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REFRACTIVE INDEX AND OPTICAL ABSORPTION COEFFICIENT OF SLAGS WITH HIGH IRON-OXIDE CONTENT

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Synopsis: Refractive index and optical absorption coefficient of amorphous Fe_2O_3-SiO_2-CaO-Al_2O_3 slags have been determined at room temperature as functions of the basicity of [mass%CaO]/[mass%SiO_2] and the Fe_2O_3 concentration. Refractive index has been measured by an ellipsometer at 546nm and absorption coefficient has been determined from transmittance measured by a spectrophotometer in the wavelength range of 350 to 1000nm. Refractive index increases with increasing basicity and the Fe_2O_3 concentration. On the other hand, absorption coefficient is increased in the near-infrared region with decreasing basicity and is increased in the measured wavelength range with increasing the Fe_2O_3 concentration. These dependences of refractive index and absorption coefficient on the basicity and the Fe_2O_3 concentration are discussed and empirical equations for estimating refractive index and absorption coefficient at 546nm are suggested.

Key words: refractive index, absorption coefficient, transmittance, slag, iron oxide, ellipsometer, basicity, ionic refraction of oxygen, charge transfer band, ligand field.

1. Introduction

The analysis of heat transfer processes in slags is very important for the effective use of energy in iron- and steelmaking industry. In the analysis radiation heat transfer should be taken into account because it can be predominant at high temperatures where the metallurgical operations are carried out. In order to calculate radiation heat flux precisely, it is necessary to have reliable data of refractive index and optical absorption coefficient of slags, especially with high iron-oxide content.

Refractive index has been reported for many transparent silicate glasses[1] but there are no previous reports of refractive index for opaque slags containing iron oxide.

On the other hand, absorption coefficient has been measured for silicates containing iron oxide in the wavelength range of visible to near-infrared rays at room temperature and/or high temperatures[2]-[6]. These silicate samples contained iron oxide of below 1 mass%. Meanwhile, Fine et al.[7] measured absorption coefficient of slags with high iron-oxide content at room temperature. They used two samples containing 7.1 and 14.2 mass% FeO. But the dependences of absorption coefficient on iron-oxide concentration and basicity were not systematically determined.

In the present study, first we determine the optical properties of refractive index and absorption coefficient of amorphous Fe_2O_3-SiO_2-CaO-Al_2O_3 slags as functions of basicity and iron-oxide concentration. Second, we discuss the dependences of the optical properties on basicity and iron-oxide concentration and suggest empirical equations for estimating refractive index and absorption coefficient of the slags at 546nm.

2. Experimental procedures

Refractive index, n, was measured with an ellipsometer at the wavelength of 546nm at room temperature in air. The angle of incidence was 70°. The errors in measuring angles of polarizer and analyzer were within ±0.1° respectively, resulting in the error of about ±0.6% for refractive index.

On the other hand, absorption coefficient, α, was determined from transmittance, τ, by means of the Lambert's law.

$$\alpha = -\ln\tau / d \tag{1}$$

where d is the thickness of samples. Transmittance was measured with a spectrophotometer in the wavelength range of 350 to 1000nm at room temperature in air. Reflection was neglected in the calculation of absorption coefficient. The error on absorption coefficient by the neglect was estimated to be below 5%.

Fe_2O_3-SiO_2-CaO-Al_2O_3 slag system was employed as samples. The concentration of Fe_2O_3 was varied from 1 to 20 mass% and the basicity defined by [mass%CaO]/[mass%SiO_2] from 0.5 to 1.5. Reagent grade Fe_2O_3, SiO_2 and Al_2O_3 were dried in alumina crucibles in air at temperatures of 400, 900 and 900K, respectively. CaO was made by thermally decomposing $CaCO_3$ in reagent grade at 1300K.

These reagents were weighed and mixed with desired compositions in a mullite mortar. The mixtures were melted in alumina crucibles at temperatures between 1600 and 1800K in air using an induction furnace with graphite as a heating element. After being degassed, they were quenched on a water-cooled copper plate in air.

Broad profiles by X-ray diffraction showed that the synthesized slags were amorphous. X-ray photoelectron spectroscopy(XPS) suggested that Fe^{3+} ions were predominant in the slags. Furthermore, Mössbauer spectroscopy revealed that the ratios of the number of Fe^{2+} ions to that of total Fe ions were 20 to 30%.

For the measurements by an ellipsometer, optically flat surfaces more than 10mm x 10 mm in area were required. The one side of synthesized slag was mechanically polished in optical flat with abrasive of 1μm in diameter.

On the other hand, for the measurements by a spectrophotometer, pieces of about 1mm in thickness were cut from synthesized slags and both sides of the pieces were mechanically polished with abrasive of 1μm in diameter. The thicknesses of polished samples were decreased to 200 to 350μm with the ununiformity of ±5μm.

3. Results

3.1. Refractive index

Figure 1 shows refractive index of 10mass%Fe_2O_3-SiO_2-CaO-18Al_2O_3 slags at 546nm as a function of the basicity of [CaO]/[SiO_2]. Square and circular marks of the plots mean refractive indices measured for as-quenched and polished samples, respectively, and the difference between the refractive indices is below 2%. On the contrary, open and full circles express refractive indices measured for different polished samples, from which the magnitude of the reproducibility of the measurements can be seen and the scattering error is around ±1%.

The refractive index increases linearly from 1.62 to 1.7 with increasing the basicity. This tendency agrees with those for binary silicate glasses reported by Iwamoto et al.[8].

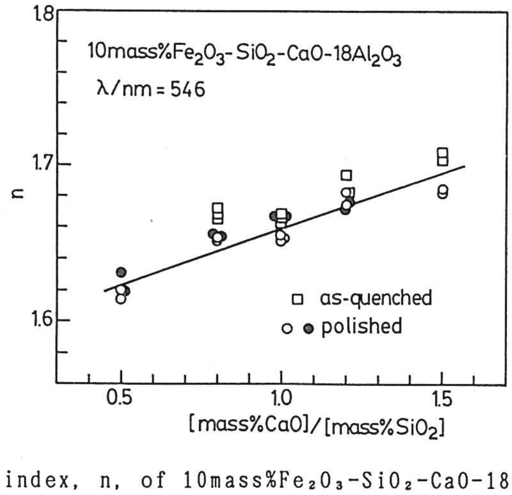

Fig.1 Refractive index, n, of 10mass%Fe_2O_3-SiO_2-CaO-18Al_2O_3 slags at 546nm as a function of the basicity of [CaO]/[SiO_2].

Figure 2 shows refractive index of Fe_2O_3-SiO_2-CaO-Al_2O_3 slags at 546nm as a function of the Fe_2O_3 concentration. The samples were synthesized by adding 1 to 20 mass% Fe_2O_3 to master slags of 40mass%SiO_2-40CaO-20Al_2O_3. The refractive index increases linearly from 1.62 to 1.72 with increasing the Fe_2O_3 concentration.

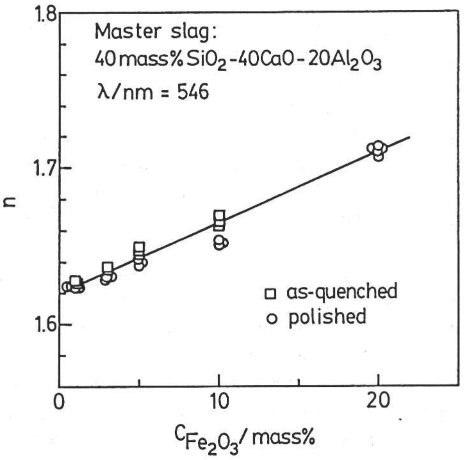

Fig.2 Refractive index, n, of Fe_2O_3-SiO_2-CaO-Al_2O_3 slags at 546nm as a function of the Fe_2O_3 concentration, C_{Fe2O3}.

3.2. Absorption coefficient

Figure 3 shows absorption coefficients of 10mass%Fe_2O_3-SiO_2-CaO-18Al_2O_3 slags as a function of wavelength. The basicity of [CaO]/[SiO_2] is varied from 0.5 to 1.5. The absorption coefficients are between 5000 and 20000m^{-1}. It is suggested that absorption coefficient is not strongly dependent on the basicity, because it has been confirmed that the scattering error is around ±15% by the measurement of two samples with the same composition.

Nevertheless, the following dependence on basicity has been suggested:
The absorption coefficient in near-infrared region increases with decreasing basicity. The steep increase of the absorption coefficient in 500 to 600nm occurs in shorter wavelength in lower basicity. This absorption is assigned to the absorption by the transition of electron from O^{2-} to Fe^{3+}, i.e., the charge transfer band[6].

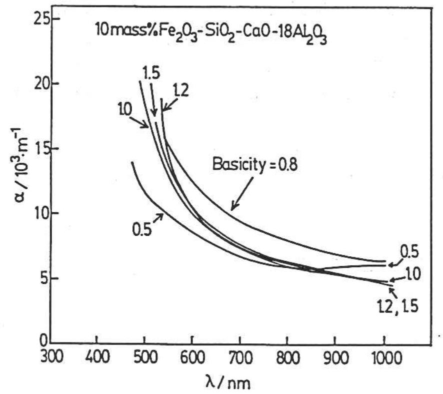

Fig.3 Absorption coefficient, α, of 10mass%Fe_2O_3-SiO_2-CaO-18Al_2O_3 slags as a function of wavelength.

Figure 4 shows absorption coefficient of Fe_2O_3-SiO_2-CaO-Al_2O_3 slags as a function of wavelength. The samples were synthesized by adding 1 to 10 mass% Fe_2O_3 to master slags of 40mass%SiO_2-40CaO-20Al_2O_3. As expected, the average absorption coefficient monotonously increases from 500 to 10000 m^{-1} with increasing the Fe_2O_3 concentration. This tendency is consistent with the result reported by Ito and Goto[6]. Furthermore, the absorption edge by the charge transfer band shifts to longer wavelength in higher Fe_2O_3 concentration.

Meanwhile, absorption coefficient of slags containing FeO has been reported by Fine et al.[7]. It has been shown that FeO-bearing slags have larger absorption coefficients in near-infrared region than Fe_2O_3-bearing slags have. The light in the region is absorbed by the ligand field of Fe^{2+}. Since the slags with Fe_2O_3 were employed in the present work, the number of Fe^{2+} is smaller than that of the FeO-bearing slags. As a result, the absorption coefficients in near-infrared region of the Fe_2O_3-bearing slags are smaller than those of the FeO-bearing slags.

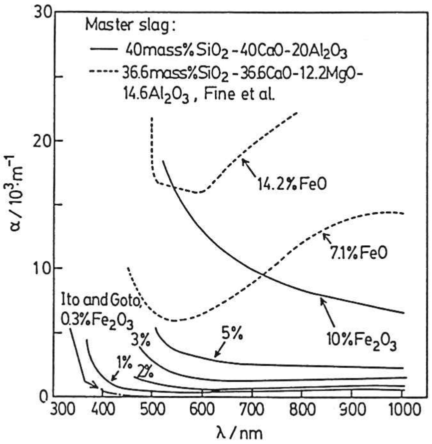

Fig. 4 Absorption coefficient, α, of Fe_2O_3-SiO_2-CaO-Al_2O_3 slags as a function of wavelength.

4. Discussion

4.1. Dependence of refractive index on basicity

Refractive index of slags expresses the magnitude of the interaction between light and ions in slags. As shown in Fig. 1, since the refractive index of slags increases with increasing basicity, it is considered that the interaction is stronger in higher basicity.

On the other hand, it is known that some oxygen atoms in slags are in the states of non-bridging oxygen ions and free oxygen ions which more strongly interact with light than bridging oxygen atoms. It is also known that the number of the two sorts of oxygen ions increases with increasing basicity.

The increase of the number of both types of oxygen ions is accordingly considered to enhance the interaction between light and the oxygen ions, resulting in the increase of refractive index of the slags.

Ionic refraction of oxygen, Ro, can express the magnitude of the interaction between light and oxygen or the electron donation activity of oxygen. In order to confirm the above consideration, Ro of each slag has been calculated by means of Eq. (2).

$$R = No \cdot Ro + \Sigma Ni \cdot Ri \qquad (2)$$

Here R expresses the molar refraction of slag and Ri the ionic refractions of respective cations. No and Ni are the numbers of moles of oxygen and respective cations contained in 1 mol of slag respectively.

R has been calculated by means of the Lorentz-Lorenz equation, i.e., Eq. (3),

$$[(n^2 - 1)/(n^2 + 2)]M/\rho = R. \qquad (3)$$

Here n, M and ρ are the refractive index, the average molecular mass and the density of slag respectively. The density is calculated on the basis of additivity. The densities for Fe_2O_3, SiO_2, CaO and Al_2O_3 have been reported by Winchell and Winchell[9].

The values of Ri for Si^{4+}, Ca^{2+} and Al^{3+} are 0.084, 1.182 and 0.137 $cm^3 \cdot mol^{-1}$ respectively[10] and that for Fe^{3+} is 2.86 $cm^3 \cdot mol^{-1}$[11]. It is assumed that the values of Ri are constant, irrespective of slag composition, and that Fe ions in each slag are in the state of Fe^{3+}. The neglect of Fe^{2+} might give some error to the absolute values of Ro but has no influence on the relationship between Ro and the basicity of [CaO]/[SiO_2].

Figure 5 shows the relation between the ionic refraction of oxygen, Ro, and the basicity of [CaO]/[SiO_2]. The ionic refraction of oxygen increases with increasing basicity. It has been confirmed that the increase of refractive index with increasing basicity results from the enhancement of the interaction between light and oxygen ions in the slags.

Iwamoto et al. [8] have reported that Ro is available as a basicity in binary silicate glasses and that glasses with larger Ro are more basic. Figure 5 has suggested that Ro can be used as a basicity also in slags containing iron oxide.

4.2. Dependence of refractive index on iron-oxide concentration

It was shown that refractive index increases with increasing the concentration of Fe_2O_3 in Fig. 2. In order to consider this behavior, the ionic refraction of oxygen has

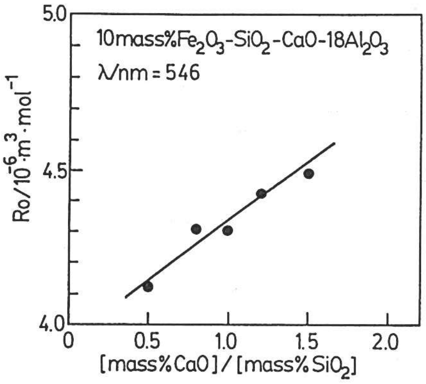

Fig. 5 Relation between the ionic refraction of oxygen, Ro, and the basicity of [CaO]/[SiO_2].

been calculated from the data in Fig. 2. The calculation has revealed that Ro increases with increasing C_{Fe2O3}. By taking account that Ro is available as a basicity of slags, the behavior can be explained as follows: Since Fe_2O_3 acts rather as a basic oxide in the slags, the number of non-bridging oxygen ions and free oxygen ions is increased by the addition of Fe_2O_3. As a result, the interaction between light and oxygen ions in the slags becomes stronger, resulting in the increase of refractive index of the slags.

4.3. Dependence of absorption coefficient on basicity

The decrease of basicity of slags results in the increase of absorption coefficient in near-infrared region and the shift of the absorption edge by the charge transfer band to shorter wavelength, as shown in Fig. 3.

The optical absorption in near-infrared region is caused by the ligand field of Fe^{2+}. Since iron has a tendency to exist preferentially in the state of Fe^{2+} in slags with lower basicity, the concentration of Fe^{2+} relatively increases in lower basicity. As a result, the absorption by the ligand field of Fe^{2+} is enhanced. This is considered to be a reason for the increase of absorption coefficient in near-infrared region in lower basicity.

On the contrary, slags with lower basicity have smaller ionic refraction of oxygen, as shown in Fig. 5. This means that O^{2-} in slags with lower basicity has smaller electron-donation activity. Since O^{2-} with smaller electron-donation activity is more difficult to release electron, the energy necessary for the transition of electron from O^{2-} to Fe^{3+}, i.e., the charge transfer becomes larger. For this reason the absorption edge by the charge transfer band is considered to shift to shorter wavelength in lower basicity.

4.4. Dependence of absorption coefficient on iron-oxide concentration

In higher Fe_2O_3 concentration the absorption edge by the charge transfer band shifts to longer wavelength, as shown in Fig. 4. This behavior can be explained on the basis of the electron-donation activity of oxygen, too. In 4.2., it has been shown that slags with higher Fe_2O_3 concentration possess larger ionic refraction of oxygen, i.e., larger electron-donation activity of oxygen. It is therefore considered that the energy necessary for the charge transfer becomes smaller with increasing Fe_2O_3 concentration, resulting in the shift of the absorption edge to longer wavelength.

4.5. Empirical equations for estimating refractive index and absorption coefficient of slags at 546nm

Refractive index of Fe_2O_3-SiO_2-CaO-Al_2O_3 slag system increases linearly with increasing the basicity of [CaO]/[SiO_2] and the Fe_2O_3 concentration, as shown in Figs. 1 and 2. From these results, an empirical equation for refractive index at 546nm has been derived as functions of [CaO]/[SiO_2] and the Fe_2O_3 concentration as follows:

$$n_{546} = 1.548 + 7.121\times10^{-2}\cdot[CaO]/[SiO_2] + 4.476\times10^{-3}\cdot[Fe_2O_3] \quad (4)$$

Here [ ] expresses the concentration by mass% of respective oxides.

Eq. (4) agrees with the average values in Figs. 1 and 2 within the error of 1 % and, furthermore, can produce refractive indices of CaO-SiO_2 binary system reported by Iwamoto et al. [8] within the error of 1 %.

Figure 6 shows the linear relation between absorption coefficient of Fe_2O_3-SiO_2-CaO-Al_2O_3 slags at 546nm in Fig.4 and the square of the Fe_2O_3 concentration. On the other hand, Fig.3 has shown that absorption coefficient is not strongly dependent on the basicity of [CaO]/[SiO_2]. From these results, an empirical equation for absorption coefficient at 546 nm has been derived as a function of the Fe_2O_3 concentration as follows:

$$\alpha \ / \ m^{-1} = 160 \cdot [Fe_2O_3]^2 \qquad (5)$$

These equations are useful for estimating refractive index and absorption coefficient in the analysis of heat transfer processes, since the light at 546nm is considered to act as a carrier of heat energy due to relative transparency of the slags at the wavelength.

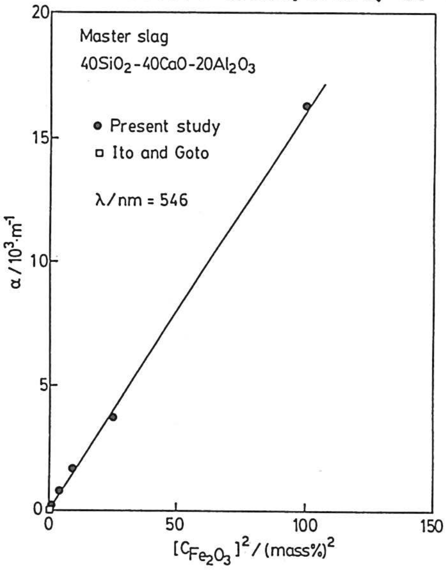

Fig.6 Relation between absorption coefficient, α, at 546nm and the square of the Fe_2O_3 concentration, $[C_{Fe2O3}]^2$.

5. Conclusion

Refractive index and absorption coefficient of amorphous Fe_2O_3-SiO_2-CaO-Al_2O_3 slags were determined at room temperature as functions of the basicity of [CaO]/[SiO_2] and the Fe_2O_3 concentration.

Refractive index of 10mass%Fe_2O_3-SiO_2-CaO-18Al_2O_3 slags increased from 1.62 to 1.7 with increasing the basicity. Refractive index of slags of 40mass%SiO_2-40CaO-20Al_2O_3 was increased from 1.62 to 1.72 by adding 1 to 20 mass% Fe_2O_3.

On the contrary, absorption coefficient of 10mass%Fe_2O_3-SiO_2-CaO-18Al_2O_3 slags was 5000 to 20000 m^{-1} in the measured wavelength range and increased in near-infrared region with decreasing the basicity. With increasing Fe_2O_3 concentration from 1 to 10 mass%, average absorption coefficient of slags of 40mass%SiO_2-40CaO-20Al_2O_3 was monotonously increased from 500 to 10000 m^{-1}.

These dependences of refractive index and absorption coefficient on basicity and Fe_2O_3 concentration were discussed on the basis of the ionic refraction of oxygen and the electron-donation activity of oxygen. Furthermore, the empirical equations for estimating refractive index and absorption coefficient at 546nm were suggested.

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