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Assessment of electrochemical methods used on corrosion of superduplex stainless steel

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ABSTRACT

This paper addresses the electrochemical parameters proposed in ISO 12732 standard that are used to quantify undesirable phases in a superduplex stainless steel. The relationship among these electrochemical parameters (listed as the maximum current and overall charges ratio during the activation and reactivation polarization curves) and the quantity of undesirable phases were evaluated. It was shown that ferrite is always preferentially corroded in that steel. For aged conditions, the undesirable phases were satisfactorily detected by Double Loop Electrochemical Potentiokinetic Reactivation. A new experimental protocol developed made possible the characterization of the attack occurring at each polarization range.

1. Introduction

Duplex and superduplex stainless steels (SDSS) are a class of biphasic austenite/ferrite steels. The percentage of each phase depends on the composition and heat treatments these steels they might have been subjected to. Most duplex and superduplex stainless steels though, present equal amounts of those two phases when in service [1]. These steels present, at the same matrix, the excellent corrosion resistance of austenite steel, and the high mechanical behaviour of ferrite ones. However, the performance presented by these materials can be drastically reduced if undesirable phases, such as sigma (σ) phase, chi (χ) phase, secondary austenite (γ_2) phase, and rich chromium precipitates like nitrides (Cr_2N) and carbides ($M_{23}C_6$, M_7C_3) are formed. Amongst those deleterious phases, the σ-phase has a particular impact in the decreasing of corrosion resistance and mechanical properties of these materials. Sigma phase is rich in chromium and molybdenum, presents high volumetric fraction and is formed by ferrite decomposition, in the temperature range between 500 °C and 1000 °C [2]. Its nucleation leads to Cr/Mo depleted areas adjacent to the ferrite/sigma interface that become susceptible to localized corrosion. Moreover, σ-phase is harder than the austenite–ferrite matrix what leads to a decrease of toughness on these steels. For this reason, investigation of the presence of this phase and its fractions has become a crucial task for guarantee the integrity and performance of duplex and superduplex steels.

Cihal et al. [3] have proposed an electrochemical method to detect the susceptibility of stainless steels to localized corrosion. This method has been described in the ISO 12732 standard [4] and has been extensively used in the literature [5–9], with several types of electrolytes, different scan rates and variation of other test parameters. The Double Loop Electrochemical Potentiokinetic Reactivation (DL-EPR), proposed by the standard, consists in polarizing the steel with a constant scan rate towards the anodic direction, ranging from the open circuit potential up to the passive region. Then, the scan is reversed towards the open circuit potential with the same scan rate. During the anodic polarization, the current reaches its maximum to a value known as *activation current* (I_a). On the reverse scan, back to the open circuit potential, the passive film formed during anodic polarization is expected to degrade firstly on the weaker areas around the deleterious phases. Therefore, another current peak will be formed, which is then called *reactivation current* (I_r). According to the standard, the ratio I_r/I_a is proportional to the degree of deleterious phases present on the electrode surface [4–9]. Another parameter that can be obtained from this electrochemical procedure is the ratio of total charges Q_r/Q_a associated with the reactivation (Q_r) and activation processes (Q_a), respectively.

The ISO 12732 standard was mainly proposed for classical stainless steel but has some recommendations for the use of duplex and superduplex steels. The solution proposed for those steels is HCl

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Table 1
Chemical composition of SDSS UNS S32750 in weight percent (wt%).

UNS	C	Cr	Ni	Mo	N	Mn	Cu	P	S	Si	Fe
S32750	0.015	25.6	6.51	3.88	0.28	0.46	0.12	0.019	0.0007	0.32	Bal.

(3 mol l^{-1}) and the scan rate recommended ranges from 2 V/h to 15 V/h. In the literature, many papers have tried to find the best electrolyte, scan rate, and test temperature to improve the use of this standard [10–13]. In particular, Angelini et al. [14], Amadou et al. [15], and more recently Deng et al. [16] have successfully correlated the presence of the undesirable phases in these dual-phase steel by DL-EPR or similar electrochemical techniques. A key point to select the good experimental condition is to find a ratio of $I_r/I_a < 0.1$ for the material under the annealing solution condition. Indeed, based on the Amadou et al. [15] and Deng et al. [16] works, this condition is necessary to improve the detection of the undesirable phases in aged conditions. These authors also proposed a screening work that consisted of using the steel under the annealing solution condition prior to working with aged materials. This practical use of the method, although time consuming, is important to minimize the value of I_r/I_a under the annealing solution condition in order to increase the possibility to associate this ratio with the presence of unwanted phases in the steel. The physical meaning of this ratio has not been explored using this approach, however. In the present work, the experimental conditions proposed by the ISO 12732 standard for duplex and superduplex steel were applied, with the purpose of exploring the physical meaning of the electrochemical parameters that can be extracted from this standard.

Table 2
Heat treatments and percentages of sigma phase and ferrite/austenite.

Heat treatment	% ferr/aust	% Sigma phase
Annealing solution (S1)	55.6/44.4	–
Annealing solution (S2)	61.2/38.8	–
Annealing solution (S3)	65.2/34.8	–
Aging 900 °C/5 min	55.0/44.4	0.56 ± 0.08
Aging 950 °C/10 min	50.7/44.4	4.90 ± 0.51
Aging 800 °C/30 min	36.9/44.4	18.75 ± 3.48
Aging 900 °C/1 h	20.6/44.4	34.97 ± 3.52

Table 3
Composition of sigma phase obtained by EDX for different heat treatments.

Heat treatment	Cr	Mo	Fe	Si	W
900 °C/5 min	30.07	9.93	46.76	0.36	–
950 °C/10 min	31.55	7.35	54.69	0.43	1.51
800 °C/30 min	31.05	11.29	49.65	0.38	3.06
900 °C/1 h	33.64	7.24	55.07	–	–

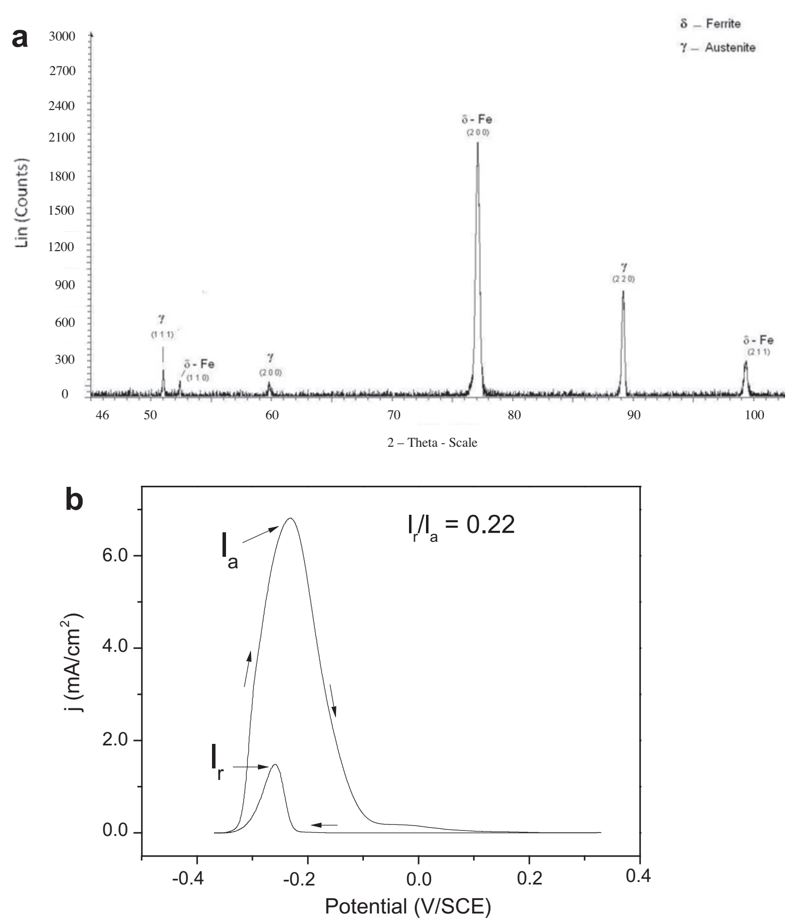

Fig. 1. Annealing solution sample (S1) (a) identification of ferrite and austenite by X-ray diffraction and (b) DL-EPR graphic.