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Author(s)	Iwamoto, Nobuya; Makino, Yukio; Endo, Shigeki
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ESR Studies on Cd^+ Centers in Alkali-silicate Slag†

Nobuya IWAMOTO*, Yukio MAKINO** and Shigeki ENDO***

KEY WORDS: (Silicate Slag) (Basicity) (Cd^+ Center) (Electron Spin Resonance)

In the welding processes using flux, slags play various important roles to improve the properties of weld metals. The roles of slags, especially their chemical roles are closely related to the structure of slags including their basicity. Therefore, the determination of basicity is very significant to improve the properties of weld metals. Untill now, various basicities have been proposed from various standpoints.[1),2)] In this study, the state of Cd^+ centers in alkali-silicate slags was investigated using electron spin resonance (ESR) spectroscopy in order to clarify the state of oxygens in these slags and examine whether or not the s-character of the unpaired electron on the 5s orbital of Cd^+ can be connected with the basicity of these slags.

Specimen slags were prepared from reagent grade Li_2CO_3, Na_2CO_3, K_2CO_3, SiO_2 and CdO. The initial content of CdO was fixed to be 1 mol%. These reagents were weighed in a desired ratio and mixed in an agate mortar and pestle using acetone as immersion liquid. After dried well, the mixed reagents were melted for 1–3 h in platinum or 20% rhodium-platinum crucibles at the temperatures 100°C higher than their liquidus temperatures. Crushed spectrosil was used for producing silica glass doped CdO. After cooling, these slags were irradiated by γ-rays from ^{60}Co for 2 h at the rate of 2×10^5 r/h at room temperature. The

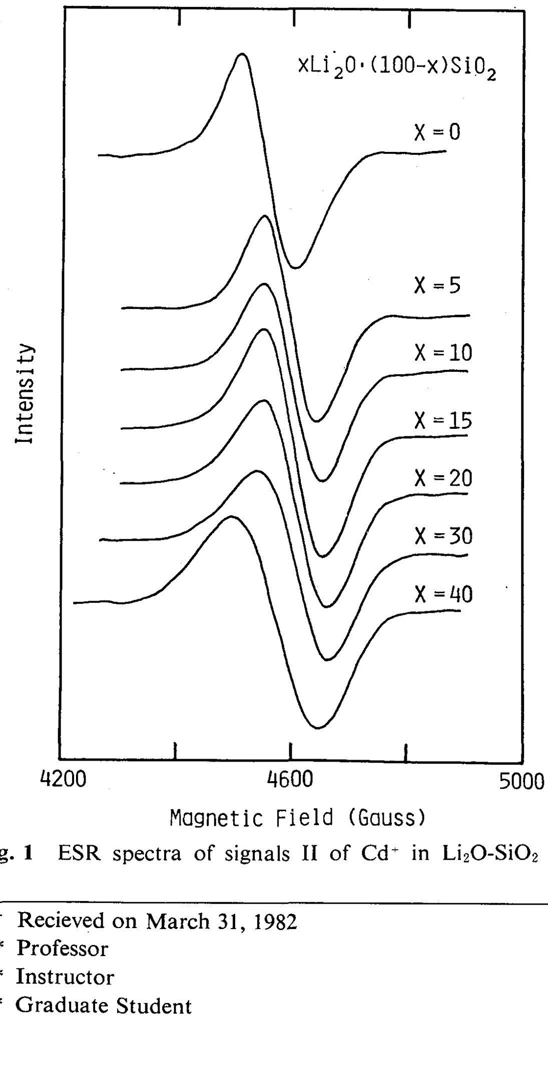

Fig. 1 ESR spectra of signals II of Cd^+ in Li_2O-SiO_2 slags.

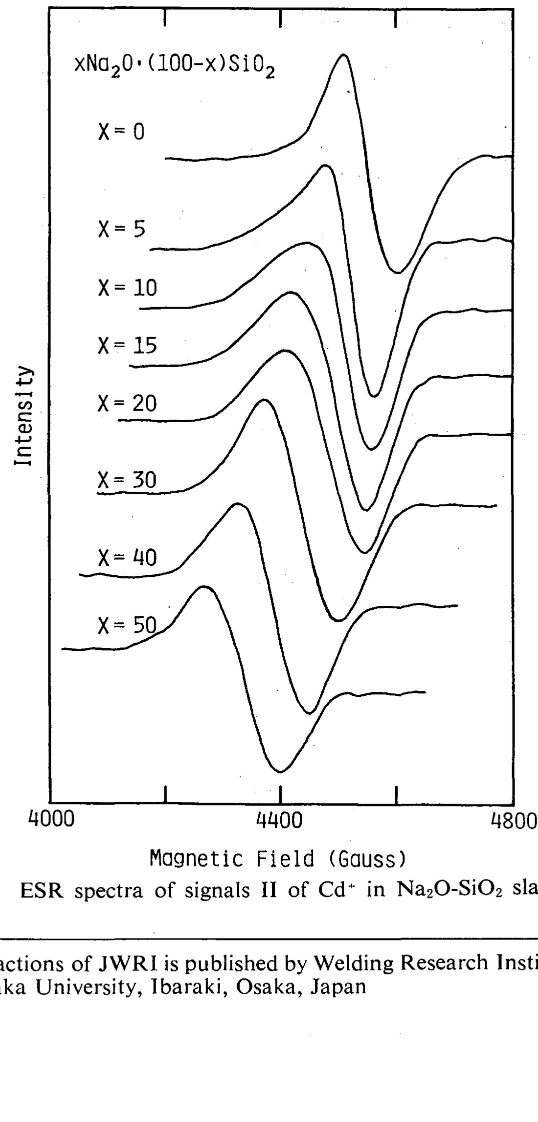

Fig. 2 ESR spectra of signals II of Cd^+ in Na_2O-SiO_2 slags.

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* Professor
** Instructor
*** Graduate Student

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ESR spectra of radiation-produced Cd^+ centers were measured using a X-band spectrometer (Varian E-109) with 100 kHz field modulation at room temperature.

ESR absorptions were observed near 3400 G (signals I) and near 4500 G (signals II). Signals II in Li_2O-SiO_2, Na_2O-SiO_2 and K_2O-SiO_2 slags are shown in **Figs. 1, 2** and **3**. Signals I are due to the zero spin nuclei and signals II are due to the other nuclei with spin $I=1/2$ (^{111}Cd, natural abundance=12.86% and ^{113}Cd, 12.34%).[3),4)] In Li_2O-SiO_2, Na_2O-SiO_2 and K_2O-SiO_2 slags, the conjugate absorption of signal II was not observed.

The g-values of signals I are determined by the following spin Hamiltonian:

$$\mathcal{H}=g\beta HS \tag{1}$$

When g tensors are approximated to scalars, g-values can be calculated from the following equation.

$$\mathcal{H}=\frac{h\nu}{g\beta} \tag{2}$$

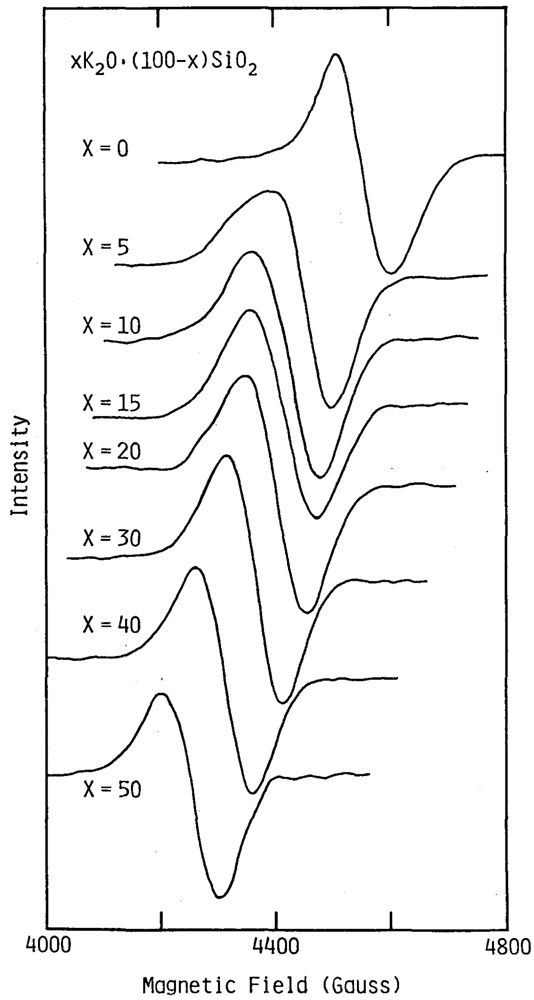

Fig. 3 ESR spectra of signals II of Cd^+ in K_2O-SiO_2 slags.

Signals II are interpreted by the spin Hamiltonian:

$$\mathcal{H}=g\beta HS+AIS \tag{3}$$

where A is a hyperfine constant. When g and A tensors are approximated to scalars, the solutions of eq. (3) are given by Breit-Rabi equation.[4)-6)] Hence, hyperfine constants can be calculated from the following equation.

$$H=\frac{2h\nu}{g\beta}\,\frac{A+h\nu}{A+2h\nu} \tag{4}$$

Because hyperfine constants have linear relation to the densities of s-electron ($|\psi(0)|^2$), the s-characters of Cd^+ can be expressed by the ratio of A to A_{free}.[7)] The s-characters of Cd^+ centers in slkali-silicate slags are shown in **Fig. 4**.

As shown in Fig. 4, the s-character in Na_2O-SiO_2 and K_2O-SiO_2 slags decreases with the increase of the alkali-oxide content. The dependence of the s-character in these slags upon alkali-oxide content is similar to that of the ionic refractivity of oxygen (R_o^{ex}).[8)] The correlation between the s-character and the ionic refractivity of oxygen is shown in **Fig. 5**.

In Li_2O-SiO_2 slags, on the other hand, the dependence of the s-character upon the alkali-oxide content

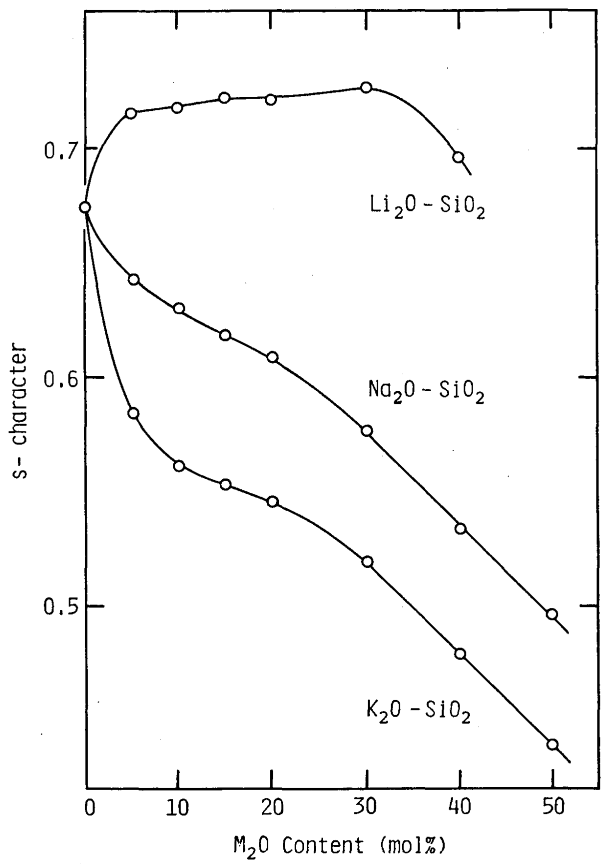

Fig. 4 The s-characters of Cd^+ in alkali-silicate (M_2O-SiO_2) slags.

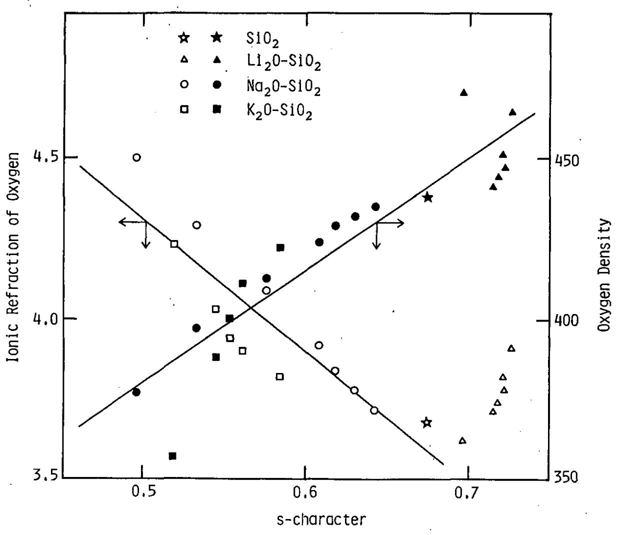

Fig. 5 The correlation of the s-character with the ionic refractivity of oxygen and oxygen density.

is converse to that in Na_2O-SiO_2 and K_2O-SiO_2 slags. Thus, it is easily expected that the s-character in Li_2O-SiO_2 slags can not be related to the average state of polarized oxygen.

Subsequently, the correlation between the s-character and oxygen density[9] is tried out in order to examine whether or not the s-character can be connected with the packing behavior of oxygen in slags. As shown in Fig. 5, a good correlation between the s-character and oxygen density is obtained. However, it is easily observed that the s-character is not linearly correlate to oxygen density. Thus, it is difficult to relate the s-character with both the polarization and the packing behavior of oxygen in slags. In further investigation, it is desired to elucidate what property of slags the s-character reflects.

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