Determination of Nitrogen in Duplex Stainless Steels by EPMA

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Abstract. We describe the quantitative determination of low nitrogen contents (< 1 %wt) in highly-alloyed, duplex stainless steels by EPMA using a calibration curve. Five monophasic stainless steels with various nitrogen concentrations were used for the calibration curve, namely, three highly alloyed steels prepared in the laboratory, with nitrogen contents 0.066, 0.565 and 1.016 %wt and two industrial alloys with nitrogen concentrations 0.174 %wt and 0.023 %wt. For these samples, the plot of nitrogen X-ray intensities versus nitrogen contents exhibited an acceptable linear relationship. Average nitrogen contents of the analysed duplex alloys were found to vary in the range 0.045–0.07 %wt in ferrite and 0.52–0.77 %wt in austenite. These results suggest that the nitrogen solubility limit in ferrite has been reached; on the other hand, nitrogen solubility in austenite increases due to the high manganese and low nickel contents.

Key words: Duplex stainless steels; nitrogen; electron microprobe analysis; calibration curve; trace analysis.

The name duplex stainless steel is commonly used to designate the stainless steels that have a two-phase ferritic-austenitic microstructure, typically separated in large grains (about 10 µm in diameter). These steels are especially valuable for applications where good mechanical and anti-corrosion properties are required simultaneously, such as refinery pipes or off-shore platforms [1].

One of the actual tendencies as regards the design of alloys is the introduction of nitrogen as an alloying element. In the case of stainless steels, nitrogen plays an important role on the main properties of these steels, such as the resistance to pitting corrosion. Moreover, nitrogen can partially replace nickel in the alloy due to its power as a γ-phase (austenite) promoter, which is a factor of economic importance. Bulk nitrogen contents in standardised duplex steels are, typically, in the range 0.15–0.35 %wt; in some experimental alloys the N contents may be as large as 0.4 %wt. In standardised duplex stainless steels the saturation of nitrogen in ferrite (α-phase) is obtained, so the remaining nitrogen goes to the austenite (γ-phase) [2, 3]. It is known that the elements chromium and manganese stabilise the nitrogen in solid solution [2].

At present, a limited number of studies have been performed to establish the partition coefficient of nitrogen (i.e. the ratio of the nitrogen contents between ferrite and austenite) especially because of the difficulties in analysing nitrogen at these low levels (see e.g. [4]). However, market demands for these materials and new steels with significantly different compositions but the same duplex structure increase the requirement for knowledge about this matter. Of interest is the behavior of nitrogen in the alloy and the role of manganese (because its high content) in the stability and the partition coefficient of nitrogen.

Wavelength-dispersive electron probe microanalysis (EPMA) is a reliable technique for the quantitative analysis of constituent phases of materials. However, EPMA of nitrogen raises numerous problems. As already pointed out in ref. [5], reliable analysis of nitrogen is possible provided extreme care is exercised during the measurements and an accurate matrix correction program (with consistent mass absorption coefficients) is used. In the case of trace content,
intensity measurement has additional difficulties, such as background subtraction. The conventional method of background estimation by linear interpolation of measurements at both sides of the peak has limitations and may lead to unacceptable errors mainly due to the strong curvature of the background and the presence of higher-order reflection lines close to the nitrogen peak. Although the use of synthetic multilayer crystals provides a substantially better peak-to-background ratio of the nitrogen peak and higher-order reflections are minimised [5], more accurate procedures for background subtraction are required. One possible solution is to use a calibration curve (see e.g. [6]), which must be obtained on reference samples having similar composition as the samples of interest. Accordingly, spectral background subtraction is not required and conversion of intensity to concentration is carried out from measured intensity. Moreover, corrections for matrix effects and peak shape differences (due to chemical state) can be assumed to be negligible.

In this work, we describe the quantitative determination of nitrogen (with contents <1 % wt) in high-alloyed, duplex stainless steels by EPMA using a calibration curve. Uncertainties of the measurement and detection limits are evaluated. The influence of the alloying elements on the nitrogen solubility limit is discussed.

**Experimental**

Classical austenitic-ferritic duplex stainless steels and newly developed ones, which have similar microstructure and are characterised by low nickel, high nitrogen and high manganese levels, were prepared in an induction re-melting unit (LIFUMAT-MET-3.3 Vac). Their global composition was determined by X-ray fluorescence analysis, XRF, (Si, Mn, Sn, Ni, Cu, Cr, P, Mo, Ti, Nb) and LECO elemental analyser (C, N, and S). The microstructure of the steels after solution treatment at 1223 K was examined by field emission scanning electron microscopy (FEG-SEM) on a LEO 982 and the ferrite phase content was measured with a ferretoscope (by magnetic measurement). The composition (major elements) of the austenitic and ferritic phases was determined in the treated state on the FEG-SEM by energy dispersive spectrometry (EDS), using a Ge detector [7].

EPMA of nitrogen was performed on a CAMECA SX-50 electron microprobe, using a Ni/C (2d = 95 Å) multilayer crystal. Measurement conditions and instrument settings were optimised as follows. Analyses were done at 10 keV electron incident energy with electron beam currents of 200 nA, in a compromise between minimum absorption of N X-rays and beam spread, and maximum counting rate. In order to minimise the influence of higher-order reflection peaks, a narrow window (2 V) was set in the pulse height analyser (PHA). Carbon contamination has to be considered when analysing nitrogen because it largely absorbs nitrogen X-rays. Therefore, care was exercised to remove surface contamination by re-polishing the samples on a soft cloth using 0.3 μm alumina and ultrasonic cleaning with alcohol before every measurement. In addition, samples were introduced in the microprobe the night before the measurement, to use vacuum as an additional cleaner. In all measurements, a liquid nitrogen cold-finger and an oxygen-jet were used. On the other hand, EPMA points were selected at random using the optical microscope in order to avoid contamination due to beam scanning. Since the microstructure of the alloys cannot be resolved by optical microscopy without selective etching, a procedure was adopted to classify the analyses (see below). Each sample was measured at least at 100 points, in automatic mode. For each point, the counting time was 40 seconds.

Conversion of measured intensity into concentration was carried out by means of a previously measured calibration curve. The reference samples available to generate the calibration curve were a combination of highly alloyed steels, prepared in the laboratory, and industrial alloys, which are summarised in Table 1. All of them have a fully monophase structure (austenite A to D or ferrite, E), which is a basic requirement for calibration purposes. In each reference sample, at least 20 measurements were performed.

**Results and Discussion**

Figure 1 shows the microstructure of a typical duplex stainless steel made up of a α-phase (ferritic) with darker contrast and a γ-phase (austenitic) with lighter contrast, obtained with the FEG-SEM. Although ferrite and austenite have slightly different compositions (see Table 3), the contrast between both phases observed in the backscattered electron micrographs is mainly due to their different crystal structure (austenite is FCC and ferrite is BCC) and the use of the FEG-SEM (which can deliver high current densities) at low incident electron energy. The black spots

<table>
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<tr>
<th>Alloy</th>
<th>Structure</th>
<th>Source</th>
<th>C</th>
<th>N</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Mo</th>
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<tr>
<td>D</td>
<td>austenite</td>
<td>industrial</td>
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<td>0.023</td>
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<tr>
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<td>experimental</td>
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<td>0.066</td>
<td>0.57</td>
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<td>0.24</td>
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<tr>
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