

Effect of TiO_2 on Viscosity and Structure of Low-Fluoride $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-Li}_2\text{O}$ Slag for Electroslag Remelting

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Abstract: The effect of TiO_2 on viscosity of low-fluoride $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-Li}_2\text{O}$ slag for electroslag remelting was investigated under continuous cooling conditions and the Fourier transform infrared (FTIR) and the Raman spectroscopy were employed to analyze the correlation between the quenched slags and corresponding structure. Results show that the slag viscosity decreases with increasing the TiO_2 content. At the TiO_2 content up to 13.1wt%, the corresponding viscosity values slowly decrease from 0.067, 0.059, 0.056 Pa·s to 0.054 Pa·s as the temperature increases from 1743, 1793, 1843 K to 1893 K and at higher temperature of 1843 K or above, TiO_2 addition has a relatively small effect on lowering the slag viscosity. The calculated activation energy of viscous flow decreases from 58.0, 47.7, 42.8 kJ/mol to 38.6 kJ/mol with increasing the TiO_2 content from 0 wt%, 4.3 wt%, 8.7 wt% to 13.1 wt%. Additionally, the FTIR results reveal that with the addition of TiO_2 , $[\text{AlO}_n\text{F}_{4-n}]$ -tetrahedral complexes and $[\text{AlO}_4]$ -tetrahedral network structures depolymerize, but $[\text{AlO}_6]$ -octahedron is not found in the slag. Simultaneously, it can be seen from the Raman spectra that with the addition of TiO_2 , the depolymerization of the Al-O-Al linkage occurs in the $[\text{AlO}_4]$ -tetrahedral network structures, the part Q^4 units transform to Q^2 units and the O-Ti-O and Ti-O-Ti chains form. These results suggest that polymerization degree of these slags decreases with increasing the TiO_2 content, which is beneficial to simplify slag structure. Finally, the changed slag structure is in good agreement with corresponding varying viscosity.

Key words: electroslag remelting; low-fluoride slag; FTIR; Raman spectra

The slag viscosity is one of the important indicators of thermophysical chemical properties for electroslag remelting (ESR) process. In order to obtain a relatively low viscosity of the melt slags, many enterprises use a large amount of CaF_2 in ESR slag systems to reduce the melting temperature and viscosity due to the pronounced characteristics of CaF_2 ^[1]. However, the used slags can produce harmful and volatile fluorides which are generated by the chemical reaction of calcium fluoride and other oxides, resulting in varying chemical composition and then affecting the viscosity of the ESR slags^[2]. Meanwhile, the slag viscosity has an effect on deep desulfurization, non-metallic inclusions and dense cast structure of metal, and also directly affects the two parameters of the velocity of molten

metal droplets and the intensity of electromagnetic stirring force^[3]. Hence, studying viscosity change of the low-fluoride slag systems is of great significance for exploring the volatile behavior of the slags and controlling the steel quality during ESR process.

Nowadays, the most extensive ESR slag systems are usually composed of different components such as CaF_2 , CaO and Al_2O_3 . To develop new slags suitable for specific smelting, such as nickel-based superalloy, a small amount of SiO_2 , MgO and Na_2O , as well as TiO_2 are added to the ternary basic slag to gain some well-defined properties such as optimal electric resistance, low viscosity, and stable content of slag. For the nickel-based superalloy containing Al and Ti, the addition of TiO_2 can regulate the influence of

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Al_2O_3 in the slag on the Al and Ti contents in the molten metal^[4]. This result is beneficial to provide stable melting conditions and obtain high quality as-cast ingot. Therefore, many previous studies have discussed the influence of a small amount of TiO_2 on viscosity and structure of metallurgical slag. Shi et al^[5] revealed the effect of TiO_2 on the ESR 51.5% CaF_2 - CaO - Al_2O_3 - MgO slag, and found that the viscosity decreases with increasing the TiO_2 content. Sohn et al^[6] investigated the influence of TiO_2 on viscous behavior of CaO - Al_2O_3 - SiO_2 - MgO slag system for the blast furnace, and the results show that TiO_2 content can lower the viscosity by depolymerizing the slag network structure. Shi et al^[7] found that TiO_2 addition can lower the viscosity of 35% CaF_2 - CaO - Al_2O_3 - MgO slag system for ESR, where $\text{CaO}/\text{Al}_2\text{O}_3$ ratio is a constant of 0.9. Li et al^[8] found that the viscosity of about 10% CaF_2 - CaO - Al_2O_3 - MgO - Li_2O - Na_2O mould fluxes for high Al steel casting decreases with increasing the TiO_2 content, whereas the highest temperature of the viscosity reaches 1723 K. Chang et al^[9] found that TiO_2 can depolymerize the CaO - SiO_2 - Al_2O_3 - MgO - MnO slag by modifying the silicate network structure and breaking the linkage between the silicate and aluminate structure to decrease viscosity of the slag, while this has little effect on aluminate structure of the slag. However, many scholars have studied the TiO_2 on viscosity and structure of the medium and fluoride-free slags but there are few researches on low-fluoride slag systems, especially when the mass fraction of CaF_2 in the slag is below 25%. This study provides an idea to study the low-fluoride slag containing TiO_2 for ESR.

In the current study, the effect of TiO_2 on viscosity and structure of CaF_2 - CaO - Al_2O_3 - MgO - Li_2O slag for electroslag remelting was investigated using rotating cylinder method. The correlation between slag structure and corresponding viscosity was analyzed by the Fourier transform infrared (FTIR) and the Raman spectroscopy.

1 Experiment

1.1 Preparation of samples

Analytical reagent-grade CaF_2 ($\geq 98.5\%$), CaCO_3 ($\geq 98.0\%$), Al_2O_3 ($\geq 99.0\%$), MgO ($\geq 98.0\%$), Li_2CO_3 ($\geq 99.9\%$) and TiO_2 ($\geq 99.0\%$) powders were prepared to design the typical slag samples for ESR. The mass ratio of $\text{CaO}/\text{Al}_2\text{O}_3$ was fixed at 0.90, and TiO_2 was varied from 0%, 4%, 8% to 12%, while chemical composition for other components maintained constant. Before batching, the CaCO_3 and Li_2CO_3 powders were calcined in a muffle furnace at 1323 and 973 K for 10 h to obtain corresponding pure CaO and Li_2O powders, respectively. Then the weighted samples were firstly mixed mechanically in a mortar and subsequently pre-melted in molybdenum crucible protected on the outside of the graphite crucible in high-temperature well-type pit furnace at 1773 K (1500 °C)

for 10 min to ensure complete melting and homogenized chemical composition. After pre-melting, the slag samples were quenched by a water-cooled copper plate rapidly, and later crushed and ground into fine powders. All-quenched slags were identified as amorphous substance by XRD analysis, as shown in Fig.1. X-ray fluorescence (XRF) spectroscopy (Rigaku ZSX Primus II, Japan) was then employed to analyze the chemical composition of the pre-melted slags. The chemical composition of the slag before and after pre-melting is listed in Table 1.

1.2 Measurements of dynamic viscosity

The HRV-1600P viscometer (Sinosteel Luoyang institute of Refractories Research Co., Ltd, Luoyang, China) was employed to determine the viscosity of the quenched slags using a rotating cylinder method. The schematic diagram of the experimental apparatus is shown in Fig.2. The dimensions of molybdenum (Mo) crucible and Mo spindle for the viscometer are presented in Table 2.

Before the viscosity measurement, the viscometer was calibrated by standard castor oil with known viscosity at room temperature. The weighed 140 g quenched slags for each sample were placed into a Mo crucible protected by graphite for 20 min in high temperature well-type pit furnace with high-load U-type MoSi_2 electric bar to homogenize the molten slags. Subsequently, the Mo spindle was immersed into molten slag bath and rotated. Of particular note was that both the Mo crucible and the spindle should be properly aligned along the axis of the viscometer as a light deviation from the axis can cause large experimental errors, and the distance between top of viscosity spindle and bottom of the Mo crucible maintained a constant value of 10 mm. Next, the slag viscosity values at a speed of 200 r/min with a Mo spindle were measured and collected, during the continuous cooling process at a rate of 3 K/min. After completing the viscosity measurement, slag sample was reheated to 1823 K to pull out the spindle for the next test of experiments. In the whole experiment of viscosity measurement, high purity argon (99.99%) was the protective gas.

1.3 Determination of structure

The quenched slag samples were performed on FTIR

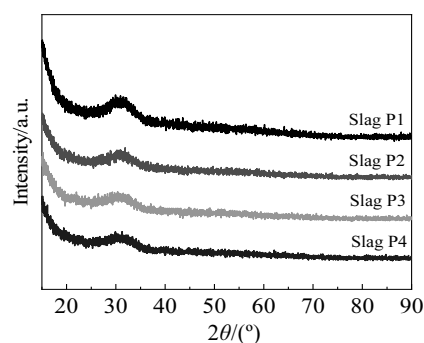
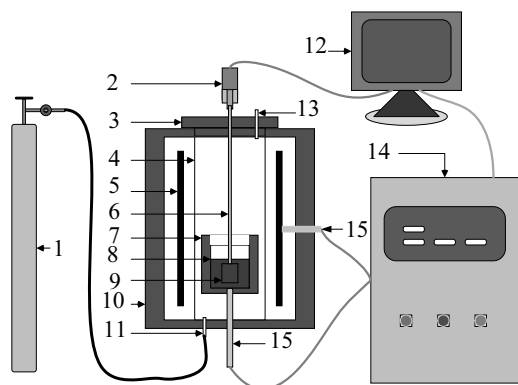


Fig.1 XRD patterns of as-quenched slag samples

Table 1 Chemical composition of studied slags before and after pre-melting (wt%)

Sample	Before pre-melting						After pre-melting					
	CaF ₂	CaO	Al ₂ O ₃	MgO	Li ₂ O	TiO ₂	CaF ₂	CaO	Al ₂ O ₃	MgO	Li ₂ O	TiO ₂
P1	23	33.6	37.4	2	4	0	17.6	39.54	37.9	2.46	2.5	0
P2	23	31.7	35.3	2	4	4	16.5	38.37	35.87	2.36	2.6	4.3
P3	23	29.8	33.2	2	4	8	15.85	37.24	33.2	2.41	2.6	8.7
P4	23	27.9	31.1	2	4	12	14.68	36.06	31.55	2.41	2.2	13.1



1-Ar gas; 2-viscometer; 3-firebrick lid; 4-alumina tube; 5-MoSi₂ heating element; 6-shaft; 7-graphite crucible; 8-Mo crucible; 9-Mo spindle; 10-refractory; 11-gas inlet; 12-computer; 13-gas outlet; 14-program controller; 15-B-type thermocouple

Fig.2 Schematic diagram of experimental apparatus

Table 2 Dimensions of the crucible and spindle

Mo crucible	Size/mm	Mo spindle	Size/mm
Inner diameter	40	Diameter	15
Outer diameter	50	Height	20
Height	80	Submerged length	20

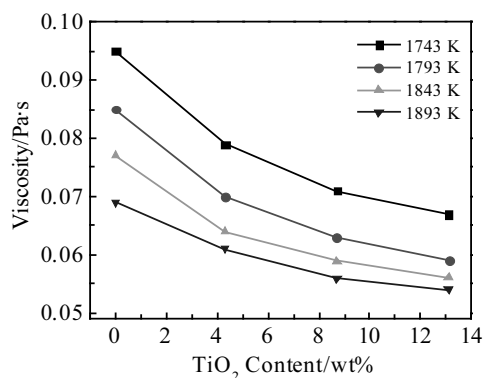
spectrometer (Nicolet iN10 MX, USA) and Raman spectrometer (LabRAM HR Evolution, HORIBA, France) to identify the influence of TiO₂ on the structure of the appointed slags. FTIR absorbance spectra of the samples was recorded within the wavenumber range of 1100~400 cm⁻¹ by an IR-spectra that equipped with potassium bromide pellets technique. The Raman spectra was collected in the frequency range of 400~1500 cm⁻¹ at room temperature using excitation wavelength of 532 nm. Furthermore, the Raman spectra was fitted by assuming Gaussian functions for the peaks of different structural units using the Peak Fit V4 Software.

2 Results and Discussion

2.1 Effect of TiO₂ content on viscosity

The influence of TiO₂ on the viscosity of CaF₂-CaO-Al₂O₃-MgO-Li₂O slag system is presented in Fig.3. It can be observed that the viscosity of quenched slags decreases with the addition of TiO₂, which is in agreement with some previous studies on different slag systems^[5-9]. when TiO₂ content reaches 13.1 wt%, viscosity values slowly decreases from 0.067, 0.059, 0.056 Pa·s to 0.054 Pa·s as the temperature increases from 1743, 1793, 1843 K to 1893 K, which is relatively stable than the viscosity with 4.3 wt% TiO₂ addition. In the meantime, at higher temperature of 1843 K and above, TiO₂ addition has only a relatively small effect on lowering the slag viscosity, which may be attributed to the fact that the slag has sufficient excess thermal energy at high temperature to modify the network structures of the slag^[10]. Additionally, since the viscosity of the melt slags is closely related to the slag structure, downward trend in viscosity with increasing the TiO₂ content seems to indicate that the addition of TiO₂ is closely related to the corresponding structure.

The effect of TiO₂ on the slag viscosity of CaF₂-CaO-Al₂O₃-MgO (CCAMT) and CaF₂-CaO-Al₂O₃-MgO-Li₂O (CCAMLT) slag is listed in Fig.4. From Fig.4, it can be noted that TiO₂ in both two slags can lower the slag viscosity, but the viscosity values in the present study as a whole is lower than that of Shi's^[7] study, with an increase of TiO₂ content. This result can be attributed to the pronounced role of Li₂O addition in the slag. What's more, Shi^[11], Kim^[12], and Qi et al^[13] have found that the slag viscosity decreases with increasing the Li₂O content, which can be used to explain the

Fig.3 Viscosities of CaF₂-CaO-Al₂O₃-MgO-Li₂O slags as a function of TiO₂ contents

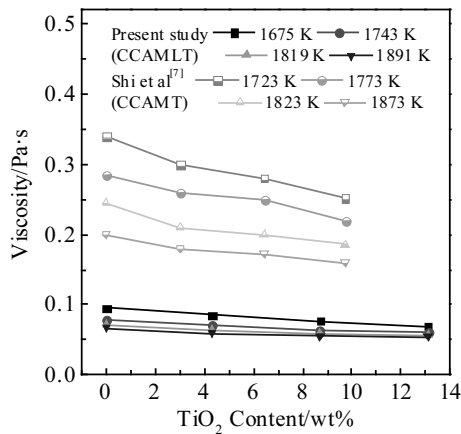


Fig.4 Effect of TiO₂ on the slag viscosity of CCAMT and present CCAMLT slag

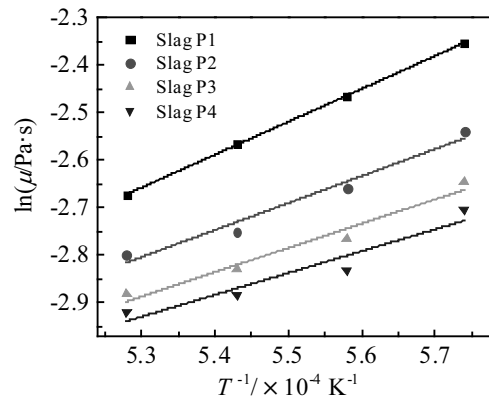


Fig.5 Temperature dependence of viscous flow of CaF₂-CaO-Al₂O₃-MgO-Li₂O on TiO₂ contents

phenomenon that the viscosity of this experiment is lower than that of Shi’s study.

According to the previous studies, TiO₂ acts as an alkaline oxide and can provide free oxygen ions (O²⁻) to break bridge oxygen in the tetrahedral structure of silicate or aluminate structures of the slag systems^[1]. However, TiO₂ also acts as an acidic oxide to increase polymerization degree of the slags^[14]. Although the slag viscosity decreases with increasing the TiO₂ content according to the experimental results of this study, the understanding of structural changes is still unclear. Therefore, the correlation between viscosity and structure will be introduced.

2.2 Temperature dependence and activation energy

For the thermophysical properties of the melt slags, the temperature dependence of the viscosity is usually described in terms of Arrhenius-type Eq.(1):

$$\mu = A \exp(E_{\mu}/RT) \tag{1}$$

where μ is the viscosity (Pa·s), A is the pre-exponential factor (Pa·s), E_{μ} is the activation energy for viscous flow (J/mol), R is the ideal gas constant, and T is the absolute temperature (K). The activation energy of viscous flow is considered as the activation energy required for the flow unit to flow from the first equilibrium position to the next one^[15].

Taking the natural logarithm on both sides of Eq.(1) and to get the following Eq.(2):

$$\ln \mu = \ln A + E_{\mu}/RT \tag{2}$$

Fig.5 presents the temperature dependence of the designed slags, and the natural logarithm of the viscosity is a fitting function of the reciprocal temperature. By acquiring the slope of fitted linear relationship in Fig.5, the activation energy of viscous flow is calculated for each low-fluoride slag.

The activation energy of viscous flow with increasing the TiO₂ content is shown in Table 3. It can be noted that the activation energy of viscous flow decreases from 58.0, 47.7, 42.8 kJ/mol to 38.6 kJ/mol with increasing the TiO₂ content

from 0 wt%, 4.3 wt%, 8.7 wt% to 13.1 wt%, which is similar to the degressive trend of experimental viscosity data of melt slags. This result indicates that polymerization degree for viscous flow of the slags decreases with the addition of TiO₂ content. Therefore, the activation energy of viscous flow can be used to test the slag viscosity or predict the change of the slag structure simply.

2.3 Effect of TiO2 content on the molten slag structure

Fig.6 exhibits the FTIR spectra of the CaF₂-CaO-Al₂O₃-MgO-Li₂O slag system as a function of wavenumber under varying TiO₂ content conditions. From the FTIR spectra in Fig.6, it can be found that the spectra can be divided into three wavenumber ranges: 940~720, 720~600 and 600~500 cm⁻¹, which correspond to the asymmetric stretching vibration of the [AlO_nF_{4-n}]-tetrahedral complexes (n=0~4), [AlO₄]-tetrahedron and [AlO₆]-octahedron, respectively^[16]. What’s more, the bending vibration of Al-O-Al linkage is also observed at the wavenumber of 450 cm⁻¹ ^[17, 18].

For the asymmetric stretching vibration of the [AlO_nF_{4-n}]-tetrahedral complexes at the wavenumber range of 940~720 cm⁻¹, the trough of the FTIR spectra for free TiO₂ content (slag P1) is significantly wider than the trough for the 4.3 wt% TiO₂ content (slag P2), which indicates that a wider trough presents a more structured aluminate tetrahedral network^[12]. In other words, degree of polymerization of the [AlO_nF_{4-n}]-tetrahedral complexes decreases with increasing the TiO₂ content. Simultaneously, due to volatility of fluoride at high temperature, it can be inferred that F⁻

Table 3 Activation energy for viscous flow of slag samples (kJ/mol)

Sample	P1	P2	P3	P4
Activation energy	58.0	47.7	42.8	38.6

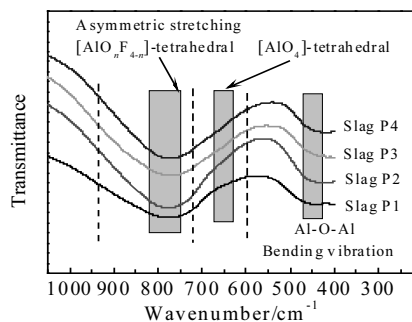


Fig.6 FTIR spectra of CaF₂-CaO-Al₂O₃-MgO-Li₂O slag system with different TiO₂ contents

in the form of [AlO_nF_{4-n}]-tetrahedral complexes in molten metal is much less than O²⁻ ions which are in the form of tetrahedral complexes based on Al³⁺ ions, which results in [AlO₄]-tetrahedral complexes accounting for a large proportion in the [AlO_nF_{4-n}]-tetrahedral complexes. Additionally, at wavenumber of approximately 660 cm⁻¹, an obvious bulge appears, and it gradually disappears with increasing the TiO₂ content. This result indicates that TiO₂ acts as a network modifier in the slag, and the [AlO₄]-tetrahedral complex network is depolymerized to relatively simple structural units^[19]. Nevertheless, the FTIR spectrum curves do not change much in the wavenumber range of 600~500 cm⁻¹ with increasing the TiO₂ contents, which may be attributed to the fact that the amount of [AlO₆]-octahedron in the slag has no residue.

Though the above analysis, the general variation of the [AlO_nF_{4-n}]-tetrahedral complexes, the [AlO₄]-tetrahedral network and [AlO₆]-octahedron are observed, but the variation of Al-O-Al linkage and other newly generated structured units are not found. Therefore, the Raman spectroscopy was employed to further analyze the structural behavior of the experiment slag system.

2.4 Raman spectra of the slag samples

The original Raman spectra of four quenched slag samples with varying TiO₂ contents at room temperature are presented in Fig.7. As shown in Fig.7, three different bands are concentrated in the frequency range of 500~600, 600~700 and 700~900 cm⁻¹. It can be observed that the spectrum peak of 700~900 cm⁻¹ gradually shifts from low frequency to high frequency with the increase of TiO₂ content, which may be due to the fact that the addition of TiO₂ results in quantitative or morphological changes of each units. Additionally, the relative intensity of each frequency range of 600~700 cm⁻¹ band in the present research is very weak compared to other bands. Accordingly, the influence of each structural unit in the 600~700 cm⁻¹ frequency region will be ignored.

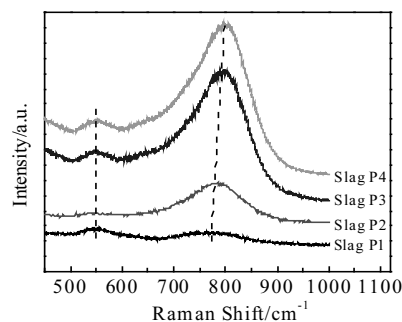


Fig.7 Original Raman spectra for CaF₂-CaO-Al₂O₃-MgO-Li₂O slag with varying TiO₂ contents

Fig.8 shows the typical deconvolution peaks of the Raman spectra with varying TiO₂ contents at room temperature. All backgrounds of the Raman signals are subtracted. The Raman spectra are deconvolved by Gaussian-Deconvolution method with the minimum correction coefficient of $r^2 \geq 0.995$. All Raman spectra are successfully fitted at the frequency range of 470~940 cm⁻¹. According to the deconvolution results, the TiO₂-free slag consists to three peaks near 550, 730, and 790 cm⁻¹. The deconvolution peak at around 550 cm⁻¹ pertains to transverse motion of bridged oxygen within Al-O-Al linkage for the [AlO₄]-tetrahedral network units^[20, 21]. The Raman spectroscopy structure of TiO₂-free aluminate shows that the peaks at about 730 and 790 cm⁻¹ are due to symmetric Al-O stretching vibration and referred to Q² (non-bridging oxygen per tetrahedrally coordinated cation, NBO/Al=2) and Q⁴ (NBO/Al=0), respectively^[20, 22]. However, when TiO₂ is added in slag, the new peak of Raman spectra of the slag appears at frequency range of 700~728 cm⁻¹ and 820~843 cm⁻¹, and the peak near 756 cm⁻¹ emerges. According to the study of Mysen et al^[23], the frequency peak in the range of 820~843 cm⁻¹ is interpreted as the presence of Ti₂O₆⁴⁺ (Ti-O-Ti stretching) chain in the melt slags, indicating that Ti⁴⁺ enters into the glasses in the form of Ti₂O₆⁴⁺ chain structure unit, and the peak in the range of 700~728 cm⁻¹ is attributed to O-Ti-O deformation vibration. Meanwhile, the emerging band at 756 cm⁻¹ is attributed to a symmetric stretching vibration of the AlO₂ units (NBO/Al=2)^[22]. This result suggests that the band of Q² unit shifts from the low frequency to high frequency with the addition of TiO₂ due to the increase of CaO content in the slag, and the phenomenon is similar to offset direction of Q² unit according to study of Shi et al^[7].

Fig.9 shows the relative fraction of Raman structural units and the relative height of Al-O-Al bond for CaF₂-CaO-Al₂O₃-MgO-Li₂O slag with varying TiO₂ contents. It can be observed from Fig.9 that the fraction height of Al-O-Al linkage decreases with increasing the TiO₂

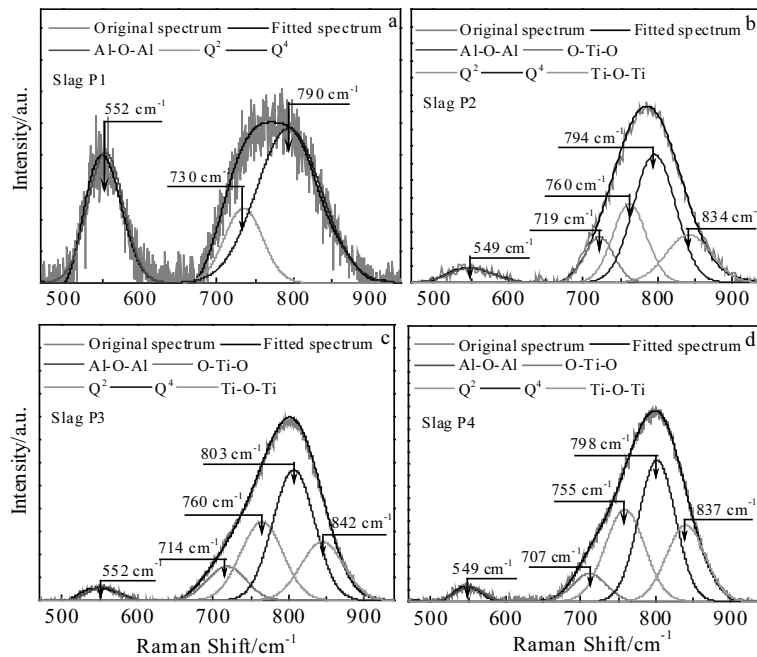


Fig.8 Typical deconvoluted peaks of the Raman spectra under varying TiO₂ contents: (a) 0 wt%, (b) 4.3 wt%, (c) 8.7 wt%, and (d) 13.1 wt%

content for the [AlO₄]-tetrahedral units. Especially when a small amount of TiO₂ is added, the fraction height of Al-O-Al linkage decreases rapidly, which can be interpreted by the decreased trend of experimental viscosity with the small amount of TiO₂ addition. Meanwhile, it can be seen that the Q⁴ units are depolymerized to aluminato structural units Q² with TiO₂ addition in the slag. This is because Q⁴ units are firstly depolymerized to instable units Q³ and it has the following relation to Q² and Q⁴: Q³ = Q² + Q⁴ [24].

Moreover, new structural bands of O-Ti-O and Ti-O-Ti chains are formed in the frequency range of 700~728 and 820~843 cm⁻¹, respectively, due to the addition of TiO₂ [23, 25]. The relative fraction of Ti-O-Ti gradually increases with increasing the TiO₂ content, which is attributed to the fact that the center of partial Al³⁺ ions in the [AlO₄]-tetrahedral network structures is substituted by Ti⁴⁺ ions to form of [TiO₄]-tetrahedron with the addition of TiO₂, and this is beneficial to simplify slag structure, according to the reports of Zhen et al [26]. Also, it can be found that when TiO₂ content is greater than 4.3 wt%, the total number of O-Ti-O and Ti-O-Ti chains basically remains constant and the relative fraction of O-Ti-O chain decreases with the addition of TiO₂, suggesting that Ti-O-Ti chains can be obtained by O-Ti-O deformation vibration.

Based on FTIR and Raman spectroscopy analysis, it can be seen that the relative amount of [AlO_nF_{4-n}]-tetrahedral complexes, [AlO₄]-tetrahedral network structure and O-Ti-O chain decreases and Ti-O-Ti chain increases, as

well as transformation from Q⁴ to Q² in [AlO₄]-tetrahedral network structure. These results are due to the use of TiO₂ in the slag as a basic oxide to provide free O²⁻ ions which destroy the bridge oxygen bond in the complex network structure and Ti⁴⁺ cations which form simple structures with other anions. Simultaneously, the complex network structure tends to be simplified, which is consistent with the decreased viscosity with increasing the TiO₂ content. Therefore, whether TiO₂ acts as acidic or basic oxides in the slag, it will directly affect the complexity of the micro network structure and the macro viscosity.

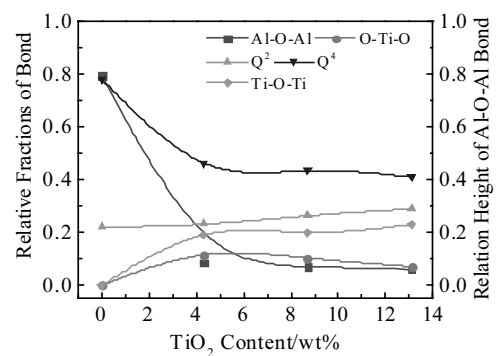


Fig.9 Relative fraction of each bond and relation height of Al-O-Al bond for CaF₂-CaO-Al₂O₃-MgO-Li₂O slag with varying TiO₂ contents

3 Conclusions

1) The viscosity of the low-fluoride slags decreases with increasing the TiO_2 content. The calculated activation energy of viscous flow decreases from 58.0, 47.7, 42.8 kJ/mol to 38.6 kJ/mol with increasing the TiO_2 content from 0 wt%, 4.3 wt%, 8.7 wt% to 13.1 wt%, indicating the decrease in polymerization degree of melt slags.

2) The FTIR results revealed that with the addition of TiO_2 , $[\text{AlO}_n\text{F}_{4-n}]$ -tetrahedral complexes and $[\text{AlO}_4]$ -tetrahedral network structures depolymerize, but $[\text{AlO}_6]$ -octahedron is not found in the slag.

3) The Raman spectra suggest that with the increase of TiO_2 , the Al-O-Al linkage in the $[\text{AlO}_4]$ -tetrahedral network structures is destroyed, the transformation of Q^4 to Q^2 unit occurs, and the new structural units of O-Ti-O and Ti-O-Ti chains form.

4) The polymerization degree of the slags decreases with increasing the TiO_2 content, and the changed structural units are consistent with the varying trend of viscosity.

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电渣重熔中 TiO_2 对低氟 CaF_2 - CaO - Al_2O_3 - MgO - Li_2O 渣黏度和结构的影响

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摘要: 研究了连续冷却条件下电渣重熔中 TiO_2 对低氟 CaF_2 - CaO - Al_2O_3 - MgO - Li_2O 渣黏度的影响, 并利用傅里叶变换红外光谱和拉曼光谱分析水淬渣和对应结构的关系。结果表明, 渣的黏度随着 TiO_2 的增加而降低, 当 TiO_2 含量达到 13.1% (质量分数, 下同), 随着温度从 1743, 1793, 1843 K 增加至 1893 K 时, 对应黏度从 0.067, 0.059, 0.056 Pa·s 降低到 0.054 Pa·s; 当温度达到 1843 K 或之上时, TiO_2 的加入对降低黏度有较小的影响。随着 TiO_2 含量从 0%, 4.3%, 8.7% 增加至 13.1%, 黏流活化能从 58.0, 47.7, 42.8 kJ/mol 降低到 38.6 kJ/mol。此外, 傅里叶变换红外光谱表明, 随着 TiO_2 的加入, 渣中 $[\text{AlO}_n\text{F}_{4-n}]$ -四面体络合物和 $[\text{AlO}_4]$ -四面体网状结构被解聚, 但没有发现 $[\text{AlO}_6]$ -八面体结构; 同时, 拉曼光谱分析表明, TiO_2 加入可解聚 $[\text{AlO}_4]$ -四面体网状结构中 Al-O-Al 键, 并且 Q^4 单元转化为 Q^2 单元, 同时形成 O-Ti-O 和 Ti-O-Ti 键。这些结果都表明 TiO_2 可降低渣的聚合度, 并且有利于渣的结构简单化。最终, 黏度变化与渣的对应结构有很好的一致性。

关键词: 电渣重熔; 低氟渣; 傅里叶变换红外光谱; 拉曼光谱

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