HEAT TREATMENT INFLUENCE ON LOCALIZED AND SELECTIVE CORROSION RESISTANCE IN A 21 Cr 1 Ni DUPLEX STAINLESS STEEL

Vittorio Di Cocco, Francesco Iacoviello, Ornella Di Bartolomeo, Donatella Cipriani

Duplex stainless steels offer a good combination of mechanical properties and corrosion resistance compared to standard austenitic grades. They are widely used in chemical, petrochemical, fertilizer and cellulose industries. These steels solidify liquid + ferritic field and it is during cooling of the solid that a partial ferrite transformation into austenite takes place. The amount of austenite and ferrite phases depends on chemical composition and cooling rate. The best combination of mechanical properties and corrosion resistance is obtained with a $\alpha/\gamma$ volume ratio near to 1. In this work, localized corrosion resistance of a rolled duplex stainless steel 21 Cr 1 Ni was investigated by means of Double Loop Electrochemical Potentiodynamic Reactivation (DL-EPR) and potentiostatic tests performed using a computer controlled system (0.5 M $\text{H}_2\text{SO}_4$ + 0.01 M KSCN aqueous solution). This procedure was optimized to investigate the austenitic stainless steels intergranular corrosion susceptibility, but it was found to be useful also for other localized corrosion mechanisms (e.g. pitting, stress corrosion cracking). Furthermore, in order to identify the main localized corrosion morphologies, specimens surfaces were investigated by means of a light optical microscope. Finally, results were compared with the localized corrosion resistance of two 22 Cr 5 Ni stainless steels (characterized by different $\alpha/\gamma$ ratios).

KEYWORDS: stainless steel, corrosion

INTRODUCTION

Duplex stainless steels offer a good combination of mechanical properties and corrosion resistance compared to standard austenitic grades [1-2], because of their austenitic-ferritic microstructure. They are widely used in chemical, petrochemical, fertilizer and cellulose industries [3]. These steels solidify liquid + ferritic field and it is during cooling of the solid that a partial ferrite transformation into austenite takes place. The amount of austenite and ferrite phases depends on chemical composition and cooling rate [4]. The best combination of mechanical properties and corrosion resistance is obtained with a $\alpha/\gamma$ volume ratio near to 1. Duplex stainless steels are characterized by many microstructure modifications (Fig. 1).

Fig. 1

T.T.T (Transformation–Time–Temperature) diagram for three different austenitic-ferritic stainless steels [3].

Diagramma TTT (Trasformazione – Tempo – Temperatura) per tre differenti acciai inossidabili austeno-ferritici [3].
Above 1050°C, austenite transforms into ferrite. This ferritization process implies a modification both in volume fraction and in partition coefficients, with an increasing of interstitial elements content (e.g. hydrogen and nitrogen) in ferrite grains [5]. Below 1050°C, duplex stainless steels shows two different critical temperature ranges. In the 600-1050°C range many carbides, nitrides, intermetallic and secondary phases could precipitate. Carbides M₇C₃ and M₂₃C₆ carbides precipitation could implies a decreasing of Cr content at grain boundaries [9, 10], with a decreasing of localised corrosion resistance considering both the intergranular attack susceptibility and a selective attack of ferrite grains. The aim of this work is the analysis of the localized corrosion resistance in a 21 Cr 1 Ni austenitic-ferritic stainless steels considering several ageing heat treatments. This resistance was evaluated by means of electrochemical potentiokinetic (EPR tests) and potentiostatic tests and compared with the resistance of two 22 Cr 5 Ni duplex [10, 13-15] with different α/γ volume fractions (equal to 1 and 1.5, respectively).

**MATERIALS AND EXPERIMENTAL PROCEDURES**

Sensitization degree investigations could be performed by both destructive and time consuming methods (e.g. ASTM A262 [16]), and non destructive, fast, quantitative, but partially standardized or not standardized electrochemical methods. Among partially standardized methods, the Electrochemical Potentiokinetic Reactivation methods (EPR) [17] are often used to investigate the degree of sensitization, allowing a quantitative analysis of this susceptibility. These methods render the functional dependence of current density in response to changes of applied potential [18]. Many types of EPR methods are available. Among them we can consider Single Loop-EPR (SL-EPR) test and Double Loop-EPR (DL-EPR) test. In SL-EPR test the curve is a reverse curve, with the potential scan from positive to negative. In DL-EPR test the curve is polarized anodically at a given rate from the corroding potential to a potential in the passive area. Then the scanning direction is reversed and the potential is decreased at the same rate to the corroding potential. This reactivation implies a preferential breakdown of the passive film corresponding to chromium depleted areas, where chromium carbides precipitation takes place. DL-EPR method has the advantage to be substantially independent on the surface finishing. Sensitization degree is evaluated as Q/S ratio (Area under reactivation peak/Area under activation peak).

A rolled “lean” austeno-ferritic duplex stainless steel characterized by an α/γ volume fraction ratio equal to 1 was considered for the investigation (Tab. 1) and results were compared with those formerly obtained considering...
a duplex stainless steel 22 Cr 5 Ni, with different α/γ volume fractions (Tab. 2 and 3). 21 Cr 1 Ni duplex stainless steel localized corrosion resistance was investigated both after solution annealing and after different tempering heat treatments (3 hours at 350, 400, 450, 460, 470, 480, 490, 500, 550, 600°C; 475°C tempering temperature was also investigated for 1000 hours). An aqueous solution 0.5M H$_2$SO$_4$ + 0.01 KSCN was considered, with an exposed area of the sample of 1 cm$^2$. After establishing of $E_{corr}$, the specimen was polarized from the initial potential (-500 mV/SCE), in the cathodic region, to a version potential of +200 mV/SCE, with a sweep rate of 50 mV/min. As soon as this potential was reached, the scanning direction was reversed and, always considering the same sweep rate, the potential was decreased to the initial potential. Tests were performed at 25°C and they were repeated five times, in order to control the results reproducibility. Working electrodes consisted of cubic samples insulated in epoxy resin, polished with a 1200 silicon carbide paper, rinsed in alcohol and dried before each measurement. A platinum counter electrode and a saturated calomel reference electrode were used. Potentiostatic tests were performed (same solution of DL-EPR tests; potential pause equal to 200 mV/SCE for 2 minutes; tests duration up to 1 hour) at potential values selected on the basis of the DL-EPR tests results. Specimens surfaces were analyzed by means of a light optical microscope (LOM), in order to identify the main attack morphologies.

**RESULTS AND DISCUSSION**

DL-EPR tests results confirms their high repeability and only one curve is sufficient to characterize the applied potential-current density behavior for all the investigated conditions. In order to evidence both activation and reactivation curves, two different diagrams are used (Fig. 4 and 5, respectively). In the investigated potential range, activation curves do not show evident secondary maxima for all the investigate heat treatments. The investigated stainless steel in solubilized conditions shows a reactiva-

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**Tab. 2**

22 Cr 5 Ni duplex stainless steel (PREN = 35); EN 1.4462: chemical composition, wt% (α/γ=1).

Composizione chimica (%peso) dell'acciaio inossidabile duplex 22 Cr 5 Ni (EN 1.4462; PREN = 35; α/γ=1).

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<th>C</th>
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**Tab. 3**

22 Cr 5 Ni duplex stainless steel (PREN = 35); EN 1.4462: chemical composition, wt% (α/γ=1.5).

Composizione chimica (%peso) dell'acciaio inossidabile duplex 22 Cr 5 Ni (EN 1.4462; PREN = 26; α/γ=1.5).
A very low current density value, corresponding to the same potential of the reactivation maxima obtained with all the investigated heat treatments. \( Q_r/Q_p \) ratio (Area under reactivation peak/Area under activation peak) as a function of the tempering temperature (3 hours) shows an evident peak corresponding to 475°C (Fig. 6). The increase of the tempering duration (between 3 to 1000 hours) correspond to an evident increase of the \( Q_r/Q_p \) value (up to a factor of two). Corresponding to tempering temperature higher than 490°C, \( Q_r/Q_p \) values sharply increase (tempering duration equals to 3 hours). Potentiostatic tests performed on 21 Cr 1 Ni tempered at 475°C (V = -380 mV/SCE, corresponding to the reactivation peak) allows to identify the attack mechanism (Fig. 7). It is evident that after an initial stage with a selective attack of ferrite grain (Fig. 7a-c), there is not the superposition of localized corrosion attack: ferrite grains selective attack develops up to 3600 seconds (figures 7d-f). An analogous attack sequence was observed considering the 475°C – 1000 hours tempered steel.

Both investigated 22 Cr 5 Ni duplex stainless steels in solubilized conditions do not show any reactivation maxima, and the activation curves depend on the \( \alpha/\gamma \) ratio (Fig. 8, [10]). Comparing their behavior with 21 Cr 1 Ni, \( \alpha/\gamma \) ratio and chemical composition influence is evident. If this value is equal to 1, only one maximum is evident in the activation curve, corresponding to an applied potential of about -240 mV/SCE, both in 21 Cr 1 Ni and in 22
Cr 5 Ni duplex stainless steel, with the “lean” steel that is characterized by a higher density current (up to a factor of one). If the considered 22 Cr 5 Ni stainless steel is characterized by an $\alpha/\gamma$ ratio equal to 1.5, the higher ferrite volume fraction implies the presence of two maxima, with higher density current values if compared to the 22 Cr 5 Ni with an $\alpha/\gamma$ ratio equal to 1: the first corresponds to about $-280 \text{ mV/SCE}$ and the second corresponds to about $-180 \text{ mV/SCE}$.

The influence of the 475°C permanence on the DL-EPR results depends on the $\alpha/\gamma$ ratio and on the steel chemical composition. Considering 22 Cr 5 Ni duplex stainless steels, if $\alpha/\gamma$ ratio is equal to 1 (Fig. 9), both the activation and the reactivation curves do not differ from the curves obtained considering the stainless steel after solubilization (Fig. 8): the activation maximum corresponds to the same potential with almost the same current density and no reactivation maxima are observed. If $\alpha/\gamma$ ratio is equal to 1.5 (Fig. 9), after a tempering treatment at 475°C for 1000 hours, it is evident an increase of the activation maximum current density (from about 4 up to about 10 mA/cm²) and a lower importance of the activation maximum at -280 mV/SCE, probably due to the increase of the first maximum. Furthermore, two different reactivation maxima are evident. The first corresponds to $-280 \text{ mV/SCE}$ with a current density of about 3.5 mA/cm² (this value is comparable with the activation maximum obtained with the solubilized steel), and the second is less evident at about $-480 \text{ mV/SCE}$, with a current density of about 0.5 mA/cm². 21 Cr Ni steel after a tempering heat treatment at 475°C for 1000 hours is characterized by an activation maximum that is analogous to the value obtained with the solubilized steel, and by a reactivation curve that is characterized by at least three peaks: the more evident one corresponds to a potential of about $-300 \text{ mV/SCE}$; the second corresponds to a potential of about $-430 \text{ mV/SCE}$; the third corresponds to a potential of about $-480 \text{ mV/SCE}$ (exactly the same value of the second maximum in the reactivation curve of the sensitized 22 Cr 5 Ni, $\alpha/\gamma = 1.5$).
third maximum (corresponding to a potential of about -430 mV/SCE) seems to be connected to a different attack morphology (Fig. 11), with austenite grains that are more evidently attacked. It is necessary to point out that this peak is observed only in 21 Cr 1 Ni steel: considering also the importance of the partition coefficients, probably this is due to the differences in chemical composition especially concerning the Ni and Mo content.

CONCLUSIONS

In the present work, localized and corrosion resistance of 21 Cr 1 Ni “lean” duplex stainless steel was investigated by means of Double Loop Electrochemical Potentiodynamic Reactivation (DL-EPR) and potentiostatic tests and LOM surface observations. 21 Cr 1 Ni stainless steel behavior was investigated after different tempering heat treatments (up to 600°C). Experimental results were compared with the behavior of two 22 Cr 5 Ni austenitic-ferritic (duplex) stainless steels characterized by different ferrite/austenite ratios (e.g. \( \alpha / \gamma = 1.5 \)) and sensitized at 475°C (up to 1000 hours). Experimental results allow to summarize the following considerations:

- Intergranular corrosion seems to be always connected to G phase precipitation, with analogous electrochemical conditions of the previously investigated 22 Cr 5 Ni steel (\( \alpha / \gamma = 1.5 \));
- Lower Ni and Mo contents that characterize the investigated 21 Cr 1 Ni “lean” duplex stainless steel implies the possibility that austenite grain are attacked, with an attack morphology that develops after ferrite grains selective corrosion.

ACKNOWLEDGMENTS

Outokumpu S.p.A. is warmly acknowledged.

REFERENCES

16) ASTM A262-86 Standard practices for detecting susceptibility to intergranular attack in austenitic stainless steel, section 3, vol.03.02.
INFLUENZA DEL TRATTAMENTO TERMICO SULLA CORROSIONE LOCALIZZATA E SELETTIVA DI UN ACCIAIO DUPLEX 21 Cr 1 Ni

Parole chiave: acciaio inox, corrosione

Gli acciai inossidabili duplex affrono una buona combinazione di proprietà meccaniche e di resistenza alla corrosione [1-2], grazie alla loro microstruttura austenito-ferritica. Sono largamente utilizzati nelle industrie chimiche, petrolchimiche, alimentari, nucleari [3]. Questi acciai solidificano formando ferrite e durante il raffreddamento si ottiene una parziale trasformazione del la ferrite in austenite. Le frazioni volumetriche di ferrite ed austenite dipendono dalla composizione chimica e dalla velocità di raffreddamento [4], con la migliore combinazione di proprietà meccaniche e resistenza alla corrosione che viene ottenuta con un rapporto volumetrico A/γ pari a circa 1. Gli acciai inossidabili duplex sono caratterizzati da numerose trasformazioni microstrutturali (Fig. 1). 

Al di sopra di 1050°C, l’austenite si trasforma in ferrite. Questo processo di raffreddamento implica una modifica sia delle frazioni volumetriche che dei coefficienti di ripartizione, con un aumento del tenore degli elementi interstizi negli grani ferritici [5]. Ai di sotto di 1050°C, gli acciai inossidabili duplex sono caratterizzati da due differenti intervalli di temperatura critici. Fra 600-1050°C, nei grani ferritici oppure in corrispondenza dei bordi grano A/γ o A/γ, possono precipitare carburati M₇C₃ (fra 950 e 1050°C) e M₇C₆ (fra 600 e 950°C), nitruri (M, Cr, N, Cr, N), fasi intermetalliche (A, x, R) ed austenite secondaria A/γ che cambiano in funzione della temperatura di rinvenimento (3 ore di permanenza) [6]. Tali precipitazioni implicano una evidente modifica delle proprietà meccaniche [7], ad esempio con una evidente diminuzione della resistenza alla propagazione della crica di fatica [8]. Nell’intervallo di temperatura compreso fra 350 e 600 °C, si verifica la decomposizione spinodale dei grani ferritici e la precipitazione della fase G in corrispondenza dei bordi grano A/γ [9, 10]. Le particelle di fase G sono caratterizzate da una composizione chimica differente dall’acciaio considerato e dalle condizioni di invecchiamento, con un tenore complessivo di Ni+Si+Mn+Mo+Al che aumenta dal 20% al 60% per una permanenza a 350°C che varia da 1000 a 3000 ore [11]. La precipitazione della fase A/γ dei carburati M₇C₃ e M₇C₆ può implicare una diminuzione del tenore di Cr a bordo grano A/γ con una diminuzione della resistenza alla corrosione localizzata (sia intergranulare che selettiva in corrispondenza dei bordi grano A/γ [10, 13-15]. Le curve di attivazione e di reattivazione sono rispettivamente ripor- tate nelle Fig. 4 e 5. Le curve di attivazione relative all’acciaio 21 Cr 1 Ni non mostrano evidenti massimi secondari per tutti i trattamenti termici investigati. Nel caso dell’acciaio solubilizzato, il massimo della curva di attivazione è caratterizzato da una densità di corrente molto bassa, con un valore del potenziale che corrisponde ai massimi delle curve di reattivazione. Il terzo massimo è stato osservato solo nell’acciaio 21 Cr 1 Ni trattato termicamente. L’evozione del rapporto Q/Q (Area del picco di reattivazione / Area del picco di attivazione) in funzione della temperatura di rinvecimento (3 ore di permanenza) mostra un massimo evidente in corrispondenza della curva di attivazione (Fig. 6). Per tempi più elevati di permanenza a 475°C (fino a 1000 ore) si ha un corrispondente incremento del rapporto Q/Q (fino a due ordini di grandezza più elevato). Per rinvecimenti effettuati al di sopra di 490°C, il rapporto Q/Q aumenta bruscamente. Le prove potenziostatiche effettuate considerando l’acciaio 21 Cr 1 Ni rinvenuto a 475°C per 3 ore (V = +380mV/SCE, in corrispondenza del picco di reattivazione) permette di identificare il meccanismo di attacco (Fig. 7). Risulta evidente che, dopo una fase iniziale cui corrisponde un attac-