

XAFS analysis of corroded metal surfaces with molten salts by conversion-electron-yield method

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We have measured XAFS spectra of metal surfaces corroded with melting salt (NaCl, KCl, and Na₂SO₄). Steel samples used were S45C, SCM435, SUS310S, and SUS304. We measured the Fe K-edge XAFS spectra for all samples and the Ni K-edge for SUS310S and SUS304 samples before and after the corrosion. The XANES spectra of samples before the corrosion show metallic structure because surface oxide thickness is thinner than probing depth with a conversion yield XAFS method. Each result of these XAFS spectra gives good agreements with the FEFF calculation in the assumption of bcc and/or fcc structure. The Fe K-edge spectra of steel samples except SUS310S after corroded treatment show existence bonding between Fe and another light element although the spectra of SUS310S samples before and after corroded treatment are much the same.

Keywords: metal, molten salts, corrosion.

Introduction

It is recently expected to operate at a higher temperature for suppression of dioxins in operating refuse incinerating power plants. However, the accelerated corrosion of structural steel is a major problem in the development of the plants. This is because passivation oxides dissolve in melting eutectic mixture salt, which is included in fly ash. In order to develop new material for such plants, it is essential to collect basic data of corroded steel surface. Despite the large number of investigations (Shardakov et. al, 1999; Okuyama et. al, 1988), there has not been a systematic microscopic study of surface structure corroded with molten salt. Therefore, we study steel surface structure corroded with molten salt by using XAFS technique. XAFS clarifies not only chemical states but also local structures of corroded surface. In our study, we used conversion electron yield method as XAFS measurement technique. This method is especially valuable for analyses of chemical system where conventional XAFS methods are not applicable. We have measured XAFS spectra of steel surfaces corroded with NaCl, KCl and Na₂SO₄ mixture that is adopted as a model of salt in fly ash. We report and discuss the results of XAFS measurements and the corrosion mechanism with molten salt.

Experimental

The chemical composition of the steel samples investigated in this study is given in Table 1. All steel sample surfaces were polishing with emery paper. To prepare the corroded samples for our measurements, we immersed the specimens in melting salt for a few seconds at a temperature 973K under an atmosphere. Equal molarity of NaCl, KCl and Na₂SO₄ powder were uniformly mixed to blended salt and melted in alumina crucibles in an electric furnace at 973K. Blended salt on the specimen was removed with filter paper for XAFS measurements after it got cool.

A conversion electron yield method was used for XAFS measurements. When a sample placed in atmospheric He gas is irradiated with X-ray photons, Auger electrons are ejected from the sample surface in proportion to the photon absorption, and there ionize He atoms. The electrons or He ions current so generated can be used for XAFS measurement. The probing depth of this method depends on Auger electron mean free path. We can estimate the probing depth at about a few 10nm. The details of our conversion electron method has been described elsewhere (Yanase et. al, 1999).

All XAFS measurements were performed at the beamline BL01B1 SPring-8 in Hyogo Prefecture, Japan. The X-ray beam was monochromatized by using Si(111) double crystal monochromators. The higher harmonics were rejected by using a rhodium coated mirror system. The sample size of 10mm x 10mm x 1mm was placed on the sample holder with conductive carbon tape. The X-ray incidence angle to the sample was fixed at 25 degree. The beam intensity was monitored with a nitrogen gas ionization chamber of 5.5 cm in path length. We measured the Fe K-edge XAFS spectra for all samples and the Ni K-edge for SUS310S and SUS304 samples before and after the corrosion treatment. The EXAFS analysis procedure used in this work has been described elsewhere (Sakane et. al, 1993).

Results and Discussion

S45C and SCM435, which are ferrite steels, have bcc structure of Fe atoms. On the other hand, SUS304 and SUS310S have fcc structure because these steels are austenite stainless steel. Therefore, we calculated k³-weighted EXAFS spectra, k³χ(k), by using FEFF7.02 code in the assumption of bcc or fcc structure. The k³χ(k) spectra obtained by our calculated and experimental results at Fe K-edge are shown in Fig. 1. The k³χ(k) spectrum of SUS310S gives good agreement with the FEFF calculation. The spectrum at Ni K-edge as shown in Figure 2 also gives good agreement. This result shows that the thickness of oxide layer on the surface is sufficiently thinner than probing depth with a conversion yield XAFS method. The result of SUS304 is different although it is the same austenite stainless.

Table 1
Chemical composition of steel used (wt.%)

Composition	Steel			
	SUS304	SUS310S	SCM435	S45C
Fe	Bal.	Bal.	Bal.	Bal.
C	≤ 0.08	≤ 0.08	0.42-0.48	0.33-0.38
Si	≤ 1.00	≤ 1.50	0.15-0.35	0.15-0.35
Mn	≤ 2.00	≤ 2.00	0.60-0.90	0.60-0.85
P	≤ 0.045	≤ 0.045	≤ 0.030	≤ 0.030
S	≤ 0.030	≤ 0.030	≤ 0.035	≤ 0.030
Ni	8.00-10.50	19.00-22.00	≤ 0.20	≤ 0.25
Cr	18.00-20.00	24.00-26.00	≤ 0.20	0.90-1.20
			Cu ≤ 0.30	Cu ≤ 0.30
				Mo 0.15-0.30

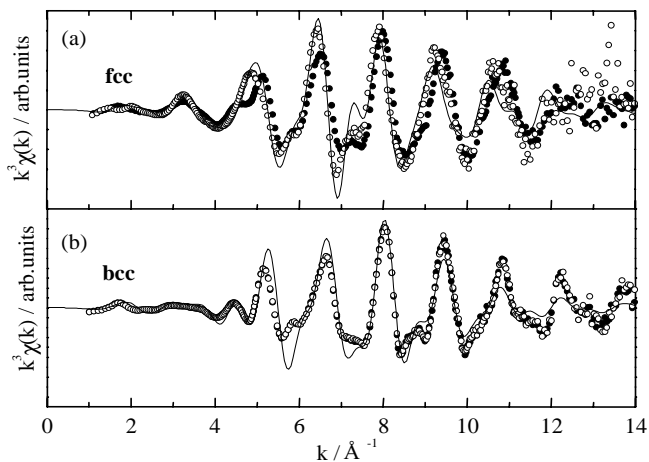


Figure 1
 $k^3\chi(k)$ spectra at Fe K-edge. (a) Open circle, close circle and solid line show the spectra of SUS304, SUS310S and FEFF calculation, respectively. (b) Open circle, close circle and solid line show the spectra of S45C, SCM435 and FEFF calculation, respectively.

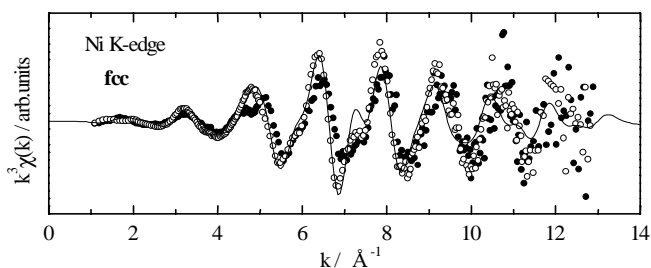


Figure 2
 $k^3\chi(k)$ spectra at Ni K-edge. Open circle, close circle and solid line show the spectra of SUS304, SUS310S and FEFF calculation, respectively.

Each of SUS304 spectra at Fe and Ni K-edge includes oscillation structure of bcc FEFF calculation spectra shown in Fig. 1(b) for Fe K-edge and Fig. 2 for Ni K-edge, respectively. This shows that ferrite phase is induced in the surface due to the polishing preparation because the austenite phase in SUS304 is unstable at room temperature owing to smaller amount of Cr and Ni than SUS310S. The $k^3\chi(k)$ experimental spectra of S45C and SCM435 are much the same. A minor difference between experimental and calculated spectra suggests that the surface contains iron oxide layer, which is thinner than probing depth.

The normalized Fe K-edge XANES spectra before and after corrosion are shown in Fig. 3. The spectra before corrosion treatment show metallic structure. This corresponds with the discussion of $k^3\chi(k)$ spectra. The XANES spectra of three steels except SUS310S have a similarity in the shape. This suggests the same corrosion behaviour of Fe element in these three steels. To investigate the details of corrosion surface reaction, we measured Ni K-edge XAFS spectra of SUS304 and SUS310S containing Ni element. The Ni K-edge XANES spectra are shown in Fig. 4. Each XANES spectrum before the corrosion nearly corresponds with the one after. This result shows that Ni element in SUS304 and SUS310S hardly reacts in molten salt our used as a model.

We calculated Fourier transformation of $k^3\chi(k)$ to discuss the detail of local structure. Figure 5 and figure 6 show the calculation results of spectra at Fe and Ni K-edge, respectively. The spectrum of SCM435 after the corrosion has the same

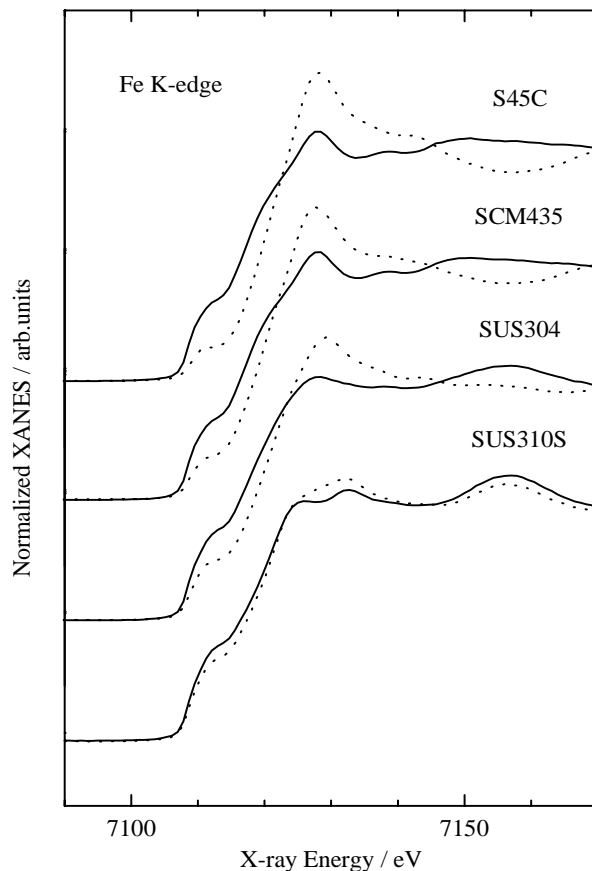


Figure 3
 The XANES spectra at Fe K-edge. Solid and dotted lines show before and after corrosion treatment, respectively.

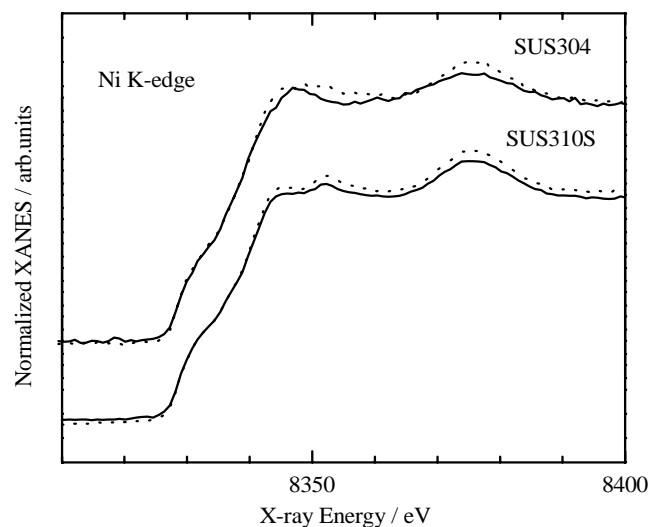
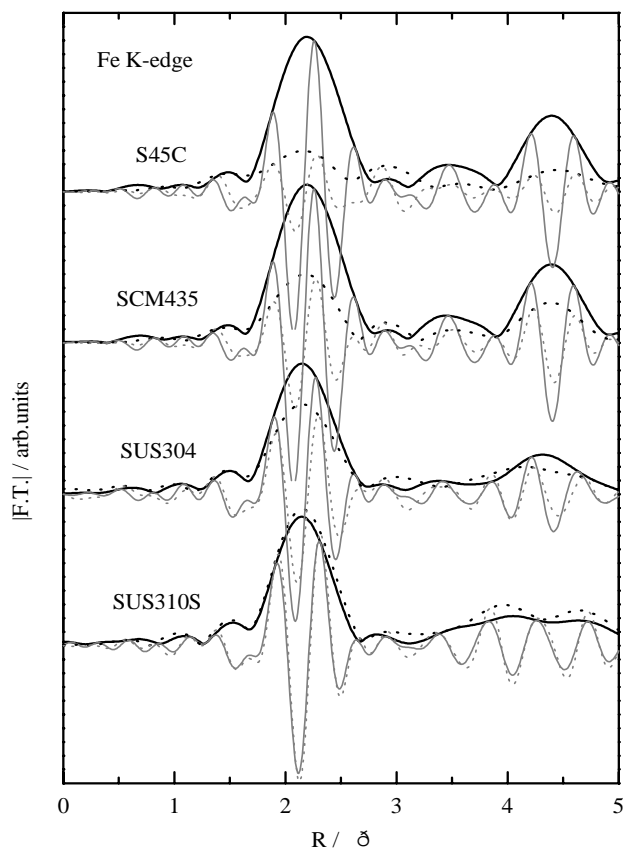


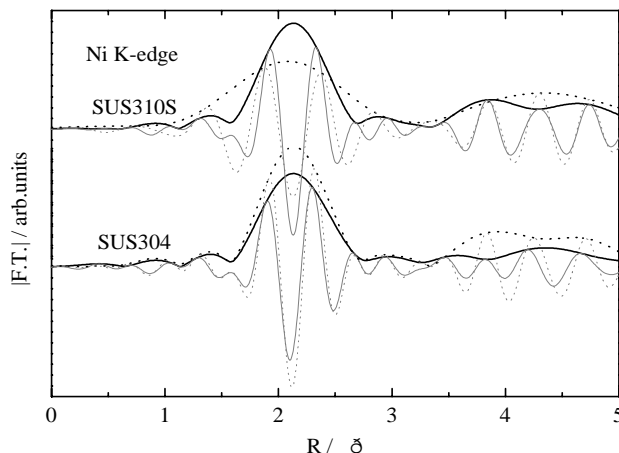
Figure 4
 Ni K-edge XANES spectra of SUS304 and SUS310S. Solid and dotted lines show before and after corrosion treatment, respectively.


Figure 5

Fourier transformation of $k^3\chi(k)$ at Fe K-edge. Solid and dotted lines show before and after corrosion treatment. Black and grey lines show the absolute and imaginary profiles, respectively. Units for R: Å.

structure as the one of S45C has. The spectrum of SUS304 after the corrosion also has the same although the spectrum before the corrosion has the difference structure. This indicates that the behaviour of corrosion reaction in these three steels is the same. It is considered that the reduction of 1st peak intensity in these spectra suggests the presence of bonds between Fe and a light element, for example, Fe-O, Fe-Cl and/or Fe-S bonds.

The behaviour of corrosion reaction in SUS310S surface is different from SUS304, which is the same austenite stainless steel. The spectrum of SUS304 at Fe K-edge before the corrosion indicates the structure mixed with bcc and fcc; it is already confirmed in the discussion of $k^3\chi(k)$. The $k^3\chi(k)$ spectrum of SUS310S at Fe K-edge also shows the structure containing bcc, which is not clarified due to a small amount before Fourier transformation calculation. This small amount is because austenite phase in SUS310S is more stable than SUS304. In the case of SUS310S, however, the $k^3\chi(k)$ structure after the corrosion is close to pure fcc. In addition to this, the structure of SUS304 at Ni K-edge after the corrosion is close to fcc phase. These results suggest that the bcc phase induced by the polishing process dissolves in melting salt. Although the $k^3\chi(k)$ spectrum of


Figure 6

Fourier transformation of $k^3\chi(k)$ at Ni K-edge. Solid and dotted lines show before and after corrosion treatment. Black and grey lines show the absolute and imaginary profiles, respectively. Units for R: Å.

SUS310S at Ni K-edge after the corrosion does not have good resolution experimentally, it is concluded from the result of XANES spectra that the surface structure of SUS310S after and before the corrosion is the same. When arranging the experimental results, fcc phase containing a large amount of Ni element is relatively stable in molten salt.

Conclusion

We measured XAFS spectra of 4 steels before and after the corrosion treatment by using conversion electron yield method. We could confirm the validity of this method for study of such a surface corrosion reaction. The results of Fe K-edge XAFS of corroded except SUS310S suggest existence bonding between Fe and another lighter element owing to the corrosion reaction. According to the discussion about the result of two stainless steel, the two samples which have slightly different Ni and Cr compositions display different spectral features suggesting that small difference in their contents noticeably influences corrosion reaction of Fe element in molten salt.

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