Determination of nitrogen partitioning coefficients in superduplex stainless steels by NRA using a nuclear microprobe

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ABSTRACT

Superduplex stainless steels (SDSSs) combine the good mechanical behavior and the high corrosion resistance of the ferrite (α-Fe) and austenite (γ-Fe) phases. The SDSSs properties depend strongly on the partitioning of the elements that form the alloy. The ferrite is generally enriched in P, Si, Cr and Mo while the content of Ni, Mn, Cu and N in the austenite phase is higher. Nitrogen is known to be a strong austenite stabilizer and its presence increases the strength and the pitting corrosion resistance of the stainless steels. While the global nitrogen content in SDSSs can be readily determined using elemental analyzers, it cannot be measured at a microscopic scale.

In this work, the nuclear microprobe of the Centro Nacional de Aceleradores (Sevilla) was used to obtain the quantitative distribution of nitrogen in SDSSs. A deuteron beam of 1.8 MeV was employed to determine the overall elemental concentration of the matrix by deuteron-induced X-ray emission, whereas the nitrogen partitioning coefficients were obtained by using the $^{14}N(d, \alpha_0)^{12}C$ nuclear reaction. Mappings of this element show that the nitrogen ratio between the ferrite and austenite phases ranges from 0.3 to 0.6 in the analyzed samples.

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1. Introduction

Due to their excellent mechanical properties and corrosion resistance [1], duplex stainless steels (DSSs) have been extensively used in many applications, such as oil extraction, paper manufacturing and other chemical industries [2]. DSSs combine the suitable properties of ferrite and austenite phases, which are equally present in DSSs. In general, alloy composition has a great influence on the phase transformation, mechanical properties and corrosion behavior of DSSs. Nitrogen is one of the most important alloying elements in these steels due to several beneficial effects. Nitrogen is known to be a strong austenite stabilizer and its presence can lead to a solid solution strengthening [3–5] and a lower stacking fault energy [6,7], increasing subsequently the strength of the steels. The nitrogen alloying can also play an important role in retarding the precipitation of intermetallic compound [8,9], raising the ferrite/austenite transformation temperature and assisting the formation of the austenite phase in the heat affected zone (HAZ) of a weldment [10]. Most important, the alloying of nitrogen into the stainless steels can greatly improve the passivation, and increase the pitting corrosion resistance in aqueous environments [11].

While the global nitrogen content in SDSSs can be readily determined using elemental analyzers, the study the nitrogen solubility inside the different metallic phases requires taking advantage of the high sensitivity of ion microbeam characterizations. The microanalysis of this kind of samples, using a nuclear microprobe, allows us to obtain the quantitative or semiquantitative elemental distribution maps of both main and trace elements.

In a previous work [12], our group performed the simultaneous measurement of the partitioning ratio, for light and heavy elements into different steels, by means of deuteron induced γ-ray emission (d-PIGE), based on the $^{14}N(d, p\gamma)^{15}N$ nuclear reaction, and deuteron induced X-ray emission (d-PIXE) respectively. In this work, the $^{14}N(d, \alpha_0)^{12}C$ nuclear reaction at a deuteron energy of 1.8 MeV is also employed to measure low nitrogen contents in steel by means of nuclear reaction analysis (NRA), and the overall composition of the phases by d-PIXE and EDX (Energy Dispersive X-ray Detection). We show that using a nuclear microprobe, it is possible to obtain the corresponding nitrogen distributions inside individual metallic grains of austenite and ferrite within the same experiment. Moreover, compared with the $^{14}N(d, p\gamma)^{15}N$ nuclear reaction, lower acquisition times are required for these

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measurements, since specific point microanalysis in each phase are not necessary.

2. Experimental

Five experimental duplex stainless steels with different Mo, W and Ni content were prepared by induction melting in a centrifugal casting furnace with controlled nitrogen atmosphere. One of the alloys corresponds to SAF 2507 (UNS S32750, EN 1.4410) type stainless steel, the most common within the superduplex grades, and it has been used for the comparative analysis with the other DSSs alloys. A homogenization treatment was performed at 1050 °C for 15 min. The resulting typical duplex microstructure, after the metallographic preparation and etching, can be observed in Fig. 1, in addition the X-ray diffraction analysis also reveals the duplex structure for all the samples. Ferrite and austenite fractions were obtained by standard metallographic techniques. Global chemical composition has been determined using GD-OES (Glow Discharge with an Optical Emission Spectroscopy) and elemental analyzers. Table 1 shows the overall chemical composition in wt% for the more relevant elements for this study. The samples have been also observed by electron microscopy (SEM) in order to check the microstructure and determine the major components, not detailed in this paper.

In order to determine the distribution of nitrogen between metallic phases, ferrite and austenite, ion beam analysis has been performed using a nuclear microprobe connected to the 3 MV Tandem accelerator of the Centro Nacional de Aceleradores [13]. Simultaneous micro d-PIXE, d-PIGE and NRA experiments have been carried out with a 1.8 MeV deuteron beam, accomplishing a lateral resolution of 5 µm. A Si(Li) detector, placed at $\theta = 135°$, was used for PIXE acquisition using a 500 µm thick Mylar funny

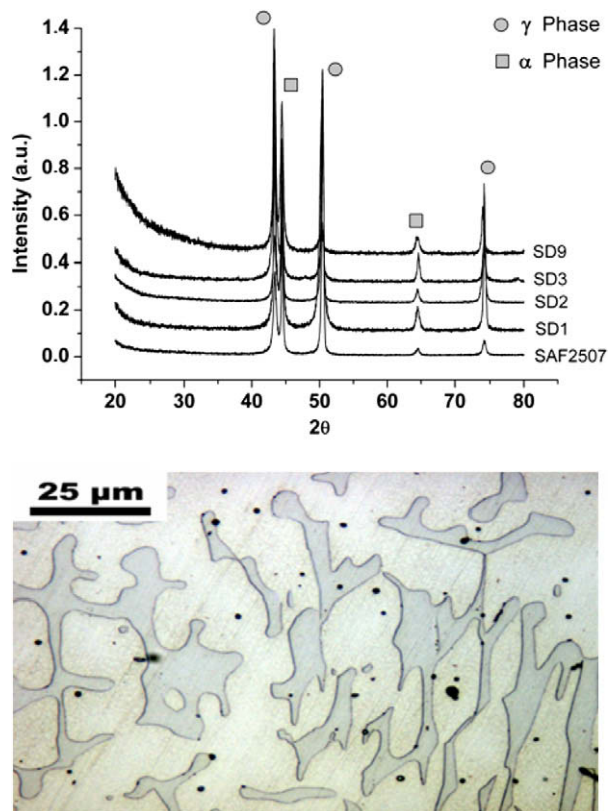### Table 1
Manufactured samples global chemical composition in wt%.

wt% samples	C	Si	Mn	Cr	Cu	Ni	w	Mo	N
SAF2507	0.015	0.5	0.2	25.3	0.3	7.2	0.0	3.8	0.39
SD-1	0.016	0.6	0.2	24.8	0.3	7.0	2.1	2.9	0.41
SD-2	0.018	0.7	0.2	27.0	0.6	6.9	4.1	1.9	0.46
SD-3	0.022	0.8	0.2	26.1	0.4	6.9	6.4	0.9	0.41
SD-9	0.014	0.6	0.2	25.2	0.3	2.9	6.1	0.8	0.43

filter (1.5 mm hole). This filter effectively reduces the pile-up due to the high Fe signal, improving the detection limit for Ni in the time consuming experiments. The γ-rays emitted by the $^{14}N(d, p\gamma)^{15}N$ nuclear reaction, were detected with a HPGe detector located outside the vacuum chamber at $\theta = 90°$. The alpha particles coming from the $^{14}N(d, \alpha_0)^{12}C$ nuclear reaction were collected with a surface barrier detector placed at $\theta = 135°$ in Cornell geometry. Despite the higher cross-section of the $^{14}N(d, \alpha_1)^{12}C$ reaction, we have selected the $^{14}N(d, \alpha_0)^{12}C$ reaction since, due to the thickness of the samples, only the peak corresponding to α_0 particles is completely isolated from other contributions and it is background free [14]. In addition, the interfering ^{14}N proton group has been displaced adjusting the thickness of the sensitive zone of the particles detector [15]. By scanning the deuteron microbeam perpendicularly to the sample, the elemental maps have been simultaneously recorded using the OM_DAQ data acquisition system [16] in list mode operation. This option avoids the uncertainty in the spectra normalization corresponding to different phases in the samples.

Previously to the microprobe experiments, macro NRA measurements were performed on several calibration samples with known nitrogen content, ranging from 0.052 to 0.20 wt%, to establish the experimental conditions for the detection of the α_0 particles. A TiN sample (20 wt% N) was used to define the signal and experimental set up. The results from the bulk specimens agreed with the theoretical values within the error of our measurements (around 5 wt%). The N concentration was determined by direct comparison of the α_0 peak area from the sample spectra with that from a steel standard, and corrected with the corresponding stopping powers, as stated in [17]. The d-PIGE experimental setup to measure N in steels is widely discussed in [12].

3. Results and discussion

The incident 1.8 MeV deuteron beam, with a current of ~800 pA, was scanned over a 100×100 µm^2 area of the samples to obtain NRA and d-PIXE elemental maps simultaneously. Fig. 2 shows typical distribution maps corresponding to the $Ni_{k\alpha}$ X-ray emission and $N_{\alpha0}$ particles detected for the SD-1 sample. The element concentration increase as the colors scale goes to warm colors (bright field). A clear correlation between both images can be established, the islets with higher Ni concentration also present a higher content of nitrogen. The molybdenum and tungsten concentrations were found higher in the ferrite phase, obtaining a negative image respect to the Ni and N distribution. This fact corroborates the N preferential dissolution on the austenite phase. We also recorded the nitrogen distribution maps taken a window in the high-energy region of the emitted γ-rays (including the 7298 and 8310 keV peaks). However, in the corresponding images we are not able to distinguish between austenite and ferrite phases. The γ-ray background is very large compared with the small N signal coming from both phases, especially for a quite long acquisition time. The Fig. 3 shows two spectra with 1.8 MeV deuteron-induced γ-ray and α_0 emitted, respectively, from the $^{14}N(d,p\gamma)^{15}N$ DIGE and the $^{14}N(d,\alpha_0)^{12}C$ NRA measured in a sample. Although the first method has been proven as an accurate way to detect nitrogen [12,18], we find that this is not the best option for our goal to

Fig. 1. XRD spectra and optical microscopy of SD1, ferrite is shown in darkness and austenite in brightness.