relative to Mg^{2+} ion [24]. This leads to the form of more stable AlO_4^{5-} tetrahedron which increases the viscosity. But, according to the above analysis, the non-bridging oxygen bonded with Ca^{2+} ion is weaker than that bonded with Mg^{2+} ion.

CaO content is higher than Al_2O_3 content, so non-bridging oxygen bonded with Ca^{2+} ion will be formed. This factor will decrease viscosity. Furthermore, the larger the value of $x_{CaO} - x_{Al_2O_3}$ is, the more non-bridging oxygen bonded with Ca^{2+} ion will be formed, and the larger the viscosity decrease will be. In Figure 3, from composition MAS-CMAS-1 to MAS-CMAS-2, there is only a little decrease of viscosity for the small value of $x_{CaO} - x_{Al_2O_3}$. But from composition MAS-CMAS-3 to MAS-CMAS-4, viscosity decreases dramatically for its large $x_{CaO} - x_{Al_2O_3}$ value.

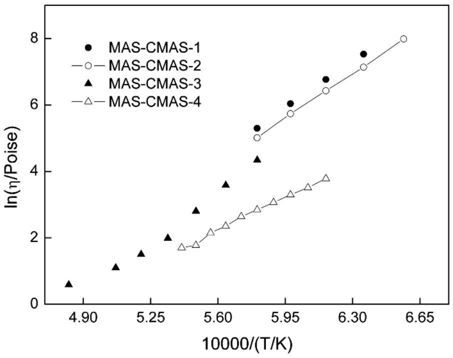

Figure 4. Variation of viscosity for MAS-CMAS group

3.5. CAS-CMAS group

All the six compositions in this group fulfill $x_{CaO} - x_{Al_2O_3} > 0$. So, all Al^{3+} ions in this group are compensated by Ca^{2+} ions. It can be seen from Figure 5 that viscosity increases when substituting part of MgO for CaO (from CAS-CMAS-1 to CAS-CMAS-2, from CAS-CMAS-3 to CAS-CMAS-4, and from CAS-CMAS-5 to CAS-CMAS-6).

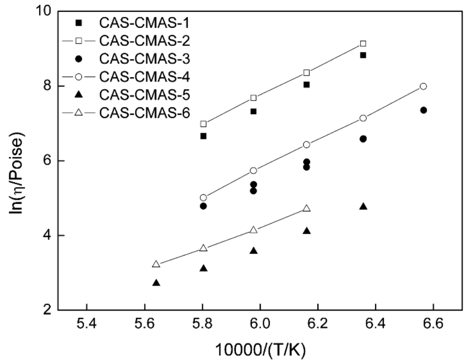

Figure 5. Variation of viscosity for CAS-CMAS group

Replacing part of CaO by MgO but keeping $x_{CaO} - x_{Al_2O_3} > 0$ can leads to two changes: part of O_{Si}^{Ca} transform to O_{Si}^{Mg} bond; part of $O_{Al,Ca}^{Ca}$ transform to $O_{Al,Ca}^{Mg}$. The two changes coexist during the substitution process. The viscosity variation of the melt is determined by the deforming abilities differences (between O_{Si}^{Mg} and O_{Si}^{Ca}, as well as $O_{Al,Ca}^{Mg}$ and) $O_{Al,Ca}^{Ca}$, as well as the relative concentration of O_{Si}^{Mg} and $O_{Al,Ca}^{Mg}$. From Table I, it can be seen that O_{Si}^{Mg} bond is stronger than O_{Si}^{Ca} bond, while $O_{Al,Ca}^{Mg}$ bond is weaker than $O_{Al,Ca}^{Ca}$ bond. Furthermore, the bond strength increment from O_{Si}^{Ca} to O_{Si}^{Mg} is smaller the bond strength decrement from $O_{Al,Ca}^{Ca}$ to $O_{Al,Ca}^{Mg}$. Meanwhile, the concentration ratio of O_{Si}^{Mg} to $O_{Al,Ca}^{Mg}$ is decided by the content ratio of SiO_2 to Al_2O_3 [24], so, when there is enough Al_2O_3 in melt, enough $O_{Al,Ca}^{Mg}$ will be formed to decrease viscosity. But if the content of Al_2O_3 is smaller relative to SiO_2, more O_{Si}^{Mg} will be formed than $O_{Al,Ca}^{Mg}$. Therefore, in this case, the viscosity increasing tendency resulted from transforming of O_{Si}^{Ca} to O_{Si}^{Mg} will be dominated, which leads to the increase of viscosity. In this group, the content of Al_2O_3 for every composition is very small relative to SiO_2, so viscosity increases when replacing part of CaO by MgO.

3.6. CMAS_1 group

It can be seen from Figure 6 that viscosity decreases as replacing part of CaO in composition CMAS_1-1 by MgO to form composition CMAS_1-2 (while keeping the mole fraction of remaining CaO higher than that of Al_2O_3). According to the analyses in CAS-CMAS group, it can be concluded that more $O_{Al,Ca}^{Mg}$ will be formed when there is a higher value of $2x_{Al_2O_3}/x_{SiO_2}$ (1mol Al_2O_3 is equivalent to 2mol SiO_2 after being charge compensated). The ratio of $2x_{Al_2O_3}/x_{SiO_2}$ in this group is approximately to be 1, so the concentrations of O_{Si}^{Mg} and $O_{Al,Ca}^{Mg}$ are almost the same [24]. However, the bond strength increment from O_{Si}^{Ca} to O_{Si}^{Mg} is smaller the bond strength decrement from $O_{Al,Ca}^{Ca}$ to $O_{Al,Ca}^{Mg}$, so the viscosity decrement will be dominated. Therefore, there is a decrease for viscosity from CMAS_1-1 to CMAS_1-2.

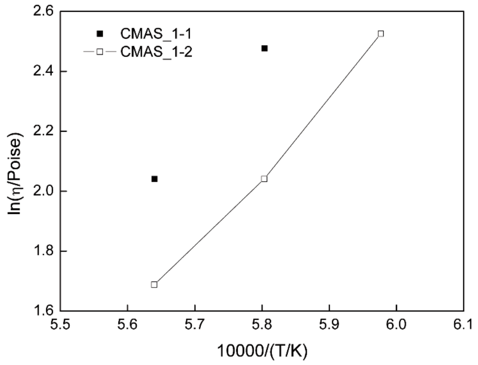

Figure 6. *Variation of viscosity for CMAS_1 group*

4. Different influences of Al_2O_3 and SiO_2 on viscosity

The influence of Al_2O_3 and SiO_2 on viscosity is discussed in CaO-Al_2O_3-SiO_2, MgO-Al_2O_3-SiO_2 and CaO-MgO-Al_2O_3-SiO_2 system by replacing part of SiO_2 by Al_2O_3 while keeping the contents of CaO and MgO unchanged.

4.1. CAS group

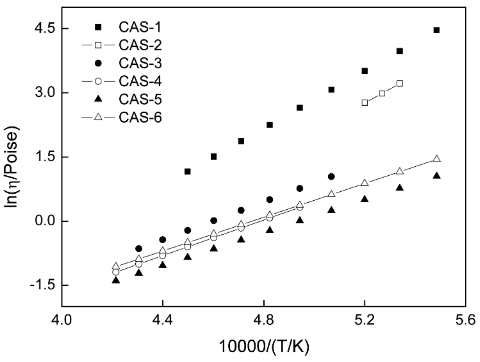

Figure 7. *Variation of viscosity for CAS group*

Figure 7 shows that viscosity decreases from CAS-1 to CAS-2, CAS-3 to CAS-4, but increases from CAS-5 to CAS-6. Combining with the composition in Table III, it can be seen the Al_2O_3 content is higher than CaO content for compositions CAS-1, CAS-2, CAS-3 and CAS-4, but lower than CaO content for compositions CAS-5 and CAS-6. Therefore, it can be concluded that when there is enough CaO to charge compensate Al^{3+} ion, the substitution of Al_2O_3 for SiO_2 will increase viscosity, while when CaO content is not adequate, the substitution will decrease viscosity. The reason for this is that when content of CaO is higher than Al_2O_3, the new added Al_2O_3 can lead to two aspects of influences on viscosity. First, it consumes equivalent mole of CaO (which originally acts as the network modifier) to charge compensate Al^{3+} ion. The compensated Al^{3+} ion incorporates into the network of SiO_2. This aspect increases viscosity. However, as substituting Al_2O_3 for SiO_2, strong Si-O bond is replaced by weak Al-O bond. This factor decreases viscosity. As the content of Al_2O_3 is small relative to CaO, all the Al^{3+} ions will be charge compensated and the viscosity increment will be larger than the viscosity decrement, so viscosity increases from CAS-5 to CAS-6. But when Al_2O_3 content is higher than CaO content, part of Al_2O_3 ($= x_{Al_2O_3} - x_{CaO}$) can not be incorporated into the SiO_2 network. This part of Al_2O_3 can dramatically decrease viscosity for the weak Al-O bond relative to Si-O. Therefore, viscosities decrease from CAS-1 to CAS-2, CAS-3 to CAS-4. In our previous paper [31], it is also found from experiments that in CaO-Al_2O_3-SiO_2 melt, viscosity first increases and then decreases as gradually replacing SiO_2 by Al_2O_3, which agrees with the conclusion of the present study.

Table 3. *Compositions for studying different influences of Al_2O_3 and SiO_2 on viscosity*

Group	No.	Composition				Refs.
		CaO	MgO	Al_2O_3	SiO_2	
CAS	CAS-1	0.216		0.216	0.568	10
	CAS-2	0.219		0.271	0.51	11
	CAS-3	0.3		0.4	0.3	10
	CAS-4	0.3		0.5	0.2	10
	CAS-5	0.512		0.188	0.3	10
	CAS-6	0.51		0.34	0.15	10
MAS	MAS-1		0.25	0.15	0.6	18
	MAS-2		0.25	0.2	0.55	18
	MAS-3		0.25	0.25	0.5	8
	MAS-4		0.35	0.05	0.6	18
	MAS-5		0.35	0.1	0.55	18
CMAS_2	CMAS_2-1	0.055	0.154	0.121	0.67	15
	CMAS_2-2	0.056	0.157	0.155	0.632	15
	CMAS_2-5	0.423	0.074	0.058	0.445	19
	CMAS_2-6	0.423	0.073	0.119	0.385	16

4.2. MAS group

Figure 8 shows that viscosity always decreases in MgO-Al_2O_3-SiO_2 system when substituting Al_2O_3 for

SiO_2 regardless of $x_{MgO} < x_{Al_2O_3}$ or $x_{MgO} > x_{Al_2O_3}$. In CaO-Al_2O_3-SiO_2 system, when the Al_2O_3 content is small, the substitution will increase viscosity. Why the opposed variation tendency of viscosity is present in MgO-Al_2O_3-SiO_2 system. It has been pointed out above that the main factor for viscosity increase in CaO-Al_2O_3-SiO_2 melt are that all Al^{3+} ions enter into stable AlO_4^{5-} tetrahedron after being charge compensated by Ca^{2+} ions and part of CaO (= $x_{Al_2O_3}$) originally acting as network modifier now charge compensate Al^{3+} ion. But the charge compensation ability of Mg^{2+} is weak (it can be seen from Table I that $O_{Al,Mg}$ bond has larger deforming ability than $O_{Al,Ca}$ bond) which means a large deforming ability under external force. Therefore, in this case, during the substitution of Al_2O_3 for SiO_2, the viscosity increment will be smaller than the viscosity decrement resulted from the substitution of weak Al-O bond for strong Si-O bond, so viscosity decreases.

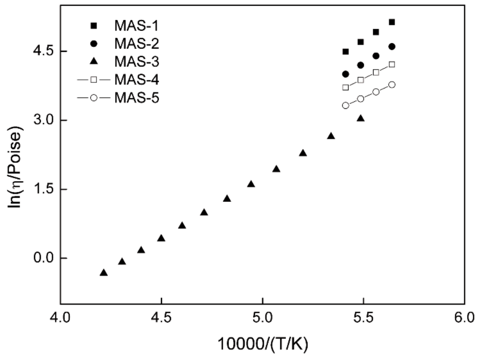

Figure 8. *Variation of viscosity for MAS group*

4.3. CMAS_2 group

From Figure 9, it can be seen that from CMAS_2-1 to CMAS_2-2, viscosity decreases; while from CMAS_2-5 to CMAS_2-6, viscosity increases. The reason for this may be that composition CMAS_2-1 and CMAS_2-2 only contain small content of CaO which is not enough to charge compensate all the Al^{3+} ions. This case is similar to the case of MAS group. Therefore, the viscosity variation law is the same as MAS group. CMAS_2-3 and CMAS_2-4 only contain small content of MgO, and CaO content is enough to charge compensate all Al^{3+} ions, so viscosity increases when substituting Al_2O_3 for SiO_2 as the case of CAS group.

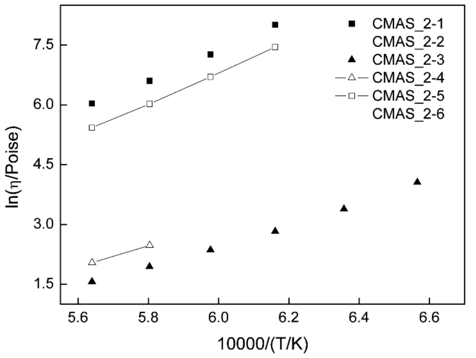

Figure 9. *Variation of viscosity for CMAS_2 group*

5. Summary

The present study focuses on the influences of different components on CaO-MgO-Al_2O_3-SiO_2 melt by combining the experimental data in the literature and our theoretical viscosity model. From the above examples, it can be seen that the complex variation behavior of viscosity is resulted from the existence of Al_2O_3. When substituting CaO for MgO, viscosity changes monotonously for melt without Al_2O_3. However, the viscosity variation becomes very complicated when Al_2O_3 is added. The present study also found that as substituting Al_2O_3 for SiO_2 in CaO-Al_2O_3-SiO_2 melt, viscosity increases when the content of Al_2O_3 is small relative to that of CaO, but decreases when there is a large substitution. However, the viscosity always decreases for MgO-Al_2O_3-SiO_2 melt as substituting Al_2O_3 for SiO_2. The weak charge compensation ability of Mg^{2+} ion for Al^{3+} ion may be the reason for this phenomenon.

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References

[1] J.O.M. Bockris and D.C. Lowe, Proc. Roy. Soc. Lond., 226 (1954) 423.
[2] J.S. Machin and T. B. Yee, J. Am. Ceram. Soc., 31 (1948) 200.
[3] P. Kozakevitch, Rev. metall., 57 (1960) 149
[4] G. Urbain, Y. Bottinga and P. Richet,Geochim. Cosmochim. Acta, 46 (1982) 1061.
[5] G. Urbain,Rev. Int. Hautes Temp. Refract., 11 (1974) 133.
[6] M. Kawahara, K. Mizoguchi and Y. Suginohara, Bull. Kyushu Inst. Technol. Sci. Technol., 43 (1981) 53.
[7] T. Licko and V. Danek, Phys. Chem. Glasses, 27 (1986) 22.
[8] V. G. Hofmaier, Berg und Hutterun. Monatsh., 113 (1968) 270.
[9] D. Sykes, J. Dickinson, E. James, R.W. Luth and C.M. Scarfe, Geochim. Cosmochim. Acta, 57 (1993) 1291.
[10] R. Rossin, J. Bersan and G. Urbain, Revue Hautes

Temperatures Refractoires, 1 (1964) 159.
[11] M.J. Toplis and D.B. Dingwell, Geochim. Cosmochim. Acta, 24 (2004) 5169.
[12] F. Johannsen and H. Brunion, Z. Erzbergbau Metallhüttenwesen, 12 (1959) 272.
[13] R. A. Lyutikov and L. M. Tsylev, Izv. Akad. Nauk SSSR Metall. Gorn. Delo, 1 (1963) 41.
[14] U.N. Mishra, B. Thakur and M.N. Thakur, SEAISI Q., 23 (1994) 72.
[15] J.S. Machin and T.B. Yee, J. Am. Ceram. Soc., 37 (1954) 177.
[16] H. Kim, W.H. Kim and I. Sohn, D.J. Min, Steel Res. Int., 81 (2010) 261.
[17] J.S. Machin and D.L. Hanna, J. Am. Ceram. Soc., 28 (1945) 310.
[18] K. Mizoguchi, K. Okamoto and Y. Suginohara, Nippon Kinzoku Gakkaishi, 46 (1982) 1055.
[19] J.S. Machin, T.B. Yee and D.L. Hanna, J. Am. Ceram. Soc., 35 (1952) 322.
[20] G. Urbain, Steel Res., 58 (1987) 111.
[21] T. Iida, H. Sakal, Y. Klta and K. Shigeno, ISIJ Int., 40 (2000) 110.
[22] Q.F. Shu, Steel Res. Int., 80 (2009) 107.
[23] L. Zhang and S. Jahanshahi, Metall. Mater. Trans. B, 29B (1998) 177.
[24] G.H. Zhang, K.C. Chou and K.C. Mills, ISIJ Int., 52 (2012) 355.
[25] G.H. Zhang, K.C. Chou, Q.G. Xue and K.C. Mills, Metall. Mater. Trans. B, 43B (2012) 64.
[26] G.H. Zhang and K.C. Chou, J. Min. Metall. B, 48B (2012) 1.
[27] G.H. Zhang and K.C. Chou, J. Min. Metall. B, 48 (2012) 433.
[28] G.H. Zhang and K.C. Chou, Metall. Mater. Trans. B, 2014, in press.
[29] G.H. Zhang and K.C. Chou, Metall. Mater. Trans. B, 43B (2012) 841.
[30] L. Pauling, The nature of the chemical bond, Cornell University Press, Ithaca, 1960.
[31] G.H. Zhang and K.C. Chou, ISIJ Int., 53 (2012) 177.