

## Corrosion Characterization of Sintered Stainless Steel Filters with Surface Films Formed in Sulfuric Acid Solutions Containing BTAH

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**Abstract:** The aim of the present work was to develop a surface film on 304L SS filters to increase their corrosion resistance in acid solutions. Film formation was carried out by immersion in sulphuric acid solution containing benzotriazole (BTAH). The filters, after surface treatment, were immersed in a solution of sulphuric acid (3 mol/L). The corrosion behaviour of the filters was evaluated by measurements of open circuit potential at increasing times, electrochemical impedance spectroscopy (EIS) versus time, and polarization curves. The filters surface treated in BTAH containing solutions had significantly more noble corrosion potentials and much lower passive current densities than the bare filters. In addition EIS results indicated stability of the film after a partial attack.

### Introduction

Stainless steel (SS) filters produced by Powder Metallurgy (P/M) find many applications in various industries, such as chemical, petrochemical, nuclear and medical. These filters are used for solid-liquid separation, gas filtering, separation of antibiotic crystals, or any application where the contaminants are detrimental to the final product. In many of these applications the filters are exposed to corrosive environments. Therefore, corrosion resistance is a desirable property of a filter [1-12]. The large surface area of filters exposed to the corrosive medium can lead to high corrosion rates, depending on the characteristics of the surface.

There are many works [13-15] studying the corrosion resistance of conventional stainless steels (SS) in acid media. These studies evaluated the effect of chemical composition, microstructure, and heat treatment on corrosion performance. Inside pores, aeration conditions differ from those observed on external areas. This fact changes the corrosion behavior of sintered SS from those of conventional ones. Excessive open porosity increases the area exposed to a corrosive environment and, consequently, induces crevice corrosion. The formation of concentration cells in the interior of pores reduces the passivity of sintered materials [16-18]. Therefore, sintered SS have inferior corrosion resistance compared to similar materials produced by conventional metallurgy, a feature of their porosity [19,20].

Rodrigues [13] studying conventional 304 SS in sulphuric acid observed general corrosion in a solution made of 2 mol/L H<sub>2</sub>SO<sub>4</sub>. The resistance of this material increased in the same solution with addition of benzotriazole (BTAH), the latter compound acting as a corrosion inhibitor. It was found that on immersion of conventional 304 SS in 2 mol/L H<sub>2</sub>SO<sub>4</sub> containing BTAH, a surface film was formed. The film increased the corrosion resistance of the 304 SS upon immersion in a H<sub>2</sub>SO<sub>4</sub> solution without BTAH.

Since BTAH is a corrosion inhibitor of conventional SS by formation of a surface film, the aim of the present work was to investigate the effect of BTAH on the formation of a film on sintered 304L SS filters, and to evaluate the corrosion resistance of the surface treated sintered filter in sulphuric acid solution.

### Experimental

*Material.* 304L stainless steel (SS) filters prepared from powder of granulometric range (35–50) mesh were used in this study. The filters were compacted in a cylindrical matrix of 14 mm diameter with a compacting pressure of 300 MPa, without addition of lubricant. After compacting, the filters were sintered under vacuum for one hour at 1200 °C. Cylindrical filters of 14.0 mm x 3.8 mm were obtained. The carbon content of the filter was 0.019 %. Fig. 1 shows one of the surfaces of the 304L SS filter used in this study.



Fig. 1. SEM of 304L SS filter used in this investigation.

Large pores are seen in the filter used. These are due to the fairly low compacting pressures used (300 MPa), besides the large grain sizes used in the filter fabrication.

*Experimental set-up.* A three electrode cell arrangement was used for the electrochemical measurements, with a large area platinum foil and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. Electrochemical Impedance Spectroscopy (EIS) measurements were accomplished with a 1255 Solartron frequency response analyzer coupled to a EG&G 273A Potentiostat. All measurements were performed in the potentiostatic mode at the corrosion potential,  $E_{\text{corr}}$ . The polarization curves were obtained after 1 day of immersion, when the specimens had reached a steady state. The polarization range used was from the corrosion potential until 1300 mV/SCE. EIS measurements were carried out at frequency range from  $10^5$  to  $10^{-2}$  Hz, and the amplitude of the perturbation signal was 10 mV. A Philips XL-30 scanning electron microscope was used for surface observation before and after corrosion testing.

*Test solutions.* 3 mol/L  $\text{H}_2\text{SO}_4$  solutions with and without BTAH were used. The solutions used were all quiescent, aerated and at a temperature of  $(25 \pm 1)$  °C.

### Results and discussion

A surface treatment to develop a film on 304L SS filters was carried out by immersion of 304L SS filters in a solution made of 3 mol/L  $\text{H}_2\text{SO}_4$  and 0,1 mol/L BTAH for 7 days. The development of the film on the filter surface was monitored by EIS measurements as a function of time, Fig. 2.

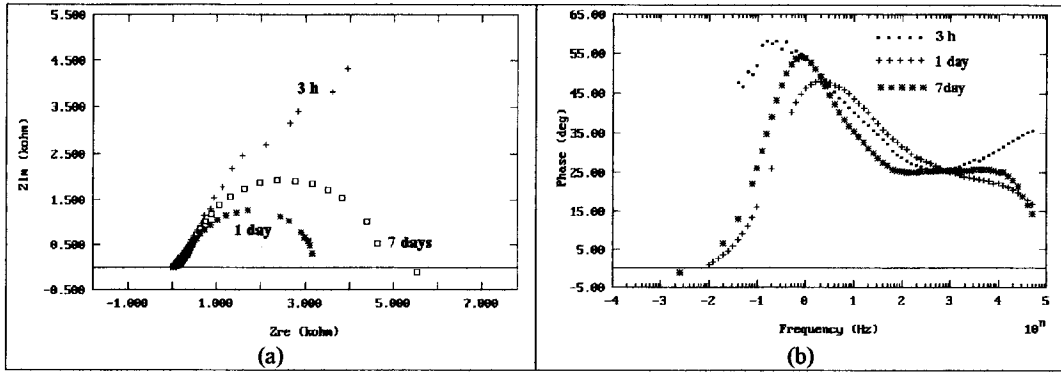


Fig. 2: EIS results at increasing times of immersion of 304L SS filter in 3 mol/L H<sub>2</sub>SO<sub>4</sub> and 0,1 mol/L BTAH. (a) Nyquist diagrams, (b) Bode phase diagrams.

The total surface area of the filters tested was measured by mercury porosimetry and a value of 173.65 cm<sup>2</sup> was obtained. The EIS results presented in Fig. 2 did not take into account the total area of filter exposed to the test solution. For comparison with literature results, the total area of the filter exposed to solution must be considered.

The results obtained after 3 hours of immersion show scattered data at low frequencies indicating that the steady state required to get reliable EIS data had not been reached. At 1 day of immersion a steady state was obtained and the Bode diagrams show two peaks, suggesting the formation of a film on the filter surface. The peak at high frequencies is likely to be related to the film, and that at low frequencies, to charge transfer processes. The resistance related to charge transfer processes (Nyquist diagrams) increased as the time of immersion in BTAH containing solution increased, from nearly  $3.3 \cdot 10^3$  ohms (1 day) to approximately  $4.7 \cdot 10^3$  ohms (7 days).

The electrochemical behavior of the 304L SS filter in both solutions, with and without BTAH, was also investigated by polarization tests. Open circuit potential measurements indicated that a stable potential was reached by specimens after 1 day of immersion in 3 mol/L H<sub>2</sub>SO<sub>4</sub>, both with 0,1 mol/L BTAH or without it. Polarization curves were then obtained for filters immersed for one day, in either solution, the results are shown in Fig. 3.

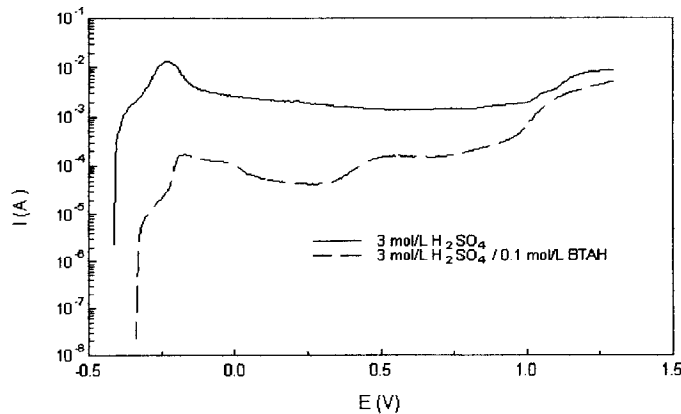


Fig. 3: Polarization curves of 304L SS filter after 1 day in 3 mol/L H<sub>2</sub>SO<sub>4</sub> solutions, with or without BTAH, at room temperature.

The polarization curves were plotted as current,  $I$ , in amperes (A) versus potential,  $E$ , in volts (V) vs. SCE. For comparison with results presented as current density,  $i$ , versus potential,  $E$ , the total area ( $173.65 \text{ cm}^2$ ) should be considered.

The corrosion potential after 1 day of immersion in 3 mol/L  $\text{H}_2\text{SO}_4$  solution was approximately  $-330 \text{ mV/SCE}$ . A slightly more noble corrosion potential was obtained for the filter immersed in the solution containing BTAH. The polarization curves for both solutions show an active behaviour near to  $E_{\text{corr}}$ . This was followed by an active-passive transition at potentials of approximately  $-200 \text{ mV/SCE}$  and  $-250 \text{ mV/SCE}$  in solutions with and without BTAH, respectively. A large passive range was seen in the polarization curve of the filter in the solution without BTAH. An increase in the current of the filter immersed in the solution with BTAH is seen at potentials around  $+300 \text{ mV/SCE}$ . The current stabilized at  $10^{-4} \text{ A}$  in the potential range from  $+500 \text{ mV/SCE}$  until transpassivation, at approximately  $+1000 \text{ mV/SCE}$ . The increase in current at potentials around  $+500 \text{ mV/SCE}$ , could have been due to partial dissolution/breakdown of the BTAH film on the filter surface. It was followed by a secondary passivation of the filter in the sulphuric acid solution. Passivation of the filter also occurred in the sulphuric acid solution without BTAH, as Fig.3 shows.

The currents measured for the filter in the BTAH containing solution were much smaller than those for the filter in the solution without BTAH, showing that BTAH also works as a corrosion inhibitor of 304L SS filter when immersed in sulphuric acid solutions. A fact which is supported by results from literature for 304 SS produced by conventional metallurgy [13].

An investigation was carried out to evaluate the ability of the film to remain on the surface after removal from the BTAH containing solution, and its effect on the corrosion resistance of 304L SS sintered filter. Specimens of 304L SS filter were removed from the solution with BTAH after 7 days of immersion and re-immersed in a solution of 3 mol/L  $\text{H}_2\text{SO}_4$  without BTAH. EIS results for surface treated specimens and bare specimens in 3 mol/L  $\text{H}_2\text{SO}_4$ , after 1 day of immersion are presented in Fig. 4.

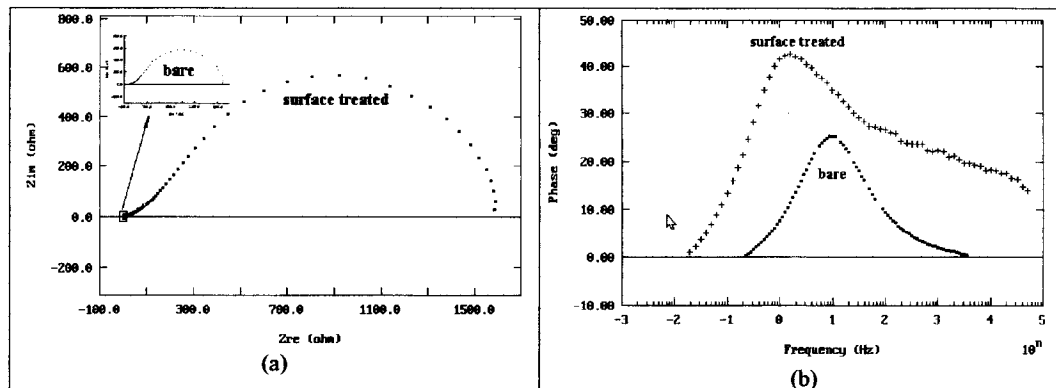


Fig. 4: EIS results for bare and surface treated 304L SS filters after 1 day in 3 mol/L  $\text{H}_2\text{SO}_4$  solution. (a) Nyquist diagrams, (b) Bode diagrams.

The Bode diagrams of the untreated specimen show behaviour typical of metal surface-electrolyte interfaces, with a peak at around 10 Hz and a resistive response at high and low frequencies. For the treated specimens a peak is seen at 1 Hz, and at higher frequencies the diagram indicates the response of a capacitive component, likely to be due to a film on the filter surface. The displacement of the peak of surface treated specimens to lower frequencies indicates that the charge transfer reactions become slower due to the surface film. These results indicate that the film remains

on the filter surface after 1 day of immersion in 3 mol/L  $\text{H}_2\text{SO}_4$ . The Nyquist diagrams show that resistance related to charge transfer processes on the filter is increased by a factor of nearly 350 times due to surface treatment in the solution with BTAH.

The electrochemical behaviour of the surface treated filter was followed by EIS measurements at increasing times of immersion in 3 mol/L  $\text{H}_2\text{SO}_4$ , and the results are shown in Fig. 5.

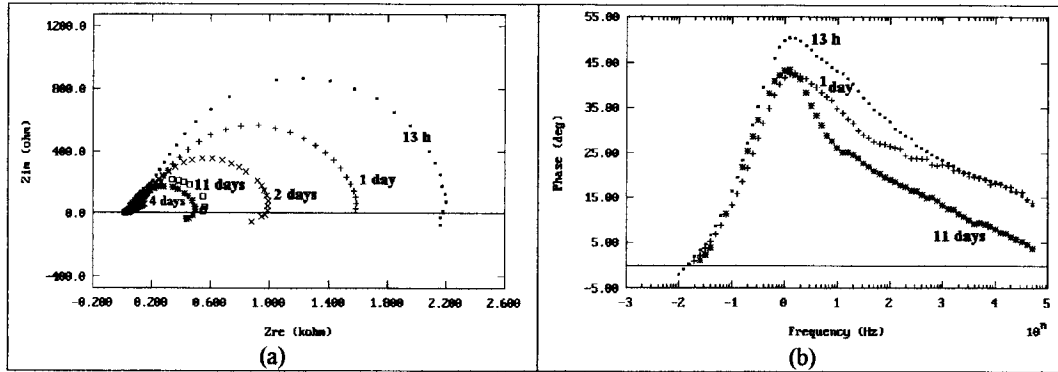


Fig. 5: EIS results of 304L SS filter treated in BTAH containing solution versus time of immersion in 3 mol/L  $\text{H}_2\text{SO}_4$  at room temperature. (a) Nyquist diagrams, (b) Bode diagrams.

The Nyquist diagrams show that the resistance related to charge transfer processes, at the filter surface, decreased from the first hours of immersion until four days. Which could be suggesting some dissolution of the BTAH film and exposure of new areas of metallic material to the electrolyte. From 4 to 11 days, the resistance did not change significantly, indicating a fairly stable state. The Bode diagrams show that the responses at higher frequencies were mainly affected by the increase in time. This result may also be indicative of a partial corrosive attack of the BTAH film. It is worthy of mention that despite the decrease in the resistance related to charge transfer reactions in the first days of immersion, after 11 days in 3 mol/L  $\text{H}_2\text{SO}_4$  it was still one hundred times larger than that of the untreated (bare) filter immersed for only 1 day in the same solution.

One of the surfaces of a 304L SS filter with BTAH film which had been exposed for 11 days in 3 mol/L  $\text{H}_2\text{SO}_4$  solution was observed by scanning electron microscopy and is shown in Fig. 6. No visible signs of corrosion were identified on the surface, indicating that the BTAH film protects the 304L SS filter when it is exposed to the sulfuric acid medium.



Fig. 6: SEM micrograph of 304L SS filter after surface treatment of 7 days in 3 mol/L  $\text{H}_2\text{SO}_4$  with 0.1 mol/L BTAH followed by immersion for 11 days in 3 mol/L  $\text{H}_2\text{SO}_4$  at room temperature.

## Conclusions

The corrosion resistance of a 304L SS filter has been improved by chemical treatment in a sulphuric acid solution containing BTAH. The formation of a film on the filter surface was indicated. This film remains on the surface after removal from the solution and increases the corrosion resistance of the filter in sulphuric acid solutions.

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## References

- [1] S. N. Molhotra, P. Ramakrishnan. MPR, 46, n° 11 (1991), p. 48.
- [2] A. L. Müller. Powder Metallurgy International, 14, n° 2 (1982).
- [3] E. Otero, A. Pardo, V. Utrilla, E. Saenz, F. J. Pérez. 12th International Corrosion Congress. Corrosion Specific Issue, vol. 3B (1993), p. 2037.
- [4] F. Velasco, J. R. Ibars, J. M. Ruiz-Roman, J. M. Torralba, J. M. Ruiz-Prieto. Corrosion, 52 n° 1 (1996), p. 47.
- [5] D. Itzhak, E. Eghion. Corrosion Science, 24, n°2 (1984), p. 145.
- [6] E. Otero, A. Pardo, E. Saenz, M. V. Utrilla, P. Hierro. Corr. Science, 38, n° 9 (1996), p. 1485.
- [7] E. Otero, A. Pardo, M. V. Utrilla, F. J. Perez, C. Merino. Corr. Science, 39, n° 3 (1997), p. 453.
- [8] L. Fedrizzi, F. Deflorian, A. Tiziani. Advances in Powder Metallurgy & Particulate Materials, 7 (1994), p. 273.
- [9] E. Maahn, S. K. Jensen, R. M. Larsen, T. Mathiesen. Advances in Powder Metallurgy & Particulate Materials, (1994), p. 253.
- [10] T. Raghu, S. N. Malhorta, P. Ramakrishnan. British Corrosion Journal, 2 (1988), p 109.
- [11] F. Velasco, J. M. Ruiz-Roman, J. M. Torralba, J. M. Ruiz-Prieto. British Corrosion Journal, 31 (1996), p. 295.
- [12] E. Klar, F. K. Samal. Advances in Powder Metallurgy & Particulate Materials, 11 (1995), p. 11.
- [13] P. R. P. Rodrigues, I. V. Aoki, A. H. P. Andrade, S. M. L. Agostinho. British Corrosion Journal, 31 (1996), p 305.
- [14] L. De Micheli; A. H. P. Andrade, C. A. Barbosa, S. M. L. Agostinho. British Corrosion Journal, 34 (1999), p. 67.
- [15] L. De Micheli; A. H. P. Andrade, C. A. Barbosa, S. M. L. Agostinho. British Corrosion Journal 35 (2000), p. 297.
- [16] T. Mathiesen and E. Maahn. Advances in Powder Metallurgy and Particulate Materials, 3 (1995), p. 45.
- [17] L. Fedrizzi, F. Deflorian, A. Tiziani, I. Cristofolini, A. Molinari. Advances in Powder Metallurgy and Particulate Materials, 7 (1994), p. 273.
- [18] A. Tremblay and R. Angers. Advances in Powder Metallurgy and Particulate Materials, 7 (1995), p. 225
- [19] A.V.C. Sobral, A. C. B. Parente, J. L. R. Muzart and C. V. Franco. Surface & Coatings Technology, 92 (1997), p. 10.
- [20] E. Maahn, S. K. Jensen, R. M. Larsen, T. Mathiesen. Advances in Powder Metallurgy and Particulate Materials, 7 (1994), p. 253.

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