Quantitative Analysis of Nb in Steel Utilizing XRF-yield XAFS Edge Jump

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X-ray fluorescence (XRF) yield x-ray absorption fine structures (XAFS) have been investigated in terms of quantitative analysis for steel sheets containing 31–2100 ppm of Nb. Nb concentrations in the samples were determined with high accuracy from the height of the K-edge jump. The detection limit was estimated down to the single digit ppm range. The combination of this technique with the conventional extended x-ray absorption fine structure (EXAFS) analysis for an identical XAFS spectrum provides both quantity and chemical state information of trace elements in the given volume of steel samples.

KEY WORDS: XAFS; XRF; EXAFS; synchrotron radiation; quantitative analysis; chemical state analysis; micro alloy; trace elements; Nb; segregation.

1. Introduction

Micro-alloying elements added to the steel matrix dramatically change properties of steel products such as strength and corrosion resistance. For example, nanometer-sized precipitates, such as carbides formed by various elements, effectively improve the strength of steel.¹⁾ It is therefore important to understand the roles these elements have on the properties of steel for designing micro-alloyed steel products of superior performance. The fundamental information about the micro-alloying elements are their quantity and chemical state, although size and distribution of precipitates are also important parameters regarding the strength of the steel if the elements form small precipitates.²⁾

XAFS is a powerful tool for clarifying chemical states and local structures of specific elements in steel.^{3–6)} X-ray fluorescence (XRF) yield XAFS techniques have the advantage of high sensitivity to trace elements. This technique is especially valuable for elements substituting matrix atoms and forming atomic level clusters or nanometer-sized precipitates. These are difficult to detect by conventional high-resolution transmission microscopy (TEM). Another advantage of XAFS analysis is that chemical states are nondestructively investigated for rather large averaged volumes (typically up to several mm² in area and tens of μm in depth) of samples.

Conventionally, quantities of added trace elements are determined by chemical analysis. When quantity and chemical state are studied by chemical analysis and XAFS, respectively, for micro-alloyed elements, one latent problem

is the inconsistency between their results caused by the difference in the measured volume for each technique. This is fatal especially for inhomogeneous or non-uniform samples. Compilation of the different information is required for identical volumes of such samples.

A study has reported the potential of XAFS as a quantitative analysis method for Cl and Br in environmental matters.⁷⁾ The concentration of Cl was successfully determined in the concentration range from single digit ppm to 1400 ppm. The authors pointed out the advantage of the simultaneous determination of quantity and chemical state for Cl and Br. Their results clearly demonstrate the quantitative ability of the XRF-yield XAFS. However, there is no such report relating to research with metals. In this paper we have investigated the quantitative factor of the XRF-yield XAFS for trace elements in steel. The XAFS spectra have been recorded for small amounts of Nb added to steel and used for the quantitative and chemical state analysis.

2. Experiment

15 low-alloyed steel samples containing 31–2100 ppm Nb were collected. The chemical composition of the base steels differed among samples. The Nb concentrations were determined by conventional chemical analysis. A sample containing 2100 ppm Nb was prepared as a reference for Nb which is substitutional in the bcc-Fe matrix by water quench from 1200°C. Nb atoms in the other samples were partly precipitated due to different treatment. All samples were cut into small pieces and mirror-polished for XAFS measurement. The XAFS spectrum for commercial NbC powder was also measured in the transmission mode. The powder

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was mixed with BN and pelletized.

The XAFS experiment was carried out at beam line BL27B, Photon Factory (2.5 GeV, Tsukuba, Japan) with a two-crystal Si (111) monochromator. The Nb-K edge XAFS spectra were recorded in the x-ray fluorescence mode using a 7-element solid-state detector. The detector window (Region of Interest; ROI) was set to the Nb-K α emission peak. A Zr filter ($\mu t=3$) was set at the front of the detector. The beam size of the incident x-ray was limited to 1 mm in height and 12 mm in width (16 mm for the sample with 31 ppm Nb) using a 4-dimension slit placed at the front of an ion chamber measuring the intensity of the incident x-ray. The dwell time was set at 4 sec/point and the spectra were measured by accumulation of from 1 to 3 cycles according to the Nb concentration. All samples were set in an identical position where the angles between sample surfaces and both incident x-ray and detector were 45 degrees. The analysis of the XAFS spectra was performed with a commercial software package (Rex 2000, Rigaku Corp.).

The edge jump determined by the difference between μ_0 ($h\nu$) and background μ_B ($h\nu$) corresponds to the net intensity of the Nb-K α emission peak excited by the x-ray with photon energy $h\nu$. Therefore, edge jump can be directly used to quantify the concentration of the target elements in the same manner as the net intensity in XRF analysis. Where μ_0 is an x-ray absorption curve for isolated atoms and is obtained by removing the EXAFS modulations caused by photoelectron interference from neighboring atoms.

The height of the Nb-K edge jump was evaluated as follows: 1) A smooth μ_0 ($h\nu$) curve was drawn using a cubic spline method. 2) A background curve μ_B ($h\nu$) above the Nb-K edge was estimated as that the difference between the μ_B ($h\nu$), which smoothly connects to the spectra below the edge region, and the μ_0 ($h\nu$) obeys the Victoreen equation as a function of wave length (photon energy $h\nu$).⁸⁾ 3) The height of the edge was determined by the difference between the μ_B ($h\nu$) and μ_0 ($h\nu$) at an identical photon energy region above the edge. In this study an average value between 19 050 eV and 19 150 eV was used. The background above the edge is estimated by an exertion from the μ ($h\nu$) curve below the edge to above the edge in the conventional method. However, this often fails for the XRF-yield mode XAFS spectra, due to the low intensity and abnormal shape of the background, and therefore Step 2) above is valuable.

3. Results

The Nb-K edge was clearly observed for all specimens using XRF-yield mode XAFS measurement. **Figure 1(a)** shows Nb-K edge XAFS spectra for the samples containing 31, 148, 450, and 2 100 ppm Nb. No Nb-K edge structure was observed for a standard specimen including no Nb (JSS1000-1) under the same experimental conditions. The height of the edge jump changes with Nb concentration. The spectrum for the steel with 2 100-ppm Nb shows typical EXAFS oscillations for solid solution elements in the bcc-Fe matrix. The spectral shape for the steel with 450-ppm Nb is actually broader than this. This shows that the chemical state of Nb in this sample differs from the solid solution in the bcc matrix. This difference was caused by differences in heat treatment between the samples and is unrelated to Nb

Fig. 1. (a) Nb-K edge XAFS spectra for the samples containing Nb of 31, 110, 500, and 2 100 ppm. I/I_0 scale is not normalized. (b) Normalized Nb-K edge XAFS spectra for the samples containing Nb of around 150 ppm (spectra a–c), Nb in the bcc-Fe matrix (spectrum d), and NbC (spectrum e).

concentration. The normalized XAFS spectra for the three samples containing approximately 150 ppm Nb are shown in Fig. 1(b) [spectra (a)–(c)]. The Nb-K XAFS spectra are different among these three samples. Spectrum (a) is similar to that for NbC [Spectrum (e)]. On the contrary, Spectrum (c) shows the characteristics of a spectrum for Nb atoms in the bcc-matrix [Spectrum (d)]. This shows that the fractions of precipitated Nb and dissolved Nb differ among samples although the Nb concentrations are in the same range.

Figure 2 shows the relationship between Nb concentration and Nb-K edge jump evaluated by the method mentioned in the previous section. In Fig. 2(a), there exists good correlation between them in the wide Nb concentration range from 31 to 2 100 ppm. The dashed line in the figure was obtained by least-square fit. The R^2 value of the line nears 1, which demonstrates that the Nb is quantified with high accuracy by Nb-K edge jump throughout such a wide concentration range. The expanded plot in the Nb concentration range of around 150 ppm is shown in Fig. 2(b). These samples belong to a series having almost the same chemical composition. A linear relationship is seen and a difference of less than 10 ppm is easily distinguished. This result suggests that higher quantitiveness is achieved when the chemical composition of matrices are similar among samples.

The fractions of precipitated and dissolved Nb were evaluated from the identical XAFS spectra used for the quantitative analysis. In this study, the fraction of Nb in the

Fig. 2. Relationship between Nb-K edge jump and Nb concentration determined by chemical analysis in a wide Nb concentration range (a) and in an Nb concentration of around 150 ppm (b). A line determined by a least squares fitting is shown with the equation and the R^2 value in Fig. (a).

bcc-matrix (x) was determined using the EXAFS analysis technique.⁶⁾ The average coordination number of Fe atoms around the dissolved Nb atoms was evaluated by a curve fitting for the inverse FT curves (k^3 -weighted) of the 1st and 2nd nearest neighbors. The ratio of the 1st and 2nd nearest neighbors was fixed to 8/6. A backscattering factor, a phase shift, and a Debye-Waller factor were derived from the analysis of the reference sample (2 100-ppm Nb) quenched from 1 200°C and fixed in the analysis of the other samples. The atomic fraction of Nb atoms in solution (x) in the bcc matrix was estimated from the coordination number assuming that the coordination number for the reference sample was 1. The fraction of precipitated Nb was determined as $1-x$. The concentration of precipitated Nb can be quantified by multiplying the factor $(1-x)$ by the Nb concentration determined using the calibration curve (Fig. 2(a)).

Recently, a simple and accurate analytical method for determining solid solution content of micro-alloying elements has been developed using the electrolytic extraction method.⁹⁾ We compared our results with those of this chemical analysis for the 11 samples having Nb concentrations of around 150 ppm. The results are shown in **Fig. 3**. There is good correlation ($R^2 = 0.912$) between the two methods for precipitated Nb of 30–120 ppm (corresponding to fractions of precipitated Nb between 22 and 84%). There are some points not following the 45-degree curve in the figure, however, these inconsistencies were caused by the differences in

Fig. 3. Relationship between concentrations of precipitated Nb estimated by XAFS analysis in this study and chemical analysis on samples including Nb of around 150 ppm.

estimated fractions of precipitated (dissolved) Nb, not in estimated Nb concentrations.

It should be emphasized that the method using XAFS is not destructive while chemical analysis is. However, we think that these two methods are complementary for inhomogeneous samples because chemical analysis provides overall average values while the XAFS provides analysis for selected local areas.

4. Discussion

The detection limit for Nb by our experimental setup was estimated from the XAFS spectrum for the 31-ppm Nb steel sample. The relationship between noise level (3σ) and the slope of the correlation curve (Fig. 2(a)) provided a detection limit of less than 3 ppm. This value is limited by the rather high noise smearing the edge jump of the spectra. Performance can be improved by increasing signal/noise (S/N) ratio making it possible to detect very weak edge jumps. In order to increase the S/N ratio, combinations of brighter synchrotron radiation sources and higher through-put x-ray detectors are advantageous. We consider that the detection limit and quantitative limit of XAFS might be better than XRF spectroscopy using solid state detectors because the former method uses many data points directly corresponding to the net intensity of the x-ray emission from target elements. This is valuable especially when the XRF peak cannot be identified due to superimposition from other x-ray emissions.

The method used in this study can be readily expanded to other metallic elements in steel or in other metallic matrices. An advantage of the method is that the quantity and chemical state of the target element are determined for identical sample volumes. In practice, samples are not always uniform or homogenous, due to segregation of elements during solidification and heat treatment, for example. Processing, such as welding and forming, may create areas where element concentrations and chemical states maybe altered from the original material. In such cases, chemical states and element concentrations should be evaluated at identical locations on each sample. The XAFS analysis mentioned here is a powerful technique in these situations.

Development of X-ray micro beams has seen progress this decade through the use of synchrotron radiation.^{10,11)} The combination of our techniques with a focused x-ray source certainly creates a novel microanalysis technique. One possible application is in the field of corrosion science. We have applied the XRF and XAFS to cross sectional analysis of the rust layer formed on a weathering steel sheet.¹²⁾ In that study, only major elements, iron and chromium, were analyzed. It is well known that trace elements such as Mo improve corrosion resistance. The micro-beam XRF yield XAFS can be applied to simultaneous determination of concentration and chemical states of trace elements in rust layers with high spatial resolutions.

5. Summary

We have investigated the quantitativity of the XRF-yield XAFS for Nb in steel. The results show that Nb can be quantified with high accuracy in the wide concentration range from 2 100 down to at least 31 ppm. The combination of the technique with conventional XAFS analysis provides information about quantity, chemical states, and local crystal structure from identical sample volumes. The technique can be applied to studies revealing inhomogeneous structures in steel and related materials.

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