Quantification of Nitrogen in Solution in Stainless Steels Using Parallel EELS

K. Yamada, K. Sato and C. B. Boothroyd[†]

Steel Research Centre, NKK Corporation, Kawasaki 210, Japan

The purpose of this work is to detect and quantify nitrogen which is dissolved in steels using parallel detection Electron Energy Loss Spectroscopy (PEELS). PEELS in the Transmission Electron Microscope (TEM) has a high detection efficiency and is potentially powerful for studying the behaviour of light elements in commercial steels with a high spatial resolution.

Type 316 stainless steels (SUS316) and high nitrogen austenitic stainless steels having a range of nitrogen (0.04–0.40 mass%) content were used. We also used a duplex stainless steel as a test specimen where partitioning of nitrogen between ferrite (α) and austenite (γ) phases was present. Typically nine spectra were recorded from the same area of the specimen and then were processed using the iterative averaging method described. This method efficiently removes the noise due to the channel gain variation in the parallel detection and allows the detection of small peaks. The intensity ratios of (I_N/I_{Cr}) or (I_N/I_{Fe}) are correlated with the atomic concentration ratios (C_N/C_{Cr}) or (C_N/C_{Fe}) where I and C denote the intensity and atomic concentration, respectively.

The measured intensity ratio and the concentration ratio have a good correlation and a common calibration curve is obtained regardless of the matrix composition which are different between type 316 and high nitrogen austenitic stainless steels. By using the calibration curve, the nitrogen content can be determined as 0.26 ± 0.04 mass% in the γ -phase of the duplex stainless steel, while that of α -phase is close to or below the detection limit of 0.04 mass%.

(Received October 16, 1991)

Keywords: nitrogen, parallel detection electron energy loss spectroscopy, transmission electron microscope, partitioning, calibration curve

I. Introduction

It is very important to detect light elements which are dissolved in commercial steels because they often have a dramatic effect on the steel's properties even when present in low concentrations. Solute nitrogen plays an important role in the stabilization of the austenitic phase in stainless steels⁽¹⁾. Moreover, nitrogen is intentionally added for economical reasons to improve the creep rupture strength and corrosion resistance in austenitic stainless steels. However, the function of nitrogen is still unclear in many ways mainly because of the lack of techniques to study low concentrations of nitrogen with a high spatial resolution.

Although EPMA (Electron Probe Micro Analysis) has been used for studying this problem⁽²⁾⁽³⁾, the spatial resolution is not high enough to detect partition behaviour of light elements in small areas. Electron Energy Loss Spectroscopy (EELS) in the Transmission Electron Microscope (TEM) is potentially powerful for detecting light elements from a small region. A theoretical estimate of the minimum detectable concentration (MDC) was as low as 0.2 at% for Boron in 50 nm-thick carbon⁽⁴⁾. More realistic values of MDC suggested by Liu and Brown⁽⁵⁾ for carbon and oxygen in iron were 3 and 6 at%, respec-

tively. The detection efficiency can be greatly improved by the use of a parallel detection EELS⁽⁶⁾ rather than a conventional serial detection system⁽⁶⁾. The acquisition of signals from the whole range of a spectrum is made possible by the use of a linear array of diodes in a parallel EELS. However, correcting the channel gain variation of the parallel detection system turns out to be essential for the detection of dilute atoms. We have already succeeded in detecting less than 0.1 mass% Boron in Ni₃Al alloy using the iterative averaging method⁽⁷⁾. The primary purpose of this work is to detect nitrogen which is dissolved in steels (0.04–0.40 mass%) reproducibly, and to obtain a calibration curve for quantification. In addition to this, various experimental difficulties in the estimation of peak intensities for quantification will be discussed.

II. Experimental

Table 1 shows the chemical composition of the samples which were used in the present work. Type 316 stainless steels (SUS 316) and high nitrogen austenitic stainless steels having a range of nitrogen content were used. We also used a duplex stainless steel as a test specimen where partitioning of nitrogen between ferrite (α) and austenite (γ) phases was present. The average chemical composition of this steel is shown in Table 2. TEM specimens were prepared by electropolishing using a 20% perchloric acid/ethanol solution.

Our spectra were obtained using a Gatan parallel EELS system (Model 666) controlled by a Macintosh II

[†] Present address: Department of Materials Science and Metallurgy, University of Cambridge, Pembroke St., Cambridge, CB2, 3QZ, UK.

Table 1 Chemical composition of stainless steels used for quantitative experiment (mass%).

		Fe	Ni	Cr	Mn	Mo	N	Si	C	B
SUS 316	N1	bal.	12.88	16.82	0.76	2.30	0.0433	0.21	0.004	0.0111
	N2		12.78	16.84	0.79	2.32	0.0620	0.18	0.004	0.0102
	N3		12.83	16.87	0.79	2.33	0.1024	0.18	0.004	0.0102
	P1		12.91	16.91	0.76	2.32	0.2000	0.19	0.008	0.0110
High N stainless steels	a	bal.	27.40	25.21	1.44		(0.113)	0.58	0.002	
	b		27.40	25.21	1.44		(0.229)	0.58	0.002	
	c		27.40	25.21	1.44		(0.325)	0.58	0.002	
	d		27.40	25.21	1.44		(0.442)	0.58	0.002	

Table 2 Average chemical composition of duplex stainless steels (mass%).

C	N	Mn	S	P	Ni	Cr	Mo	Si	Cu
0.011	0.11	1.06	0.001	0.016	4.8	22.1	2.74	0.53	0.03

computer. This system was attached to a Philips EM420T microscope. The accelerating voltage of the electron microscope was 120 kV and the current density at the second condenser aperture was between 80–150 A/cm². Spectra were collected in the diffraction mode for high count rates. The EELS aperture used was 3 mm in diameter and the FWHM (Full Width Half Maximum) of the zero loss peak was kept at around 1.0 eV. The collection semiangle β was about 15 mrad and an energy dispersion of 0.5 eV/ch was used. The specimen thickness of the areas analyzed was estimated to be less than 100 nm from the intensity ratio of the zero loss to the first bulk plasmon peak.

Eight to nine spectra shifted by several channels with respect to each other were collected from almost the same area of a specimen. Each spectrum was acquired for a total of 100 s using a diode integration time of 0.2 s. These spectra were then processed using the iterative averaging method described by Boothroyd *et al.*⁽⁷⁾ Normally three iterations were enough to eliminate the effects of the channel gain variation of the acquisition system. Secondary electron background subtraction was carried out for the processed spectra after iterative averaging using power law fitting. A top hat filter was applied, when the nitrogen peak was small, to obtain spectra in the second differential form.

The intensities of the N-K, Cr-L and Fe-L edges were determined by summing the counts of 5 channels (2.5 eV) around the peak top. The net intensities were estimated by measuring the counts above the linear base line connecting the onset of the peak and the minimum at the higher energy loss side of the peak as shown in Fig. 2. The intensity ratio of (I_N/I_{Cr}) or (I_N/I_{Fe}) were correlated with the atomic concentration ratios (C_N/C_{Cr}) or (C_N/C_{Fe}) where I and C denote the intensity and atomic concentration, respectively.

III. Results

1. High nitrogen austenitic stainless steel

Figure 1 shows spectra obtained from 0.113 mass%N austenitic stainless steel using different methods of data processing. Figure 1(a) is a raw spectrum acquired for 100 s and Fig. 1(b) is after divided by the gain spectrum measured with the diodes uniformly illuminated. Figure 1(c) is obtained from nine spectra similar to Fig. 1(a) shifted by from 10 to 40 channels and then averaged over corresponding energy losses. Figure 1(d) is calculated by applying the iterative averaging method for the nine spectra used in Fig. 1(c). Although the simple averaging technique, which has been firstly proposed by Shumann *et al.*⁽⁸⁾, is useful in reducing the effect of channel gain variation, it is demonstrated that the use of nine spectra is not enough to quantify nitrogen at this level. It is clearly seen that the channel gain variation is satisfactorily corrected by the iterative averaging method to allow detection of 0.1 mass% nitrogen. It should be emphasized that acquisition of only about ten spectra is needed in this procedure, which can reduce experimental error due to specimen contamination and drift when compared to the hundreds of spectra required by the method of Shumann *et al.*⁽⁸⁾

Figure 2 shows a series of spectra obtained from four

Fig. 1 Energy loss spectra of high nitrogen austenitic stainless steel after dark current background subtraction. a) One spectrum acquired for 100 s at 0.5 eV/channel and b) after dividing by gain spectrum. c) Average of 9 spectra similar to a) shifted by from 10 to 40 channels with respect to each other. d) After iterative averaging.

Fig. 2 The change of N-K peak intensities normalized by the Cr-L intensity in EELS spectra (after background subtraction) obtained from high nitrogen austenitic stainless steels (Fe-25%Cr-28%Ni) having a range of nitrogen content.

Fig. 3 Integrated intensity ratios $I(N)/I(Cr)$ obtained from Fig. 2 using a 2.5 eV integration window versus atomic concentration ratios (C_N/C_{Cr}) for high nitrogen austenitic stainless steels.

different 25Cr-28Ni steels. These spectra are normalized by the intensity of the Cr-L₃ edge after secondary electron background subtraction. The intensity of the N-K peak increases as the nitrogen concentration increases. In the case of these samples, we can estimate the peak intensity directly from the spectra in which only background are subtracted. We plotted the intensity ratios of (I_N/I_{Cr}) versus atomic concentration ratios (C_N/C_{Cr}). Although the data are scattered around the line which is extrapolated to zero, there is a strong correlation between (I_N/I_{Cr}) and (C_N/C_{Cr}) as shown in Fig. 3.

2. Type 316 stainless steel (SUS 316)

Figure 4 shows a series of second differential spectra obtained from SUS 316 stainless steels. Because the nitrogen content was lower in the type 316 stainless steels than in the high nitrogen alloys described in the previous section, spectra in the second differential form have to be used for quantification. A top hat filter (shown inset in Fig. 4) is used to obtain spectra in the second differential form. Three peaks are observed around 400 eV energy loss region in this figure. They are assigned as N-K (397 eV), Mo-M₃ (394 eV) and Mo-M₂ (410 eV), respectively from a comparison with XPS (X-ray photo electron spectroscopy) spectrum of a 0.20 mass%N SUS316 specimen. Each energy loss value is determined by assuming that the energy loss of Fe-L₃ edge is 708 eV, which is the value for metallic iron. As is clear from Fig. 4 the intensity of the N-K peak relative to the Mo-M₃ peak increases as the nitrogen concentration increases. The intensity of each peak is measured in the same manner as for the high nitrogen austenitic stainless steels. A narrow energy window of 2.5 eV (i.e. 5 channels) is chosen to avoid contributions from the Mo-M₂,₃ peaks.

Figure 5 shows the peak intensity ratios (I_N/I_{Cr}) versus atomic concentration ratios (C_N/C_{Cr}) obtained from two types of stainless steels which have different matrix compositions. The intensity ratios for the 25Cr-28Ni alloys

Fig. 4 Second differential spectra for SUS316 specimens (Fe-17%Cr-13%Ni-2%Mo) obtained using the inset filter (figures in channels). Arrows indicate N-K (↑) and Mo-L (↓) peaks, respectively.

Fig. 5 Integrated intensity ratios $I(N)/I(Cr)$ versus atomic concentration ratios (C_N/C_{Cr}) for type 316 stainless steel (Fe-17%Cr-13%Ni-2%Mo) with varying nitrogen contents; (○) measured from second differential spectra. The intensity ratios for the austenitic stainless steels (Fe-25%Cr-28%Ni) are also shown for comparison; (●). The dotted line is a straight line fitted to the data.

this time estimated from the spectra in the second differential form are also plotted for comparison. The dotted line [$I_N/I_{Cr}=0.5 (C_N/C_{Cr})$] is the best fit to the data. The intensity ratio and the atomic concentration ratio have a good correlation and a common calibration curve seems to be valid regardless of the matrix composition. Thus the calibration curve shown in Fig. 5 can be used for estimating nitrogen concentration relative to chromium concentration of unknown areas for most stainless steels. At present, nitrogen concentrations as low as 0.04 mass% are quantifiable by the use of the iterative averaging method. Although a theoretical estimation is still being done, the concentration of 0.04 mass% seems to be the detection limit for nitrogen with our instrument where LaB_6 source is used.

It should be pointed out that the calibration curve shown in Fig. 5 for second differential spectra is not identical to that shown in Fig. 3. The values of I_N/I_{Cr} are higher when they are determined from the second differential spectra. This results from the sharpening effect of the second differential calculation. Thus depending on which spectra are used for quantification, background subtracted or second differential, either of the two calibration curves should be chosen. For the quantification of low concentrations, second differential spectra combined with the curve in Fig. 5 should be used.

3. Duplex stainless steel

Partitioning of alloying elements occurs in a duplex stainless steel. When an alloy with a large grain size ($>5 \mu m$) is studied, a conventional technique such as EPMA can be used for quantification. However when small grain sizes, as found in weld metals or γ -phases precipitated at around 700°C are of interest, a method with a higher spatial resolution must be used. Partition-

Table 3 Analysis of α (ferrite) and γ (austenite) phase by TEM/EDX (mass%).

	Si	Cr	Mn	Fe	Ni	Mo
γ phase	1.0	23.2	1.8	66.3	5.4	2.2
α phase	0.5	24.8	1.7	66.6	3.3	3.1

Fig. 6 Second differential spectra obtained using the inset filter (figures in channels). a) α (ferrite) phase, b) γ (austenite) phase in a duplex stainless steel.

ing of metals can be estimated by TEM/EDX as shown in Table 3; Cr and Mo enriches in the α -phase, whereas Ni enriches in the γ -phase. Si is known to enrich in the α -phase rather than in the γ -phase. Although the result obtained in our experiment is not consistent with this expectation, we do not discuss the reason here. Attempts are made here to apply PEELS to the quantification of nitrogen.

Figure 6 shows the second differential spectra obtained from the α and γ phases in duplex stainless steel. The intensity of the two Mo-M peaks in each phase is consistent with the results of TEM/EDX (see Table 3); Mo is enriched in the α -phase. Moreover, the partitioning of nitrogen between the α and γ phase is clearly seen, as expected the nitrogen concentration is much higher in the γ -phase. The measured I_N/I_{Cr} ratio is from 0.03 to 0.04 for the γ -phase. By using the calibration curve shown in Fig. 5, this intensity ratio leads to concentration ratios from 0.050 to 0.065 for the γ -phase. Since the chromium content is estimated to be 23 mass% (24 at%) in the γ -phase, the nitrogen content can be determined as 0.26 ± 0.04 mass% ($\sim 1.0 \pm 0.2$ at%) in the γ -phase of the duplex stainless steel. The error value is derived from 5-time measurements. Although a tiny "shoulder" is observed in the α -phase, it is not possible to determine the nitrogen concentration in the α -phase. Consequently we conclude that the nitrogen concentration in the α -phase is close to or below the detection limit of 0.04 mass%.

IV. Discussion

In this section we discuss sources of errors in quantification.

a) Background-subtraction

Background-subtraction is one of the most important parts of the data analysis when the intensities of the peaks are compared. In particular, when a peak is present at the lower energy loss side of the peak of interest, we must check whether the power law fitting curve is appropriate or not. When conventional background subtraction becomes unreliable, we have resorted to the simpler baseline method described in section II. This has the advantage that a uniform background above the peak is not required, and although the peak area is underestimated the area obtained is still proportional to the edge area.

b) Surface oxidized layer

Contributions from the surface oxidized layer on the specimens are not negligible in some cases. I_N/I_{Cr} is plotted for the γ -phase in the duplex stainless steels as a function of specimen thickness in Fig. 7. The values of peak height ratio H_O/H_N (H_O is the oxygen peak height and H_N is the nitrogen peak height) are also plotted in the figure. H_O/H_N clearly decreases as the thickness of the specimen increases indicating that a surface oxidized layer is present. I_N/I_{Cr} increases as the thickness decreases due to the underestimation of the Cr-L intensity. This is because it is not possible to fit the background to allow precise estimation of the Cr-L intensity when the O-K peak whose position is only 40 eV lower than the Cr-L peak is present. In order to avoid this, it is necessary to eliminate the surface oxidized layer by ion milling. When it is difficult to remove oxidized layer it is better to use the Fe-L peak rather than the Cr-L peak. Figure 8 is a graph similar to Fig. 3 showing the ratio $I(N)/I(Fe)$ as well as $I(N)/I(Cr)$.

Fig. 7 The change of integrated intensity ratios $I(N)/I(Cr)$; ($\circ$) and peak intensity ratios $H(O)/H(N)$; ($\bullet$) versus specimen thickness for the γ phase in duplex stainless steel.

Fig. 8 Comparison between the integrated intensity ratios $I(N)/I(M)$ and atomic concentration ratios (C_N/C_M), where M is Cr; ($\circ$) or Fe; ($\bullet$).

Although normally a very thin area should be used for EELS analysis, when a surface oxide layer is present thicker areas will give better results as long as the thickness does not exceed about 1 plasmon mean free path.

c) Amount of energy shift between spectra

A periodic oscillation in the second differential spectra is frequently observed, as exemplified in some of the spectra in Fig. 4. This phenomenon occurred because the amount of the energy shift applied when collecting a series of spectra was almost the same for each spectrum. These artificial peaks can hamper the detection of peaks of interest. To avoid this problem, spectra for averaging should be collected by shifting with a different number of channels for each spectrum and we have to check for the presence of periodic features after each iterative averaging procedure.

d) Change of sample thickness

The iterative averaging method gives good results when the spectra used for analysis have a similar shape to each other. Thus a change of sample thickness during the experiment results in a poor correction of the channel gain variation, particularly in the low energy loss region. Consequently the electron probe must be positioned on the same area for every spectrum in a series during spectra acquisition. Specimen drift is not a serious problem in our experiments because we use a large electron probe ($0.5 \mu\text{m}$ in diameter) for detecting nitrogen in the matrix.

A thickness change due to the growth of a carbon contamination layer must also be avoided for the same reason. A cold stage was useful for reducing the effect of contamination in our experiments. When a small probe is used for studying, for example, segregation at grain boundaries, specimen drift and contamination growth should be minimized.

e) Total electron dose

The detection limit primarily depends on the signal to noise ratio of a spectrum, i.e. the number of electrons which enter the spectrometer⁽⁹⁾⁽¹⁰⁾. Although the peak intensity ratio (I_N/I_{Cr}) is basically independent of the total current, the statistical accuracy of the area of a N-K peak becomes worse as the total current decreases. Therefore it is necessary to have the highest current possible for the probe size wanted. Boothroyd *et al.*⁽⁷⁾ reported that when a probe of 20 nm ϕ was used the boron K-edge from Ni₃Al containing 0.1 at%B was just visible. When analyzing a small area such as a grain boundary, which is of course the advantage of a TEM, the use of a high intensity electron source such as a field emission gun seems to be essential.

V. Conclusions

(1) We have detected nitrogen down to about 0.04 mass% in stainless steels using the iterative averaging method.

(2) The iterative averaging technique for parallel EELS has proved to be a powerful tool for the detection of dissolved nitrogen in metals with high spatial resolution.

(3) The relative intensity of N to that of Cr or Fe determined by our base line method is proportional to the atomic concentration ratios (C_N/C_{Cr}) or (C_N/C_{Fe}). A calibration curve thus obtained can be used to quantify nitrogen in stainless steels with different matrix compositions.

(4) By using the calibration curve shown in Fig. 5 the nitrogen concentration of the γ -phase in duplex stainless is estimated to be 0.26 ± 0.04 mass%, whilst the nitrogen content of the α -phase is below the detection limit of 0.04 mass%.

Acknowledgments

The authors would like to thank Prof. M. Kikuchi (Tokyo Institute of Technology) for preparing the high nitrogen austenitic stainless steels and Mr. Minami (NKK) for the provision of the type 316 stainless steels.

REFERENCES

- (1) M. Kikuchi and R. Tanaka: *Tetsu-to-Hagané*, **69** (1983), A83–A88.
- (2) M. Kikuchi, S. K. Choi and R. Tanaka: *Zairyo Kagaku*, **21** (1985), 358.
- (3) M. Kikuchi, T. Urabe, G. Cliff and G. W. Lorimer: *Acta Metall. Mater.*, **38**, (1990), 1115.
- (4) R. F. Egerton: *Electron Energy-Loss Spectroscopy in the Electron Microscope*, Plenum Press, New York and London, (1986), p. 333.
- (5) D. R. Liu and L. M. Brown: *Int. Phys. Conf. Ser.*, ed. by M. J. Goringe, London, The Institute of Physics, **61** (1981), 201.
- (6) A. J. Bourdillon, W. M. Stobbs, K. Page, R. Home, C. Wilson, B. Ambrose, L. J. Turner and G. P. Tebby: *Int. Phys. Conf. Ser.*, ed. by G. J. Tatlock, Bristol, Adam Hilger, **78** (1985), 161.
- (7) C. B. Boothroyd, K. Sato and K. Yamada: *Proceedings of the XIIth International Congress for Electron Mic.*, San Francisco Press, **2** (1990), 80.
- (8) H. Shumann and P. Kruit: *Rev. Sci. Instr.*, **56** (1985), 231.
- (9) R. F. Egerton: *Ultramicroscopy*, **5** (1982), 387.
- (10) H. Kurata, I. Kubo, S. Isoda and T. Kobayashi: *Proceedings of the 47th Conference of Japan Electron Mic.*, (1991), p. 187.