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Local structural analysis of Fe and Mn in steel-making slag

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1 Introduction

Characteristics of molten slag, such as viscosity and wettability are affected by its silicate network structure. Basicity, CaO/SiO_2 (mass ratio) is generally used as a simple index for slag characteristics. Local structure of silicate is affected by additive cations. Some cation species, which can be tetrahedrally coordinated by oxygen atoms play as the network former and substitute Si in the SiO_4 units in the silicate network. others, which are coordinated by more than five oxygen plays as network modifier. Since steel-making slag contains various cation species other than Ca, *e.g.,* Mn, Al etc., the basicity should be described as [Network modifier / Network former] strictly. In this study, local structure of each cation in steel-making slag was investigated by XANES spectroscopy, to judge whether these elements are the network former or the modifier.

2 Experiment

Steel-making slag samples were taken from the test converter. Part of chemical analysis results of the sample were shown in Table 1. Reagent grade α-Fe_2O_3, Fe_3O_4, FeO and MnO, MnO_2, Mn_2O_3, Mn_3O_4 were used as references. Each sample and reference was powdered with an agate mortar and pestle then mixed with hexagonal boron nitride (BN) powder and hand pressed into a tablet with 7mm-thick in diameter and 2-3mm in thickness so as to $\Delta\mu t$ at the target absorption edge become nearly equal 1.

Fe *K*-edge and Mn *K*-edge XAFS and XANES measurements were carried out at the 9A beam line in Institute of Materials Structure Science, High Energy Accelerator Research Organization (IMSS, KEK). All the measurements were made in air at room temperature with the transmission mode. Incident X-ray was monochromated with a Si(111) double-crystal monochromator, and high harmonics were eliminated by detuning the monochromator as the primary X-ray intensity become 70% of that at full tuned. The energy resolution was about 0.4 eV. The intensities of incident and transmitted X-rays were measured with a 170-mm-long and a 310-mm-long ion chambers those were filled with 100% N_2 gas. The X-ray energy was calibrated by setting the first inflection of the Fe *K*-edge for an iron metal foil to 7.112 keV.

The EXAFS date analyses were performed using REX2000 ver2.5.6 [2]. The backgrounds of XAFS spectra in the pre-edge and post-edge regions were removed by a Victreen function and a cubic spline function. The environmental radial distribution functions (RDF) around Fe and Mn were obtained by Fourier transformation of the background removed XAFS spectra in the range $20 \leqq k \leqq 105\ \mathrm{nm}^{-1}$.

Table 1: Chemical composition of sample (mass%)

Sample	Total Fe	MnO	SiO_2	CaO	C/S
Slag A	12.3	12.4	13.7	42.9	3.1

3 Results and Discussion

Figure 1 shows normalized Fe *K*-edge XANES spectra ($\Delta\mu t$=1) of Slag A and references. Although, peak position of pre-edge and white line for slag A are close to those of $Fe^{II}O$, peak intensity of pre-edge of sample A is stronger than that of FeO. Figure 2 shows environmental radial distribution function (RDF) around Fe (RDF_{Fe}) obtained by Fourier transformation of Fe *K*-edge XAFS spectra. The RDF_{Fe} of slag A shows both Fe^{II}-O correlation in Fe^{II} oxides and Fe-Fe correlations in metal Fe. This results indicate that slag samples contain both Fe^{II} and Fe^{0}.

$Fe^0/(Fe^0 + Fe^{II})$ ratio of slag A is 8, which calculated by the least-square fitting of XANES spectra as sums up of those of metal Fe and $Fe^{II}O$. Considering oxidation reaction occurred in the converter during the oxygen blowing process, impurity elements in molten iron are oxidized and floated into molten slag layer. Also, iron would be partially oxidized and molten iron particle may be included in slag samples in this study.

Figure 3 shows normalized XANES spectra ($\Delta\mu t$=1) of Slag A and references. Pre-edge position and oscillation features of slag A were close to $Mn^{II}O$. Figure 4 shows RDF around Mn (RDF_{Mn}) obtained by Fourier transformation of Mn K-XAFS spectra. The RDF of slag A show Mn^{II}-O and Mn-Mn correlations correspond to Mn oxides, and Mn-Mn correlation correspond to metal Mn was not observed.

Comparing energy position of pre-edge of reference Mn oxides, pre-edge position of slag A was observed at energy correspond to Mn^{II}, and the absorption edge was between MnO and Mn_3O_4. Thus Mn in steel making slag A is Mn^{II} and may be octahedrally coordinated and play as the network modifier.

Both of Fe^{II} and Mn^{II} cations may work as network modifiers in the silicate network. Thus, in case of properties of slag was discussed with ratio of network modifier and network former cations, basicity of slag A can be expressed as molar ratio; $(Ca+Fe^{II}+Mn^{II})/Si$.

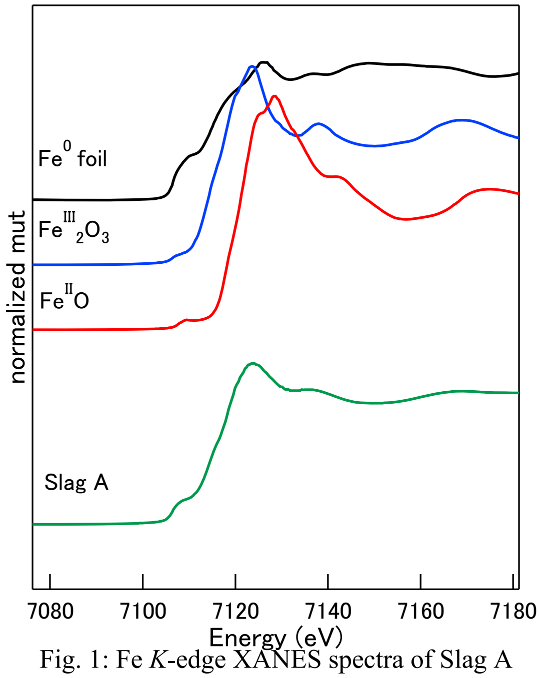

Fig. 1: Fe *K*-edge XANES spectra of Slag A

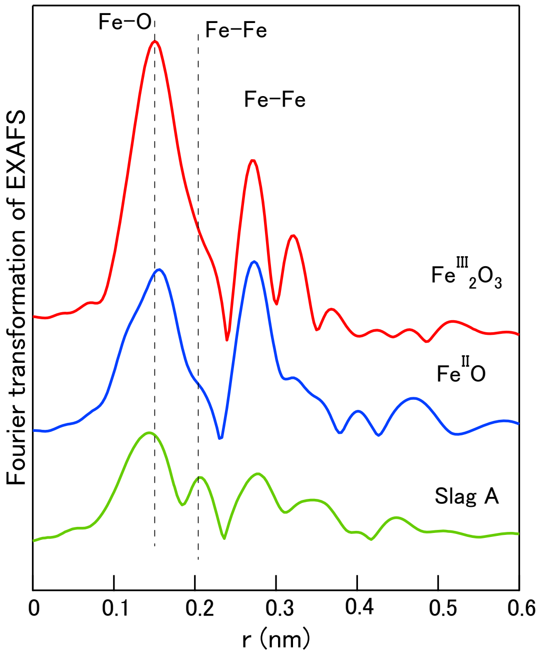

Fig.2: Radial distribution function around Fe obtained from Fourier transformation of EXAFS spectra.

Steel-making slag contains various cation species to some extent, and EXAFS analysis has been shown one of powerful method for analyze each cation species. Further study will be conducted to clarify process dependence of local structure of cation species in steel-making slag.

References
[1] E. Verein Deutscher, "Slag atlas 2nd ed.", Verlag Stahleisen, 1995.
[2]T. Taguchi, *et al.*, Phisica Scripta, **T115**, 205-206, 2005..

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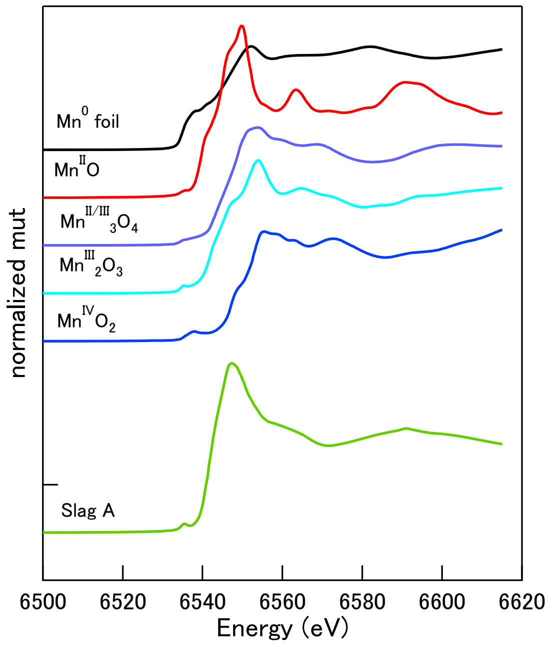

Fig. 3: Mn *K*-edge XANES spectra of Slag

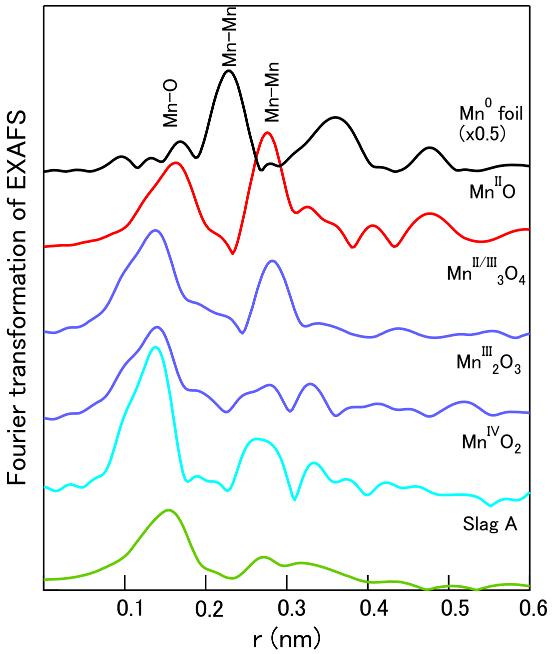

Fig. 4: Radial distribution function around Mn obtained from Fourier transformation of EXAFS