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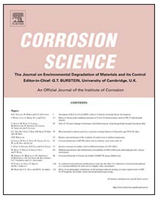

Study of stainless steels corrosion in a strong acid mixture. Part 2: anodic selective dissolution, weight loss and electrochemical impedance spectroscopy tests

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ABSTRACT

The corrosion resistance of austenitic stainless steels AISI 316L, AISI 904L and Sanicro 28 and duplex stainless steels SAF 2205, SAF 2507 and SAF 2707, was studied at 40 and 60 °C in a strong acid mixture containing tartaric acid saturated solution, H_2SO_4 and HCl. Anodic selective dissolution, weight loss and electrochemical impedance tests were performed. The results show that all stainless steels corrode actively and the micro-galvanic coupling, present on duplex stainless steels and 316L, determines severe selective corrosion and impairs their tendency to passivate. 904L and Sanicro 28 showed this tendency and the lowest corrosion rates.

1. Introduction

As considered in Part 1 of this work [1], AISI 316L stainless steel (SS) was subjected to a severe corrosion in contact with a strong acid mixture in an industrial plant for the production of tartaric acid, as a by-product of grape pressing. The acid mixture consists of a tartaric acid saturated solution, containing also H_2SO_4 and HCl, which operates at the temperature range of 22–60 °C. In order to substitute 316L components of this plant, different SSs were considered and tested in this investigation: the super austenitic stainless steels (ASSs) AISI 904L and Sanicro 28 (S28) and the duplex stainless steels (DSSs) SAF 2205, SAF 2507 and SAF 2707.

These materials were previously examined [2] through the qualitative comparison of their anodic characteristics and the weight loss tests. Subsequently, by means of the analytical method shown in Part 1 of this work [1], the characteristic potentials and current densities were obtained from anodic polarization curves and a quantitative comparison of the tested SSs was carried out. Part 1 of this work was also dedicated to studying the effect of temperature and SS alloying elements on the current/potential parameters. In addition, simplified anodic characteristics of the SSs were proposed. From the results obtained, 904L, S28 and 2707 were found to be the SSs with the best anodic characteristics throughout the entire testing temperature range [1]. In particular, the corrosion behaviour of 2707 DSS was found sensibly dependent on surface finishing because a pure passive characteristic turned to an active-passive one with the increase of surface roughness [2]. In any case, more specific indications on the corrosion mechanisms of all these SSs have not yet been provided, in order to give clear information on their durability.

DSSs steels have a high tendency to passivate in particular in alkaline environments, when for example they are used as reinforcements [3,4]. In these conditions, they form a passive film, enriched in Cr(III) and Mo(IV) and in Ni underneath it [4], which guarantees corrosion resistance higher than that of ASSs, in terms of pitting and stress corrosion cracking, in presence of chlorides [5,6]. In acid media, these alloys suffer selective corrosion which significantly impairs their corrosion resistance. A number of papers were devoted to studying this phenomenon in aqueous solutions of H_2SO_4 and HCl [3,6–12], paying particular attention on the effect produced by DSSs microstructure [3,8] and composition [3,11]. Furthermore, the effect determined by the composition of H_2SO_4/HCl mixes have been considered [7,9]. Almost all authors agree on the fact that the most active phase of DSSs in different acid solutions, which initiates the corrosion, is the ferritic (α) phase, while the noblest phase is the austenitic (γ) one. An inversion of this galvanic couple has been observed for 2205 alloy in HNO_3 solutions by other authors [10]. Taking into account that in the present study, apart from tartaric acid, a mix of H_2SO_4 and HCl is present in the testing acid solution, similar to that used by other authors, the selective corrosion of the studied DDSs is expected. In the previous work [2], only a few observations of the preferential dissolution of α phase on 2507 DSS were reported.

904L high-alloy SS (20Cr-25Ni-4Mo-1.4Cu), when compared to 300-series SSs, shows higher corrosion resistance in severe corrosion environments, including the acid ones [2]. High Ni, Cr, Mo and Cu

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contents guarantee such a high corrosion resistance especially in sulfuric acid [13]. In particular, the effect of copper in this environment is well-documented [13–18] even if the mechanism of its action is not completely known: only a small number of hypotheses were done on the formation of a protective copper containing layer on the surface [14], which promotes the active-passive transition of SSs [15].

S28 is a high-alloy multipurpose ASS (27Cr-31Ni-3Mo-1Cu) [1,2,19], characterized by a high corrosion resistance in strong acids, developed for the heat exchangers in the manufacturing process of phosphoric acid [20,21]. This material presents performances similar to those of 904L, due to the presence of Cu [16], but in critical corrosive environments it gives better protection than 904L [19,20].

The aim of this work is to assess the durability of 316L, 904L, S28, 2205, 2507 and 2707 SSs in a tartaric acid saturated solution, containing also H_2SO_4 and HCl, at 40 °C and 60 °C. The selective corrosion of DSSs was studied by means of an anodic selective dissolution (ASD) method. DSSs were electrochemically characterized through anodic polarization curves performed on the samples of these biphasic alloys and also on the separate α and γ phase electrodes, obtained by ASD in accordance to other authors [10,11]. Weight loss tests were carried out on all SSs having a surface finishing of 1200 grit and the results were compared with those obtained on as-received SS samples [2]. This comparison was done to study the effect of surface finishing. Finally, the corrosion behaviour of the SSs was monitored in the testing acid mixture at 60 °C by means of electrochemical impedance spectroscopy (EIS) for an exposure time of three days, to observe the difference in the corrosion mechanism of the examined alloys. To complete this study, optical microscopy (OM), scanning electron microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) were also performed.

2. Experimental

The six SSs examined in this work and the testing strong acid mixture are the same as in Part 1 [1]: the chemical composition of the alloys are reported in Table 1, while the mixture (density = 1.276 g/cm^3 and pH = −0.66) was formed by tartaric acid saturated solution, H_2SO_4 (3.42 wt%; 0.35 M) and HCl (0.45 wt%; 0.12 M), respectively. Almost all tests were performed at 60 °C, i.e. under the most severe corrosion conditions. Only the electrochemical characterization of the DSS phases was carried out at 40 °C. The temperature was maintained in the range of ± 2 °C using a thermostatic bath.

The presence of two electrochemically different phases in the studied DSSs is revealed by the two anodic peaks in the active-passive transition region of the polarization curve recorded in the strong acid mixture, just above the corrosion potential (E_{corr}), as shown in Fig. 1. The potentials E_1 and E_2 reported in Fig. 1 correspond to the maxima of current densities for the first peak (phase 1) and the second peak (phase 2), respectively. The correspondence between these two anodic peaks and the phases α and γ of the DSSs was found thanks to the electrochemical characterization of two separate phase electrodes, which were produced by means of two separate potentiostatic ASDs [10,11] of the initially unknown phase 1 and phase 2. Fig. 2 shows a scheme of the effect produced by the ASD method on a DSS. In particular, Fig. 2a shows a generic picture of a DSS cross-section with the distribution of the grains corresponding to the phases 1 and 2, before the application of ASD. In order to obtain the phase 2 electrode (Fig. 2b), the samples of DSSs, having an exposed surface of 2.55 cm^2 (2507, 2707) or 0.31 cm^2 (2205), ground with emery papers up to 1200 grit, were initially submitted to a potentiodynamic scan at 0.166 mV/s in the testing solution by means of an AMEL 5000 potentiostat. The polarization started from a cathodic potential of −0.03 V with respect to E_{corr} and proceeded toward anodic potentials. To perform this polarization, a Pt spiral wire as the counter electrode and a saturated calomel electrode (SCE, +0.241 V vs SHE at 25 °C) as the reference electrode were used. The latter was placed in a Luggin capillary in such a way that it remained outside the cell at room temperature, while the capillary tip was immersed in the testing solution close to the working electrode surface. The scan was manually stopped at the potential E_1, corresponding to the first anodic peak (Fig. 1), as soon as the current density, upon reaching a maximum value, started to decrease slightly. This potential was held to perform the potentiostatic ASD for the time necessary (from few hours for 2205 to 1 day for 2507 and 2707) to dissolve at E_1 the phase 1 up to a depth of 10–20 μm, verified by OM. The potentiostatic ASD was performed at 60 °C where the two anodic peaks resulted to be more separated than those observed at 40 °C.

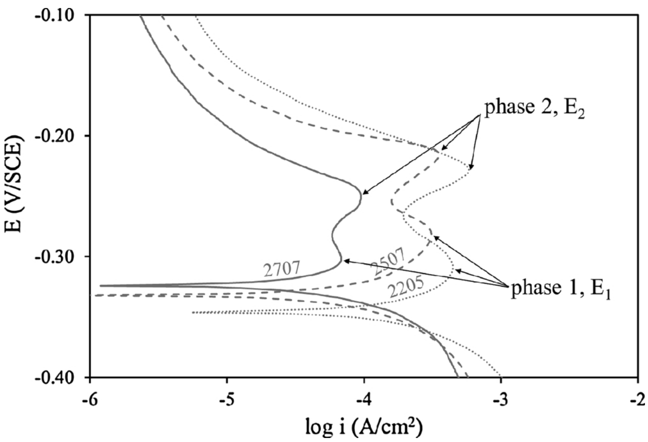

Fig. 1. Anodic polarization curves (scan rate 0.166 mV/s) performed on 2205, 2507 and 2707 DSSs in the testing acid mixture at 40 °C.

Table 1
Chemical composition[a] of the studied SSs (wt%).

Alloy	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Ti
316L	0.03	0.52	1.09	0.04	0.01	17.23	1.97	10.91	0.15	0.18
904L	0.02	0.32	1.44	0.03	0.01	20.28	4.14	25.39	1.42	0.01
S28	0.02	0.40	1.61	0.03	0.06	26.57	3.06	31.60	0.98	0.01
2205	0.03	0.50	0.76	0.03	0.01	22.49	3.13	5.99	0.11	0.01
2507	0.03	0.31	0.42	0.04	0.07	25.82	4.05	6.99	0.14	0.01
2707	0.03	0.27	0.89	0.04	0.01	27.02	5.00	6.57	0.13	0.01

[a] The rest is Fe.

After the ASD, the cavities left by the dissolved phase 1 were filled by a high flowing transparent epoxy resin (r in Fig. 2b), which was pink-red in colour, obtained with an organic substance, in order to facilitate the observation by OM that the filling operation has occurred. Before the observation, the sample was carefully ground with emery papers up to 1200 grit, to remove the excess of hardened epoxy resin present on the top of the sample surface. Following the same procedure, but stopping the scan at potential E_2, which was maintained for a sufficient time as to produce the dissolution of phase 2, an electrode with the only phase 1 was obtained, as well (the cross-section is represented in Fig. 2c).

Phase 1 and phase 2 separated electrodes were identified as α and γ phases by means of SEM observations and EDX analysis (Zeiss Supra 40 microscope coupled with a Bruker Quantax serie 5000L N_2-free XFlash). Furthermore, the separate phase electrodes were electrochemically characterized by recording anodic polarization curves in the same experimental conditions used for recording the curves of Fig. 1. The tests were carried out at 40 °C, which is a suitable operating temperature for the epoxy resin used for filling the cavities, because its glass transition temperature is around this value. All anodic curves were corrected for the ohmic drop (3–10 Ω) between working and reference electrodes.

Weight loss measurements were carried out on different samples of the examined SSs, prepared with a surface finishing of 1200 grit, immersed in the testing acid mixture, kept in an oven at 60 ± 3 °C for 3–10 days. Average corrosion rates in mm/year were calculated [22]. To study the effect of the surface finishing, these results were compared