Available online at www.sciencedirect.com

ScienceDirect

Procedia Structural Integrity 3 (2017) 269–275

Structural Integrity Procedia

www.elsevier.com/locate/procedia

XXIV Italian Group of Fracture Conference, 1-3 March 2017, Urbino, Italy

Analysis of the intergranular corrosion susceptibility in stainless steel by means of potentiostatic reactivation tests

Francesco Iacoviello*, Vittorio Di Cocco, Laura D'Agostino

Università di Cassino e del Lazio Meridionale, DICeM, via G. Di Biasio 43, 03043 Cassino (FR), Italy

Abstract

Intergranular corrosion cracking in stainless steels is a selective corrosion attack due to a local (grain boundary) Cr depletion. An undesired Cr carbides ($Cr_{23}C_6$) precipitation after heat treatment in the sensitization temperature range (usually between 550 and 850°C, depending on the steel chemical composition) is obtained with a kinetics that is mainly influenced by the C content.
In this work, the sensitization susceptibility of four sensitized stainless steels was investigated by means of potentiostatic reactivations tests. In addition, chronoamperometric tests and scanning electron microscope (SEM) observations of the specimens surfaces were performed in order to analyze the evolution of the corrosion morphologies.

Keywords: Stainless steels; Intergranular corrosion cracking; Potentiostatic reactivation tests.

1. Introduction

Intergranular corrosion is a selective attack that initiated and propagates in the vicinity of the grain boundaries of sensitized stainless steels. $Cr_{23}C_6$ carbides can locally precipitate due to heat treatments or welding procedures with a sensitization temperature that ranges between 550 and 850°C, depending on the steel chemical composition, Outukumpu handbook (2013). This localized corrosion attack is quite difficult to quantify, considering that the weight loss is really low and that the dimensions of the attacked zones are really reduced. The Electrochemical Reactivation Test (EPR test) is able to quantify the stainless steel sensitization degree and its susceptibility to an

* Corresponding author. Tel.: +39.07762993681.
E-mail address: iacoviello@unicas.it

Copyright © 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Peer-review under responsibility of the Scientific Committee of IGF Ex-Co.
10.1016/j.prostr.2017.04.032

integranular corrosion attack, Cihal (2001). It allows to perform measurements both in laboratory conditions and in situ, and, compared to the conventional corrosion test, EPR test is quicker, more sensitive and more accurate, especially investigating low sensitized conditions, Prohaska (2010). Two different EPR procedures are usually followed: single loop test (SL-EPR) and double loop test (EPR-DL). In SL-EPR tests, a potential scan from the passive range to open circuit potential is followed. Instead, in DL-EPR tests a cyclic polarization curve is applied on a metallographically prepared specimen: the polarization curve consists in a forward scan followed by a reverse scan starting at the active open circuit potential (Fig. 1). This procedure is standardized for AISI 304 and 304L, ASTM G108 (2015).

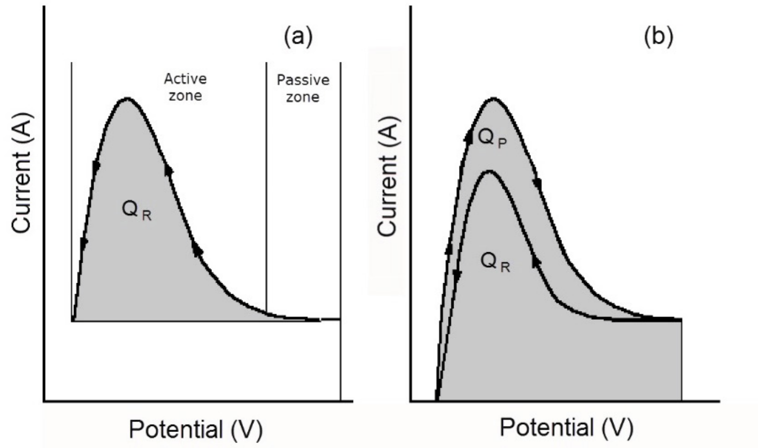

Fig. 1. (a) SL-EPR test; (b) DL-EPR test.

Considering the DL-EPR test, the sensitization degree of a stainless steel can be evaluated considering the ratio between the area of the reactivation stage and the area of the activation stage (e.g, Q_R/Q_P).

In this work, four stainless steels with different microstructures were considered and their susceptibility to the intergranular corrosion was investigated after sensitization at 800°C by means of DL-EPR tests, chronoamperometric tests and SEM specimens surface observations.

2. Investigated steels and experimental procedures

Four stainless steels were considered with different microstructures: one austenitic stainless steel (AISI 304L), two ferritic stainless steels (AISI 409 and AISI 430) and one austeno-ferritic (duplex) stainless steel (with analogous ferrite and austenite volume fractions). Investigated steels chemical compositions are shown in Tab.1-4.

Table 1. Austenitic stainless steel chemical composition AISI 304L (wt%).

C	Cr	Ni	Mn	Si	S	P
0.03	18	10	2.0	1.0	0.03	0.04

Table 2. Ferritic stainless steel chemical composition AISI 409 (wt%).

C	Cr	Mn	Si	S	P
0.08	12	1.0	1.0	0.04	0.04

Table 3. Ferritic stainless steel chemical composition AISI 430 (wt%).

C	Cr	Mn	Si	S	P
0.12	17	1.0	1.0	0.03	0.04

Table 4: Austeno-ferritic (duplex) stainless steel S31803 (2205) chemical composition (wt%; %α/%γ = 1).

C	Cr	Ni	Mo	N	Cu	Mn	S	Co	Si	P	O_2(ppm)
0.025	22.78	5.64	2.94	0.129	0.148	1.43	0.011	0.16	0.385	0.028	49/54

Focusing the austeno-ferritic stainless steel, it is worth to note that the ferrite and austenite grains have different composition depending on the temperature (element partitioning phenomenon): ferrite grains are enriched in P, W, Mo, Si and Cr, and austenitic grains are enriched in N, Ni, Cu and Mn, Tab. 5. The element partitioning implies a different electrochemical behavior of the austenitic and ferritic grains.

Table 5. Partitioning coefficients ([α])/([γ]) for a 2205 duplex stainless steel, Charles (1991).

Cr	Ni	Mo	Si	Cu	Mn	P
1.1	0.1	1.6	1.6	0.7	0.6	2.1

According to Tab.5, neither the ferritic nor the austenitic stainless steels can be considered as a perfect physical simulation of the ferritic and austenitic grains in the duplex stainless steel, but, anyway, their chemical compositions are not too far. The investigated stainless steels are characterized by different critical temperatures for the sensitization phenomenon, but, considering that 800°C is the most critical temperature for the duplex stainless steel (with the most evident ductility and toughness decrease), in this work this temperature was chosen as sensitizing temperature. Different heat treatment durations were considered (Tab. 6).

Table 6: Sensitizing duration at 800°C for the four investigated stainless steels (hours).

AISI 304L	0	1	3	10	100
AISI 409L	0	-	-	10	-
AISI 430	0	-	-	10	100
S31803 (2205)	0	1	3	10	100

DL-EPR tests were performed according to the following procedure:

- after being sensitized, specimens with a surface of 1 cm^2 were metallographically prepared;
- a 0.5 M H_2SO_4 + 0.01 KSCN aqueous solution was considered, Iacoviello (1997). Bubbling argon was used to stir the solution and ensure an oxygen-free electrolyte;
- Before polarizing the samples, the open circuit potential was measured for 2 min.
- Investigated potential range: -500 mV/SCE - +200 mV/SCE (Sweep rate: 50 mV/min).

In order to control results repeability, DL-EPR tests were repeated five times (confirming the very high repeability of the results obtained with DL-EPR testing procedure).

Corresponding to some electrochemical conditions (defined on the basis of the results of the DL-EPR tests) some chronoamperometric tests were performed and the specimens surfaces were observed by means of a SEM.

3. Experimental results and discussion

Considering the austenitic stainless steel AISI 304L (Fig. 2), it is possible to observe that the steel after solubilization shows two activation peaks. The first one (really evident) corresponds to -195 mV/SCE and is connected to the activation of the austenitic grains. The second one (almost hidden by the first one) corresponds to -340 mV/SCE and is probably due to the activation of a small volume fraction of ferrite that is present in the investigated steel. The 800°C sensitization implies some consequences:

- secondary peaks at -340 mV/SCE progressively disappear;
- reactivation peaks at about -190 mV/SCE are more and more evident (Fig. 2, right).

Considering the reactivation peaks, it is worth to note that the maximum current density is already obtained for a 800°C sensitization duration of 3 hours.

Also 2205 duplex stainless steel is characterized by the presence of two activation peaks (Fig. 3, left). The more

evident one is observed between – 240 mV/SCE (solubilized conditions) and – 180 MV/SCE (sensitized conditions). The second one is about at -300 mV/SCE. The reactivation peaks are less evident if compared to the reactivation peaks observed in the AISI 304L.
Both investigated ferritic stainless steels (Fig. 3, right) are characterized by very high current densities, considering both the activation and the reactivation stages. Focusing the reactivation stage, the current densities in ferritic stainless steels are higher than a factor of one with respect to the austenitic stainless steel and a factor of two with respect to the duplex stainless steel.

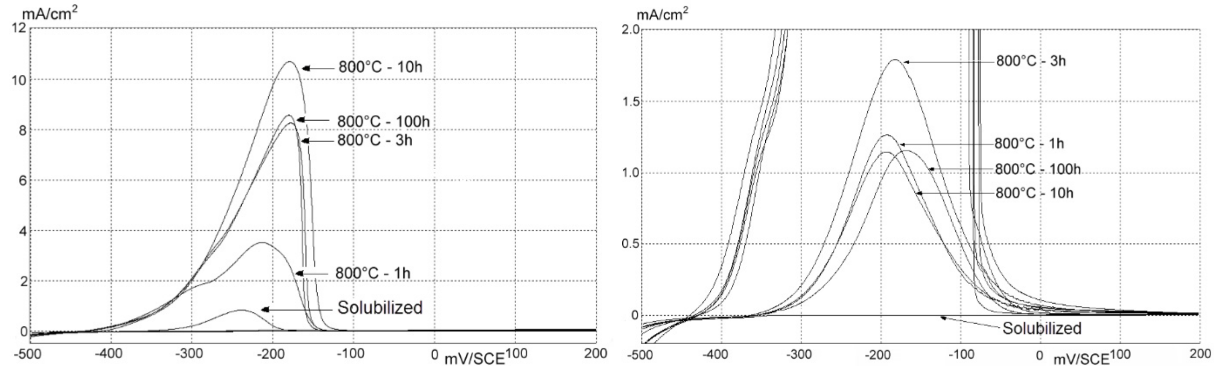

Fig. 2. DL-EPR tests results for AISI 304L: (left) activation curves; (right) reactivation curves.

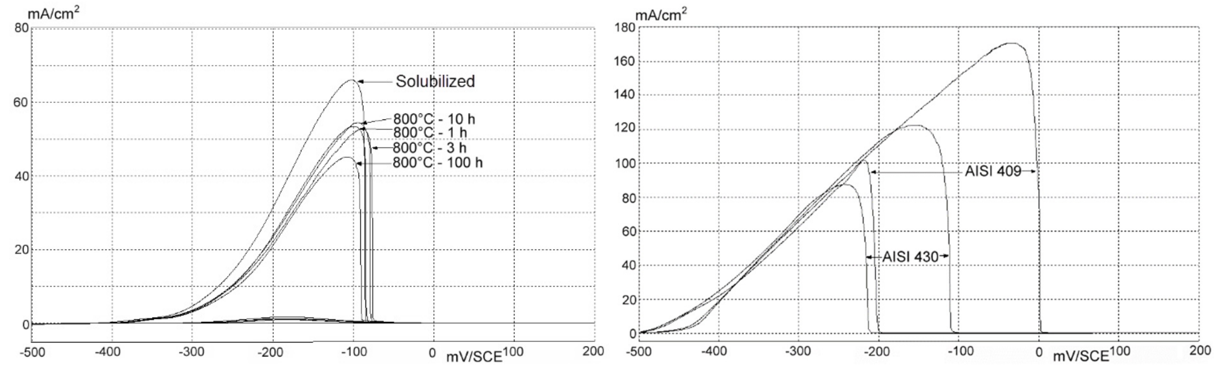

Fig. 3. DL-EPR tests results: 2205 stainless steel (left); ferritic stainless steels (right).

Considering the sensitizing index Q_R/Q_P, the microstructure influence is evident, especially considering longer sensitizing treatments (Fig. 4). The highest values of the Q_R/Q_P are always obtained after three hours at 800°C, with the 2205 duplex stainless steel that is always characterized by the lowest values. Although the Cr content in the investigated stainless steels ranges between 12 and 23%, the C content plays a key role. Considering the more critical investigated sensitizing conditions (800°C-10h), the evolution of the Q_R/Q_P ratio with the C content in Fig. 5 confirms this role: the decrease of the Q_R/Q_P ratio with the decrease of the C content is really evident.
SEM observations on the specimens after chronoamperometric tests allowed to define the different corrosion morphologies. For example, in Fig. 6, the evolution of the current density in a 800°C sensitized duplex stainless steel is shown.
Considering the duplex stainless steel, it is possible to observe that at -300 mV/SCE the intergranular attack initiates and propagates with a selective attack of the ferritic grains.

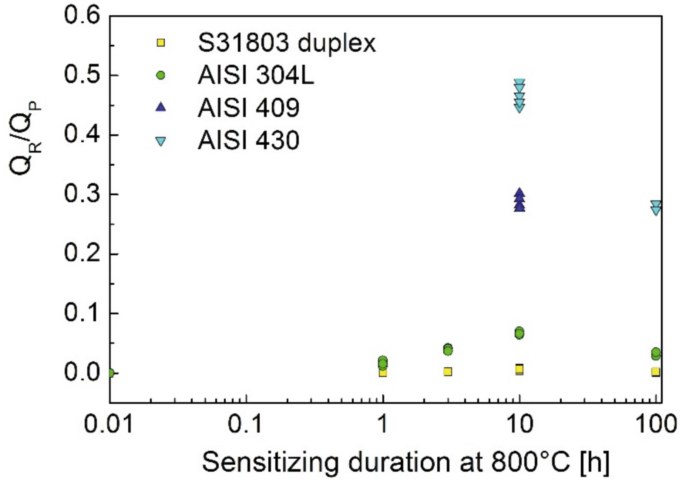

Fig. 4. Sensitizing index Q_R/Q_P evolution with the 800°C sensitizing treatment for the four investigated stainless steels.

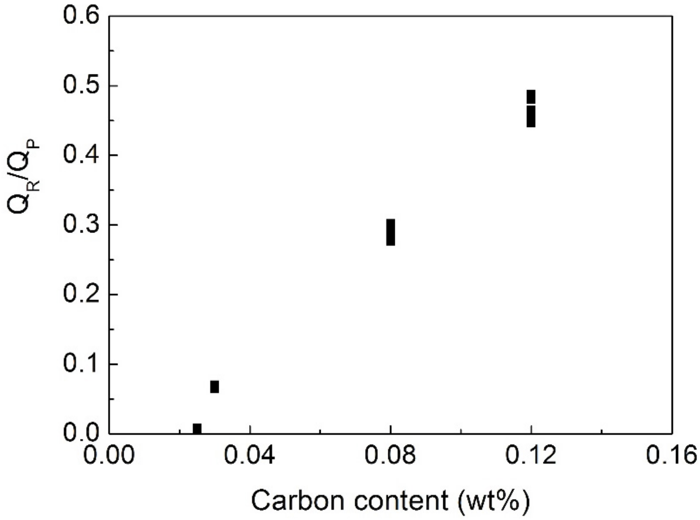

Fig. 5. Sensitizing index Q_R/Q_P evolution with the C content for the four investigated stainless steels.

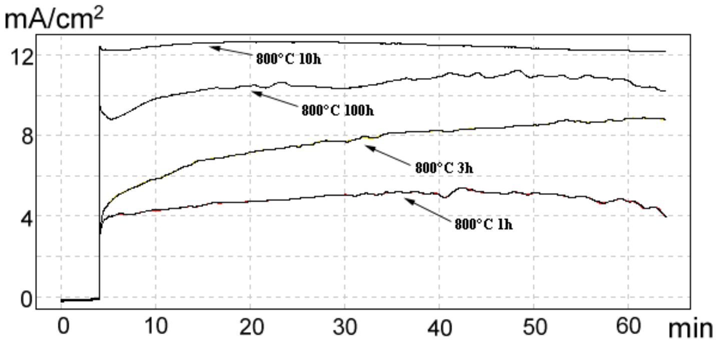

Fig. 6. 2205 duplex stainless steel: chronoamperometric tests (-300 mV/SCE).

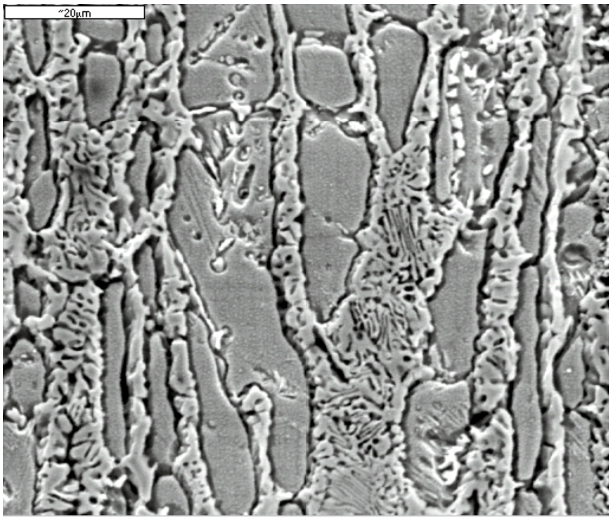

Fig. 7. 800°C -100h sensitized 2205 duplex stainless steel after a chronoamperometric test (-300 mV/SCE): SEM observation.

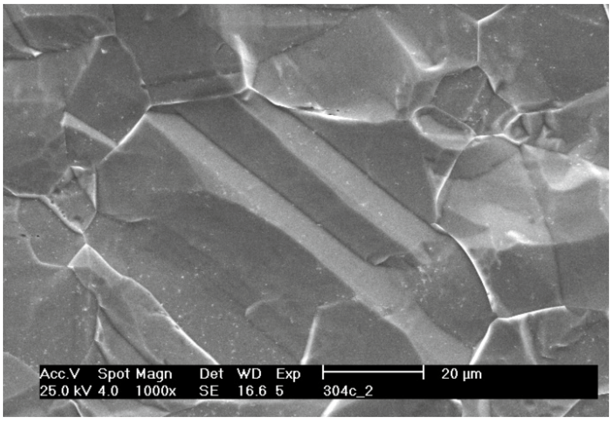

Fig. 8. 800°C -10h sensitized AISI 304L after a chronoamperometric test (-100 mV/SCE): SEM observation.

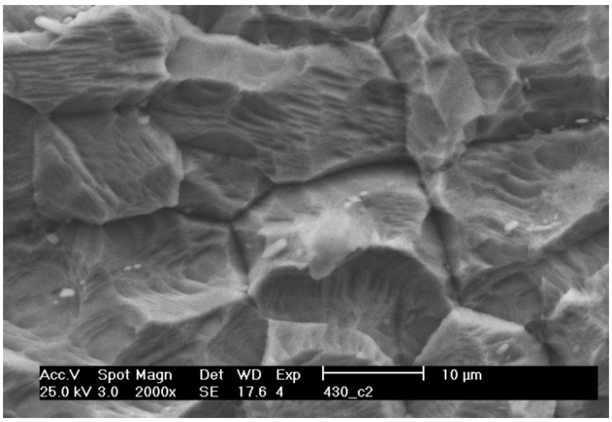

Fig. 9. 800°C -10h sensitized AISI 430 after a chronoamperometric test (-400 mV/SCE): SEM observation.

Considering the austenitic stainless steel, the intergranular attack is observed together with a selective attack corresponding to twins (Fig. 8). Instead, ferritic steels are characterized by a general corrosion superposed to the intergranular attack (Fig. 9, AISI 430).

4. Conclusions

In this work, the sensitization susceptibility of four stainless steels (AISI 304L, AISI 409, AISI 430 and SAF 2205) was investigated by means of Double Loop – Electrochemical reactivation tests and Chronoamperometric tests followed by a SEM observations of the specimens surfaces. According to the obtained results, it is possible to summarize the following conclusions:

- DL-EPR test procedure is confirmed as a high repeability test with a very good sensitivity also for low sensitized steels (e.g., duplex after 1 hour at 800°C);
- The evolution of the sensitizing susceptibility is well quantified by the Q_R/Q_P ratio. The decrease of the values of the Q_R/Q_P values after 10 hours at 800°C is probably due to a more generalized attack of the specimen surface (Cr carbides are no more localised only at grain boundaries);
- Duplex stainless steel is confirmed as characterized by the lowest susceptibility to the sensibilization phenomenon if compared to the monophasic steels (both austenitic and ferritic). Anyway, this is mainly due to its low C content rather than to its duplex structure. In fact, the influence of the duplex structure is more evident in the selective attack of the ferritic grains.

References

ASTM G108 – 94, 2015. Standard Test Method for Electrochemical Reactivation (EPR) for Detecting Sensitization of AISI Type 304 and 304L Stainless Steels.

Charles, J., 1991. The duplex stainless steels: materials to meet your needs. Duplex Stainless Steel 91, Beaune, France, Editions de Physique, 3-48.

Cihal, V., Stefec, R., 2001. On the development of the electrochemical potentiokinetic method. Electrochimica Acta, 46(24-25) , 3867-3877.

Iacoviello, F., 1997. Fragilisation par l'hydrogéne de l'acier inoxydable austeno-ferritique Z2CND2205- rôle de la microstructure. Ph.D. Thesis, Ecole Centrale Paris, 39-1997.

Outukumpu handbook, 2013. http://www.outokumpu.com/sitecollectiondocuments/outokumpu-stainless-steel-handbook.pdf.

Prohaska, M., Wernig, T., Perek, J. P., Mori, G., Tischler, G., Grill, R., 2010. Application of the DL-EPR - method for detecting sensitization to intergranular corrosion in thermomechanically rolled corrosion-resistant alloys 316L, 825L and 926L. 2nd International Conference Corrosion and Material Protection, 1-8.