

Determination of Refractive Index and Absorption Coefficient of Iron-Oxide-Bearing Slags

MASAHIRO SUSU, FUTAO LI, and KAZUHIRO NAGATA

The refractive index and absorption coefficient of amorphous $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO-Al}_2\text{O}_3$ slags have been determined at room temperature as functions of the basicity of $[\text{mass pct CaO}]/[\text{mass pct SiO}_2]$ and the Fe_2O_3 concentration. The refractive index has been measured by an ellipsometer at 546 nm, and the absorption coefficient has been determined from transmittance measured by a spectrophotometer in the wavelength range of 350 to 1000 nm. The refractive index increases with increasing basicity of $[\text{CaO}]/[\text{SiO}_2]$ and the Fe_2O_3 concentration. On the other hand, with decreasing basicity of $[\text{CaO}]/[\text{SiO}_2]$, the absorption coefficient is increased in the near-infrared region, and the absorption edge by the charge transfer band is shifted to a shorter wavelength. With increasing Fe_2O_3 concentration, the absorption coefficient is increased in the measured wavelength range, and the absorption edge by the charge transfer band is shifted to a longer wavelength. These dependences of refractive index and absorption coefficient on the basicity and the Fe_2O_3 concentration are discussed.

I. INTRODUCTION

THE effective use of energy is more important in newer iron- and steelmaking processes, such as smelting reduction. For this purpose, the analysis of heat-transfer processes in slags is a key subject. In the analysis, the heat transfer by radiation should not be negligible, because radiation conduction can be the predominant mode of heat transfer at high temperatures where the metallurgical operations are carried out.

If a slag phase is optically thick and if a temperature gradient is small, the radiation heat flux, q_r , in the slag phase can be calculated by the equation

$$q_r = -16n^2\sigma T^3\nabla T/3\alpha \quad [1]$$

Here, n and α are the refractive index and optical absorption coefficient of slag, respectively, σ the Stefan-Boltzmann constant, and T absolute temperature. In order to conduct precise calculations, it is necessary to have reliable data of the refractive index and absorption coefficient of slags, especially with high iron-oxide content.

Refractive index has been reported for many transparent silicate glasses.^[1] Iwamoto *et al.*^[2,3] have also measured the refractive index of binary and ternary transparent silicate glasses at room temperature, with respect to basicity. They have shown that the ionic refraction of oxygen calculated from refractive index can be used as a basicity of silicate glasses and proposed the concept of refraction basicity which is defined by the ratio of ionic refraction of oxygen in silicate glass to that in silica glass. However, there are no previous reports of measurements of refractive index for opaque slags containing iron oxide.

On the contrary, absorption coefficients have been measured for silicates containing iron oxide in the wave-

length range of visible to near-infrared rays at room temperature and/or high temperatures.^[4-8] These silicate samples contained iron oxide of below 1 mass pct, because most of these studies were carried out in relation to the ligand field theory. On the other hand, the absorption coefficients of slags with high iron-oxide content have been measured at room temperature by Fine *et al.*^[9] They used two samples which contained 7.1 and 14.2 mass pct FeO. But the dependences of absorption coefficient on iron-oxide concentration and basicity were not systematically determined.

Meanwhile, Ito and Goto^[8] have experimentally determined the dependences of absorption coefficient of slags with Fe_2O_3 of below 1 mol pct on basicity and Fe_2O_3 concentration and discussed the mechanism for optical absorption of the slags in detail. They have pointed out that the optical absorption of the slags in the wavelength range of visible to near-infrared rays is predominantly assigned to the ligand field of Fe^{2+} and the transition of electron from O^{2-} to Fe^{3+} , *i.e.*, the charge transfer band. But no physicochemical explanation has been given for the dependences of absorption coefficient on basicity and Fe_2O_3 concentration.

On the other hand, the interaction of light with ions in slags causes the decrease in the velocity of the transmitted radiation and its change in direction, which results in refraction of light, and refractive index expresses the magnitude of the interaction. Therefore, the determination of refractive index as functions of basicity and Fe_2O_3 concentration helps the understanding of the absorption characteristics.

In the present study, we have determined the optical properties of the refractive index and absorption coefficient of amorphous $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO-Al}_2\text{O}_3$ slags in wide basicity and iron-oxide concentration ranges and discussed the dependences of the optical properties on basicity and iron-oxide concentration in the viewpoint of ionic refraction of oxygen and electron donation activity of oxygen.

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II. EXPERIMENTAL

A. Measurement

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

On the contrary, the absorption coefficient, α , was determined from transmittance, τ , by Lambert's law,

$$\alpha = -\ln \tau/d \quad [2]$$

where d is the thickness of samples. Transmittance was measured with a spectrophotometer in the wavelength range of 350 to 1000 nm at room temperature in air.

In the calculation of absorption coefficient, reflection at a sample surface and multiple reflection in a sample were neglected. As a result, the error in the absorption coefficient was estimated to be below 5 pct at the wavelength of 546 nm. This estimation was carried out by the comparison of α determined by Eq. [2] with α' by Eq. [3] in which reflection was taken into account.

$$\tau = (1 - R)^2 \exp(-\alpha' d) / [1 - R^2 \exp(-2\alpha' d)] \quad [3]$$

Here α' is the absorption coefficient in which reflection is taken into account, and R , reflectance, can be calculated from Fresnel's law for perpendicular incidence of light, *i.e.*, Eq. [4].

$$R = [(1 - n)^2 + k^2] / [(1 + n)^2 + k^2] \quad [4]$$

Here, k , the extinction coefficient, is an imaginary part of the complex refractive index and related to α by the equation

$$k = \alpha\lambda/4\pi \quad [5]$$

where λ is the wavelength of light. Because k is smaller by a factor of about 10^{-4} than n , R is predominantly determined by n and thus converges on a constant value in the calculation of Eqs. [4] and [5].

B. Sample Preparation

Fe_2O_3 - SiO_2 - CaO - Al_2O_3 slags were employed as samples. The concentration of Fe_2O_3 was varied from 1 to 30 mass pct and the basicity defined by $[\text{mass pct CaO}] / [\text{mass pct SiO}_2]$ 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 900 K, respectively. CaO was made by thermally decomposing CaCO_3 in reagent grade at 1300 K.

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 1800 K 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 all of 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 pct.

For the measurements by an ellipsometer, optically flat surfaces of greater than 10×10 mm in area were required. One side of the synthesized slag was mechanically polished in optical flat. Figure 1 shows scanning electron microscope (SEM) view of slag surfaces polished with the different diameter of abrasives. The samples were 30 mass pct Fe_2O_3 -46 SiO_2 -24 CaO slags. The surface of the sample which was polished with abrasive of $1 \mu\text{m}$ in diameter seems to be the same as the surface of the as-quenched sample.

Figure 2 shows the relation between refractive index, n , of 30 mass pct Fe_2O_3 -46 SiO_2 -24 CaO and the diameter, d , of abrasives. The refractive index tends to increase with decreasing the diameter of abrasives. This is due to the reduction of diffused reflection of light at sample surfaces. The refractive index of the sample polished with abrasive of $1 \mu\text{m}$ in diameter is in good agreement with that of the as-quenched sample. Moreover, the refractive index of the as-quenched sample is very close to that estimated from specific refractions of the component oxides.^[10] This means that diffused reflection can be almost eliminated by polishing sample surface with abrasive of $1 \mu\text{m}$ in diameter. On the basis of the above results, samples for ellipsometry were finally polished with abrasive of $1 \mu\text{m}$ in diameter.

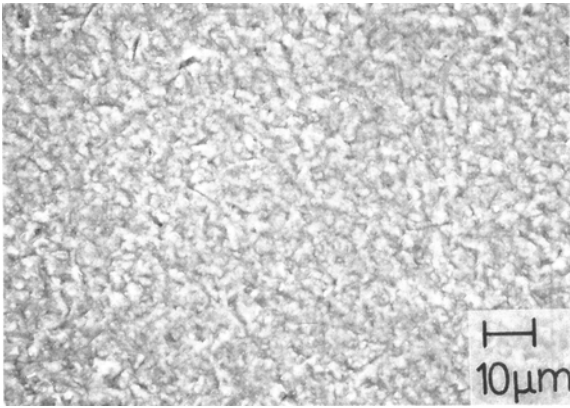
On the contrary, for the measurements by a spectrophotometer, 1-mm-thick pieces were cut from synthesized slags, and both sides of the pieces were mechanically polished in order to eliminate the energy loss of light by diffused reflection at sample surfaces. Figure 3 shows the relation between absorption coefficient, α , of 3 mass pct Fe_2O_3 -38.8 SiO_2 -38.8 CaO -19.4 Al_2O_3 and the diameter, d , of abrasives. The value of α for $d/\mu\text{m} = 1$ is smaller by a factor of about 20 pct than that for $d/\mu\text{m} = 5.6$ due to eliminating diffused reflection. It was decided that samples for transmittance measurements were finally polished with abrasive of $1 \mu\text{m}$ in diameter. The thicknesses of polished samples were 200 to 350 μm , and the nonuniformity for the thickness of a sample was about $\pm 5 \mu\text{m}$.

III. RESULTS

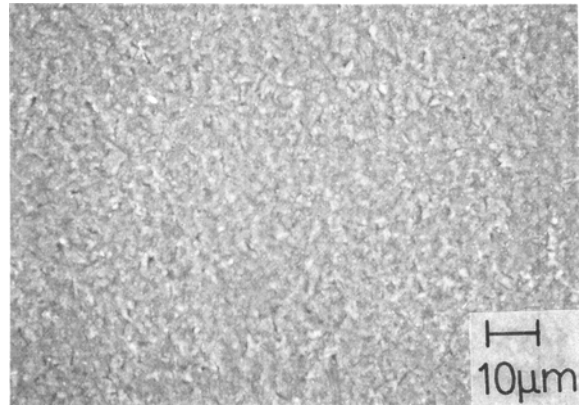
A. Refractive Index

Figure 4 shows refractive index of 10 mass pct Fe_2O_3 - SiO_2 - CaO -18 Al_2O_3 slags at 546 nm as a function of the basicity of $[\text{CaO}]/[\text{SiO}_2]$. 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 pct. 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 pct.

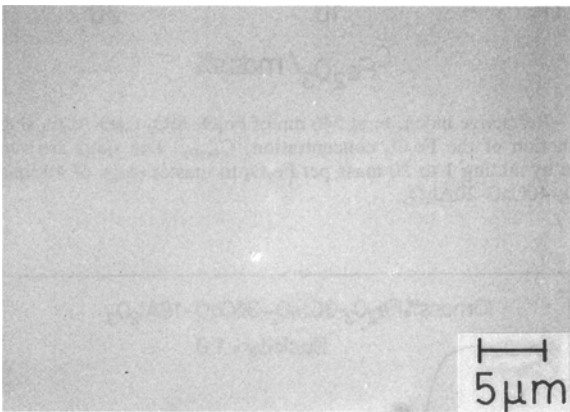
The refractive index increases from 1.62 to 1.7 with increasing the basicity of $[\text{CaO}]/[\text{SiO}_2]$ from 0.5 to 1.5. This tendency agrees with those for Na_2O - SiO_2 , K_2O - SiO_2 , CaO - SiO_2 , SrO - SiO_2 , and BaO - SiO_2 reported by Iwamoto *et al.*^[2]



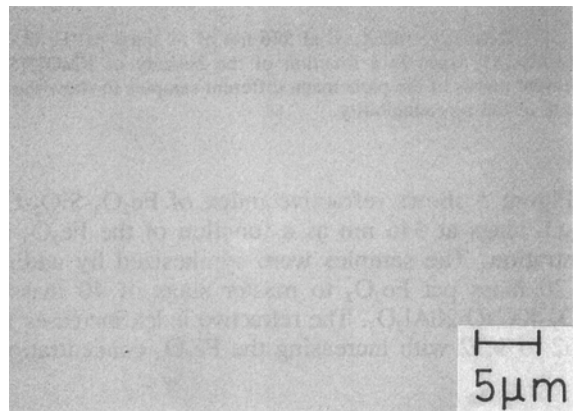
$d/\mu\text{m} = 5.6$



$d/\mu\text{m} = 3$



$d/\mu\text{m} = 1$



as-quenched

Fig. 1—SEM views of slag surfaces polished with the different diameter, d , of abrasives.

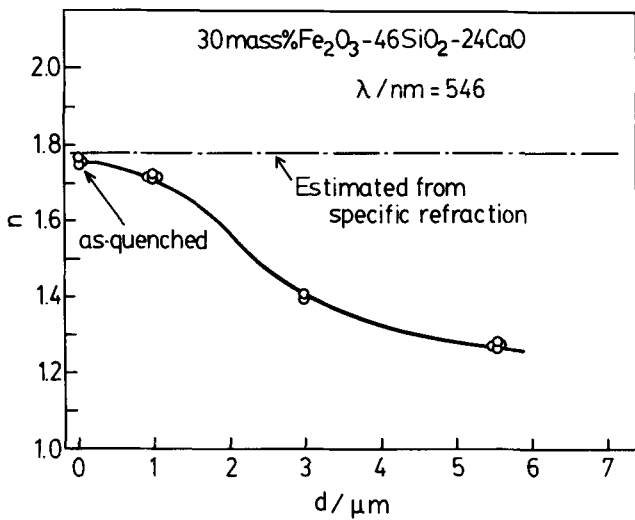


Fig. 2—Relation between refractive index, n , of 30 mass pct Fe₂O₃-46SiO₂-24CaO slag and the diameter, d , of abrasives.

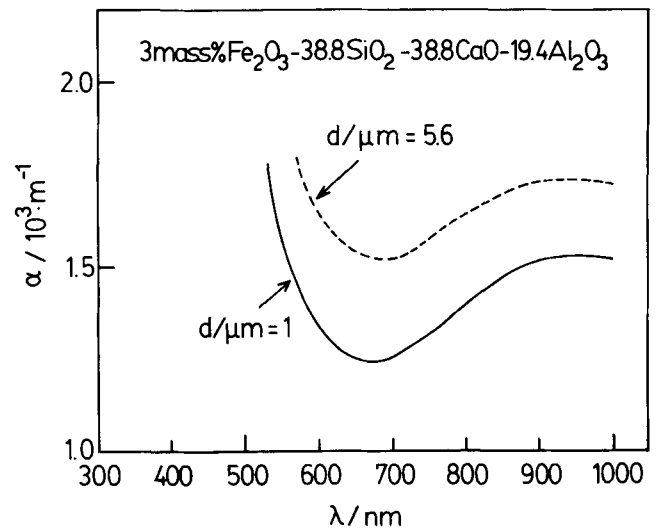


Fig. 3—Relation between absorption coefficient, α , of 3 mass pct Fe₂O₃-38.8SiO₂-38.8CaO-19.4Al₂O₃ slag and the diameter, d , of abrasives.

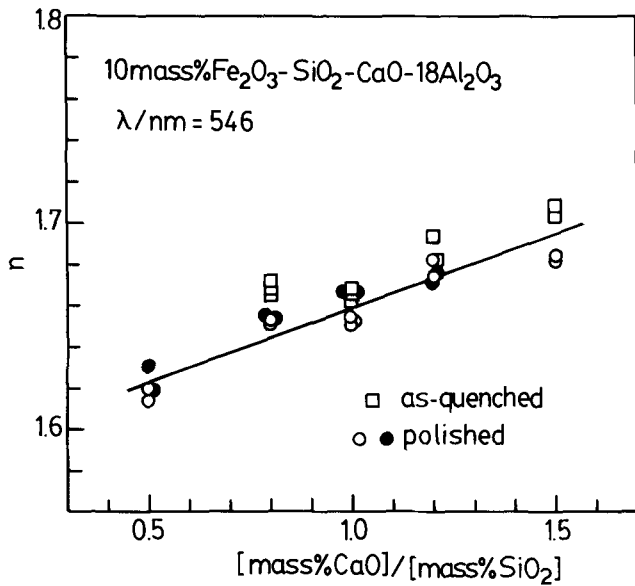


Fig. 4—Refractive index, n , at 546 nm of 10 mass pct $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO-18Al}_2\text{O}_3$ slags as a function of the basicity of $[\text{CaO}]/[\text{SiO}_2]$. Different marks of the plots mean different samples to show the magnitude of the reproducibility.

Figure 5 shows refractive index of $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO-Al}_2\text{O}_3$ slags at 546 nm as a function of the Fe_2O_3 concentration. The samples were synthesized by adding 1 to 20 mass pct Fe_2O_3 to master slags of 40 mass pct $\text{SiO}_2\text{-40CaO-20Al}_2\text{O}_3$. The refractive index increases from 1.62 to 1.72 with increasing the Fe_2O_3 concentration.

B. Absorption Coefficient

Figure 6 shows the absorption coefficient of 10 mass pct $\text{Fe}_2\text{O}_3\text{-36SiO}_2\text{-36CaO-18Al}_2\text{O}_3$ slags. Two samples with the same composition were used in order to confirm the reproducibility. It has shown that the scattering error is around ± 15 pct over the measurement range.

Figure 7 shows absorption coefficients of 10 mass pct $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO-18Al}_2\text{O}_3$ slags as a function of wavelength. The basicity of $[\text{CaO}]/[\text{SiO}_2]$ is varied from 0.5 to 1.5. It is not significant to discuss the difference of absolute values of absorption coefficients, since these absorption coefficients are $5000 \sim 20,000 \text{ m}^{-1}$ and almost equal within the scattering error of ± 15 pct, irrespective of the basicity.

However, the following dependence on basicity has been suggested. The absorption coefficient in near-infrared regions increases with decreasing basicity. The steep increase of the absorption coefficient in 500 to 600 nm 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.^[8] The shift of this absorption edge has already been reported,^[8] but the reason has not been clarified yet.

Figure 8 shows the absorption coefficients of $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO-Al}_2\text{O}_3$ slags as a function of wavelength. The samples were synthesized by adding 1 to 10 mass pct Fe_2O_3 to master slags of 40 mass pct $\text{SiO}_2\text{-40CaO-20Al}_2\text{O}_3$. As expected, the average absorption coefficient monotonously increases from 500 to $10,000 \text{ m}^{-1}$

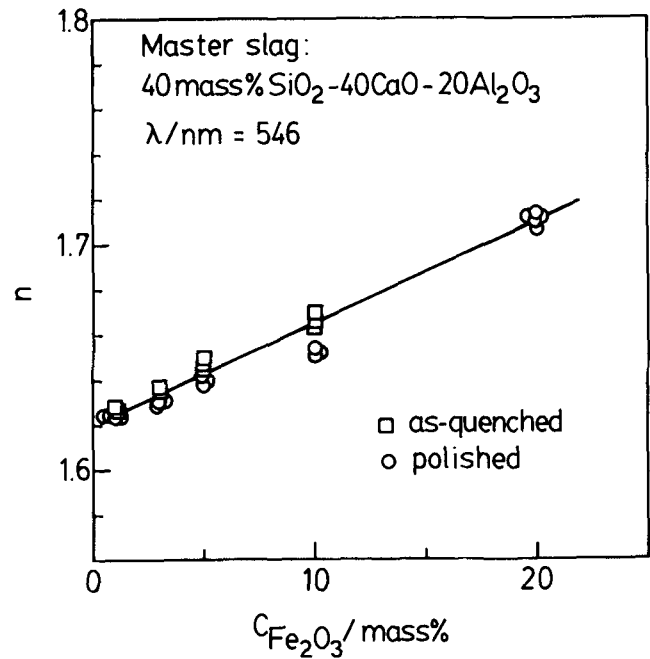


Fig. 5—Refractive index, n , at 546 nm of $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO-Al}_2\text{O}_3$ slags as a function of the Fe_2O_3 concentration, $C_{\text{Fe}_2\text{O}_3}$. The slags are synthesized by adding 1 to 20 mass pct Fe_2O_3 to master slags of 40 mass pct $\text{SiO}_2\text{-40CaO-20Al}_2\text{O}_3$.

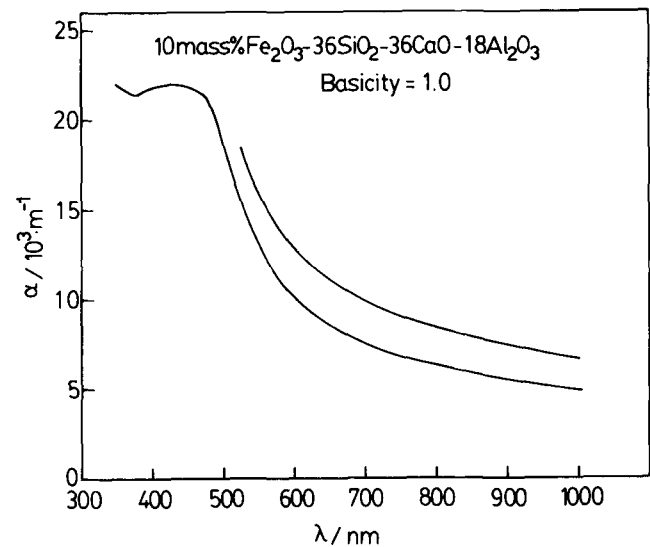


Fig. 6—Absorption coefficient, α , of 10 mass pct $\text{Fe}_2\text{O}_3\text{-36SiO}_2\text{-36CaO-18Al}_2\text{O}_3$ slag as a function of wavelength. The basicity is defined by $[\text{CaO}]/[\text{SiO}_2]$.

with increasing the Fe_2O_3 concentration. This tendency is consistent with the result reported by Ito and Goto.^[8] Furthermore, the absorption edge by the charge transfer band shifts to longer wavelength in higher Fe_2O_3 concentration. The shift of this absorption edge has also been reported,^[8] but no physicochemical explanation has been given for the phenomenon.

On the contrary, the absorption coefficient of slags containing FeO have been reported by Fine *et al.*^[9] 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+} , *i.e.*, $T_{2g} \rightarrow E_g$.^[8] 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 the near-infrared region of the Fe_2O_3 -bearing slags are smaller than those of the FeO-bearing slags.

IV. DISCUSSION

A. Dependence of Refractive Index on Basicity

When light propagates in a substance, for example, in a slag, light interacts with ions. Refractive index is related to the magnitude of the interaction. As shown in Figure 4, since refractive index of slags increases with increasing basicity, it is considered that the interaction is stronger in higher basicity.

On the contrary, it is known that some oxygen atoms in slags are in the states of nonbridging oxygen ions and free oxygen ions which more strongly interact with light than bridging oxygen atoms. It is also known that with increasing basicity, the number of the two sorts of oxygen ions increases and the electron donation activity of oxygen is higher.

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, R_O can be used as a measure of the magnitude of the interaction between light and oxygen or the electron donation activity of oxygen. In order to confirm the above consideration, the ionic refraction of oxygen in each slag has been calculated by subtracting the ionic refractions of the respective cations from the molar refraction of slag, R , calculated by the Lorentz-Lorenz equation, *i.e.*, Eq. [6],

$$[(n^2 - 1)/(n^2 + 2)]M/\rho = R \quad [6]$$

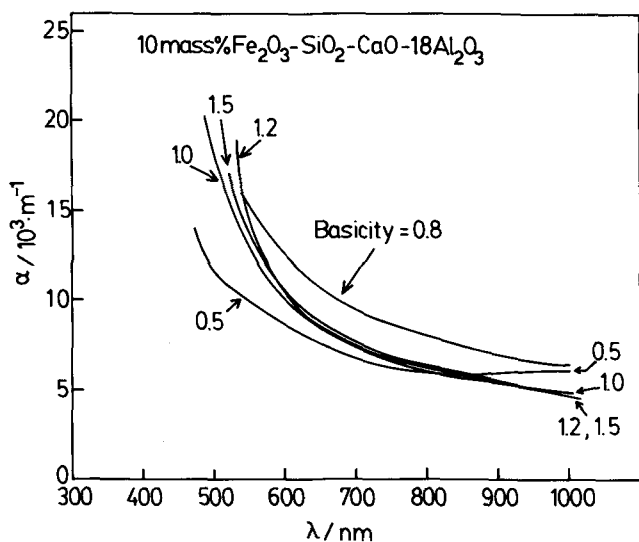


Fig. 7—Absorption coefficient, α , of 10 mass pct Fe_2O_3 - SiO_2 - CaO - $18\text{Al}_2\text{O}_3$ slags as a function of wavelength. The basicity of $[\text{CaO}]/[\text{SiO}_2]$ is used as a parameter.

where 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.^[11] The ionic refractions reported by Kordes^[12] are used for Si^{4+} , Ca^{2+} , and Al^{3+} and the ionic refraction by Fajans and Joos^[13] for Fe^{3+} .

In the calculation of R_O , it is assumed that the ionic refractions of cations 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+} may give some error to the absolute values of R_O but has no influence on the relationship between R_O and the basicity of $[\text{CaO}]/[\text{SiO}_2]$.

Figure 9 shows the relation between the ionic refraction of oxygen, R_O , and the basicity of $[\text{CaO}]/[\text{SiO}_2]$. 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.*^[2] have reported that R_O is available as a basicity in binary oxide glasses. In order to consider if R_O can be a basicity also in iron-oxide-bearing slags in complex compositions, an examination has been carried to determine the relation between the ionic refraction of oxygen and the theoretical optical basicity which indicates basicity of the whole system.

Figure 10 shows the relation between the ionic refraction of oxygen, R_O and the theoretical optical basicity, Λ_{th} . The theoretical optical basicity has been calculated by the equation^[14]

$$\Lambda_{th} = X_{\text{Fe}^{3+}}/\gamma_{\text{Fe}} + X_{\text{Si}^{4+}}/\gamma_{\text{Si}} + X_{\text{Ca}^{2+}}/\gamma_{\text{Ca}} + X_{\text{Al}^{3+}}/\gamma_{\text{Al}} \quad [7]$$

Here, $X_{\text{Fe}^{3+}}$ and so on are the equivalent fractions of the respective cations, and γ_{Fe} and so on are the basicity-moderating parameters of the cations. The basicity-moderating parameters reported by Nakamura *et al.*^[15] are employed. Iron is assumed to be in the state of Fe^{3+} .

There is a relationship between R_O and Λ_{th} . It is consequently considered that the ionic refraction of oxygen can also be available as a basicity in slags containing iron oxide.

B. Dependence of Refractive Index on Iron-Oxide Concentration

It was shown that refractive index increases with increasing the concentration of Fe_2O_3 in Figure 5. In order to consider this behavior, the ionic refraction of oxygen has been calculated from the data in Figure 5.

Figure 11 shows the relation between the ionic refraction of oxygen, R_O , and the concentration of Fe_2O_3 , $C_{\text{Fe}_2\text{O}_3}$. The value of R_O increases with increasing $C_{\text{Fe}_2\text{O}_3}$. By taking account of the fact that R_O 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 nonbridging oxygen ions and free oxygen ions are increased by the addition of Fe_2O_3 . As a result, the interaction between light and oxygen ions in the slags becomes stronger, which results in the increase of refractive index of the slags.

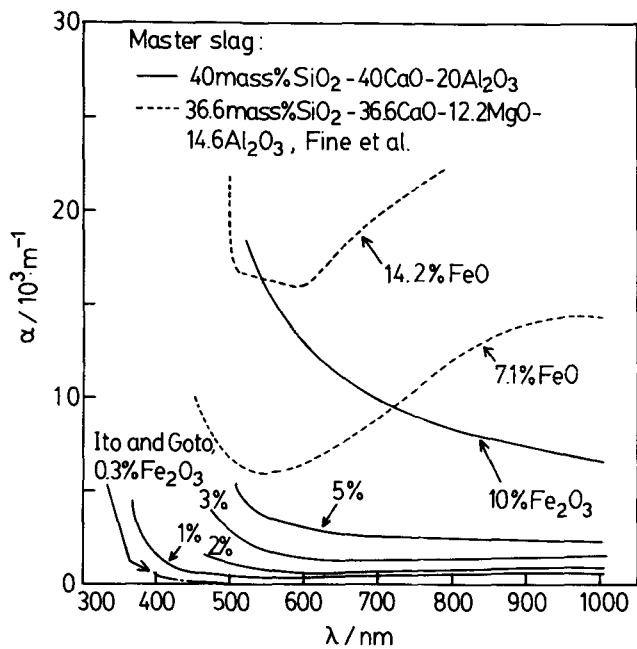


Fig. 8—Absorption coefficient, α , of $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-CaO-Al}_2\text{O}_3$ slags as a function of wavelength. The slags are synthesized by adding 1 to 10 mass pct Fe_2O_3 to master slags of 40 mass pct $\text{SiO}_2\text{-40CaO-20Al}_2\text{O}_3$. The Fe_2O_3 concentration, $C_{\text{Fe}_2\text{O}_3}$, is used as a parameter.

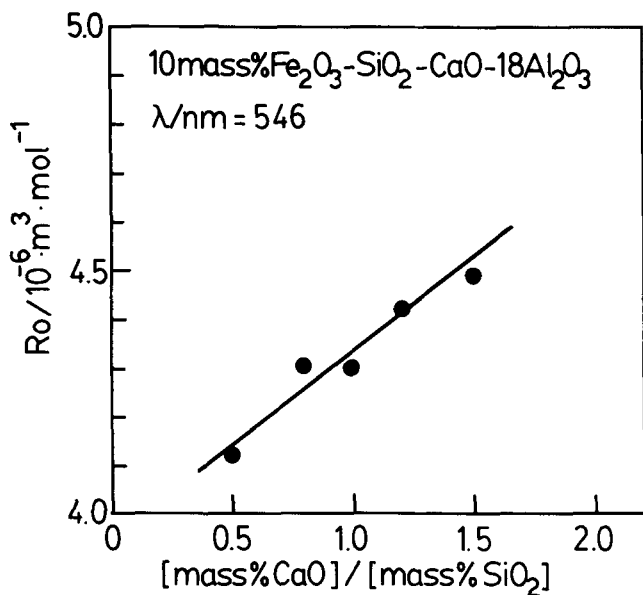


Fig. 9—Relation between the ionic refraction of oxygen, R_o , and the basicity of $[\text{CaO}]/[\text{SiO}_2]$.

C. Dependence of Absorption Coefficient on Basicity

The decrease of basicity of slags results in the increase of absorption coefficient in the near-infrared region and the shift of the absorption edge by the charge transfer band to shorter wavelength, as shown in Figure 7.

The optical absorption in the 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

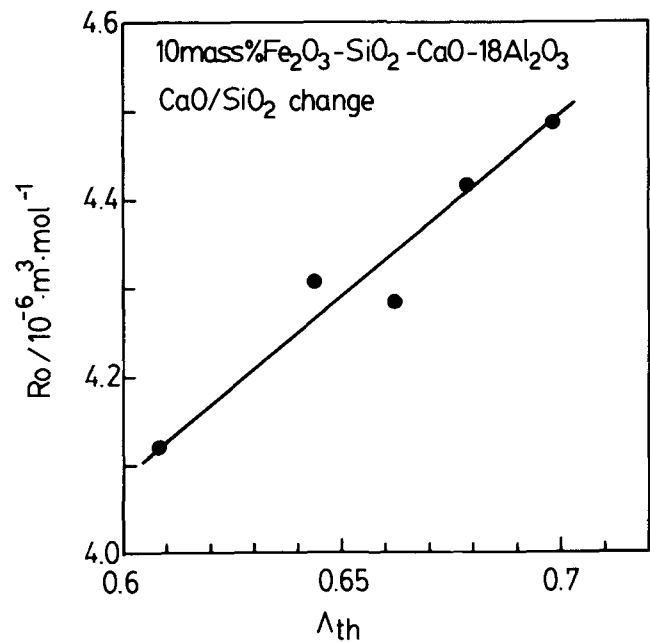


Fig. 10—Relation between the ionic refraction of oxygen, R_o , and the theoretical optical basicity, Λ_{th} .

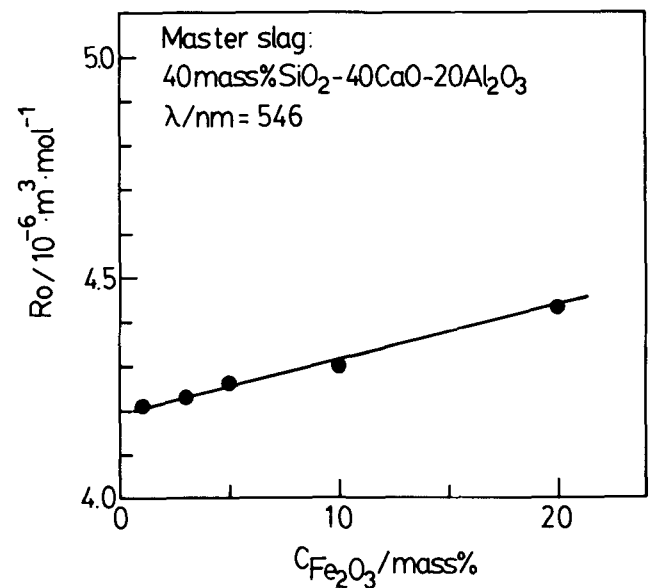


Fig. 11—Relation between the ionic refraction of oxygen, R_o , and the Fe_2O_3 concentration, $C_{\text{Fe}_2\text{O}_3}$.

considered to be a reason for the increase of absorption coefficient in the near-infrared region with decreasing basicity.

On the contrary, slags with lower basicity have less ionic refraction of oxygen, as shown in Figure 9. This means that O^{2-} in slags with lower basicity has smaller electron-donation activity. Since O^{2-} with smaller electron-donation activity releases electron less easily, 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 the slags with lower basicity.

D. 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 Figure 8. This behavior can be explained on the basis of the electron-donation activity of oxygen, too. Figure 11 has shown that slags with higher Fe_2O_3 concentration possess larger ionic refraction of oxygen, *i.e.*, larger electron-donation activity of oxygen. Therefore, it is 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.

V. CONCLUSIONS

The 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 $[\text{CaO}]/[\text{SiO}_2]$ and the Fe_2O_3 concentration. The refractive index was measured by an ellipsometer at 546 nm, and the absorption coefficient was determined from transmittance measured by a spectrophotometer in the wavelength range of 350 to 1000 nm. The refractive index in 10 mass pct Fe_2O_3 - SiO_2 - CaO -18 Al_2O_3 slags increased from 1.62 to 1.7 with increasing the basicity of $[\text{CaO}]/[\text{SiO}_2]$ from 0.5 to 1.5. The refractive index of master slags of 40 mass pct SiO_2 -40 CaO -20 Al_2O_3 was increased from 1.62 to 1.72 by the addition of Fe_2O_3 from 1 to 2 mass pct.

On the contrary, the absorption coefficients of 10 mass pct Fe_2O_3 - SiO_2 - CaO -18 Al_2O_3 slags were 5000 to 20,000 m^{-1} in the measured wavelength range and increased in the near-infrared region with decreasing the basicity of $[\text{CaO}]/[\text{SiO}_2]$. The absorption edge by charge transfer band was shifted to shorter wavelength by the decrease of the basicity. With increasing Fe_2O_3 concentration from 1 to 10 mass pct, the average absorption coefficient of master slags of 40 mass pct SiO_2 -40 CaO -

20 Al_2O_3 was monotonously increased from 500 to 10,000 m^{-1} in the measured wavelength range and the absorption edge by charge transfer was shifted to longer wavelength. 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.

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REFERENCES

1. O.V. Mazurin, M.V. Streltsina, and T.P. Shvaiko-Shvaikovskaya: *Handbook of Glass Data, Part A*, Elsevier, Amsterdam, 1983.
2. N. Iwamoto, Y. Makino, and S. Kusahara: *J. Non-Crystall. Solids*, 1984, vol. 68, pp. 379-88.
3. N. Iwamoto, Y. Makino, and S. Kusahara: *J. Non-Crystall. Solids*, 1984, vol. 68, pp. 389-97.
4. F.J. Grove and P.E. Jellyman: *J. Soc. Glass Technol.*, 1955, vol. 39, pp. 3-15.
5. F.J. Grove: *J. Am. Ceram. Soc.*, 1961, vol. 44, pp. 317-21.
6. F.N. Steele and R.W. Douglas: *Phys. Chem. Glasses*, 1965, vol. 6, pp. 246-52.
7. M. Coenen: *Glastech. Ber.*, 1968, vol. 41, pp. 1-10.
8. T. Ito and K.S. Goto: *Tetsu-to-Hagané*, 1974, vol. 60, pp. 184-91.
9. H. Alan Fine, T. Engh, and John F. Elliott: *Metall. Trans. B*, 1976, vol. 7B, pp. 277-85.
10. E.S. Larsen and H. Berman: *The Microscopical Determination of Nonopaque Minerals*, 2nd ed., U.S. Geological Survey Bull. 848, U.S. Government Printing Office, Washington, DC, 1934, pp. 30-32.
11. A.N. Winchell and H. Winchell: *The Microscopical Characters of Artificial Inorganic Solid Substances*, Academic Press, New York, NY, 1964.
12. E. Kordes: *Z. Phys. Chem.*, 1939, B44, pp. 249-60.
13. K. Fajans and G. Joos: *Z. Physik.*, 1924, vol. 23, pp. 1-46.
14. J.A. Duffy: *J. Non-Crystall. Solids*, 1986, vol. 86, pp. 149-60.
15. T. Nakamura, Y. Ueda, and J.M. Toguri: *J. Jpn. Inst. Met.*, 1986, vol. 50, pp. 456-61.