

Corrosion Resistance of Powder Injection Moulded AISI 316L and 17-4PH Stainless Steels in Acid Rain Environments

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Abstract: This paper describes corrosion studies in simulated acid rain environments carried out on AISI 316L and 17-4PH stainless steel specimens prepared by powder injection moulding. Corrosion characterization was carried out using a cyclic salt spray test to accelerate the effects of corrosion caused by acid rain. This consisted of wetting and drying cycles using a solution of composition typical of acid rain found in a polluted urban atmosphere. The solution used was concentrated to accelerate corrosion. The results were compared to results from literature for salt spray testing (ASTM B117). In addition, polarization tests and electrochemical impedance spectroscopy (EIS) measurements were performed in the same solution used in the cyclic salt spray test. The results showed that AISI 316L and 17-4PH steels produced by PIM technology are very resistant to corrosion in acid rain environments. Inspection of the surfaces of these steels revealed no corrosion products after 2600 hours of cyclic testing in simulated acid rain solution. Polarization and EIS results in the same solution, indicated a passive state and no pitting tendency of both steels in the test environment.

Introduction

Many reports have shown that sintered stainless steels are less corrosion resistant than those produced by conventional metallurgy [1-5]. Recently, a new powder injection moulding (PIM) technique was developed to produce sintered materials with extremely high corrosion resistance. This PIM technology has been commercially used for manufacturing small components with a high degree of complexity such as orthodontic materials [6].

The corrosion properties of these components in artificial saliva has been investigated [7]. Braces are usually manufactured to be self-adhesive, for direct bonding with the teeth. The metallic materials often used for injection moulded orthodontic devices are 316L and 17-4 PH steels. This technology can be considered as a complement to microfusion and it represents an important technological evolution in powder metallurgy.

In this investigation, the corrosion resistance of PIM steels, AISI 316L and 17-4 PH, was evaluated by means of a cyclic salt spray test using a solution of composition typical of acid rain, one thousand times concentrated. The aim of this study was to envisage other potential applications for these steels, such as a part of devices subjected to polluted urban atmospheres. Additionally, potentiodynamic polarization tests were carried out to investigate the susceptibility of the steels to localized corrosion.

Materials and Methods

Materials: The materials used in this study were PIM steels, 316L and 17-4PH, supplied by Lupatech S/A - Div. Steelinject, Brazil. The chemical compositions of steels tested are given in Table 1. The steels were made by powder injection moulding, pre-sintering and sintering. An outline of the injection moulding process can be found elsewhere [8,9]. The pre-sintering and sintering parameters are shown in Table 2.

Table 1. Chemical composition (in wt %) of 316L and 17-4PH injected stainless steel.

| Stainless Steel | C | Si | Mn | P | S | Ni | Cr | Mo | Cu |
|-----------------|-------|------|------|-------|-------|------|-------|------|------|
| 316L | 0.013 | 0.80 | 0.20 | 0.031 | 0.003 | 13.5 | 16.40 | 2.2 | - |
| 17-4PH | 0.05 | 0.76 | 0.25 | 0.026 | 0.020 | 4.0 | 16.70 | 0.30 | 3.95 |

Table 2. Pre-Sintering and sintering parameters.

| Process | Steel | T (°C) | Time (h) | Sintering atmosphere |
|---------------|------------------------|--------|----------|-------------------------------------|
| Pre-Sintering | 316 L | 980 | 1 | H ₂ |
| | 17-4 PH | 980 | 1 | H ₂ |
| Sintering | 316L ^(a) | 1300 | 4 | Low pressure (Ar + H ₂) |
| | 17-4 PH ^(b) | 1350 | 3 | Low pressure (Ar + H ₂) |

Density of the sintered samples: ^(a) 7,59 and ^(b) 7,61 (g.cm⁻³)

The average particle sizes of the starting powders of 316L and 17-4PH steels were 6.6 μm and 9.2 μm, respectively. The porosity after sintering of the steels was estimated as 4% and 3%, for 316 L and 17-4 PH steels, respectively.

Surface preparation: The surfaces of the working electrodes were prepared by grinding using emery papers from 220 to 1000 mesh, in water suspension. The surfaces were then polished to a mirror finish in an alumina slurry (0.25 μm). Finally, the electrodes were rinsed in water, alcohol, and dried, prior to immersion in 3% NaCl solution.

Cyclic salt spray test to simulate atmospheric corrosion under acid rain: The cyclic salt spray test was carried out using acid rain solution of composition given in Table 3, one thousand times more concentrated to accelerate corrosion, by alternating between 1 hour spraying and 1 hour drying periods. During the drying periods, the cabinet was heated to 35° C with constant air flow, and the temperature was reduced to room temperature during the spraying period. The pH of the acid rain solution was adjusted to 4.5 with NaHCO₃.

Table 3. Average composition of acid rain of Sao Paulo city [11].

| Composition | Concentration (μM) |
|---|--------------------|
| H ₂ SO ₄ | 8.5 |
| (NH ₄) ₂ SO ₄ | 14.5 |
| NaNO ₃ | 10 |
| HNO ₃ | 10 |
| NaCl | 8.7 |

Electrochemical tests: Potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) measurements were carried out in a solution of composition typical of the acid rain of Sao Paulo city (composition given in table 2), that was concentrated one thousand times to accelerate corrosion. A three electrode cell arrangement was used, with a saturated calomel electrode (SCE) as the reference electrode and a graphite rod as the auxiliary electrode. Prior to polarization and EIS measurements, all the samples remained immersed for 1 hour in the test solution and the open circuit potential was measured until a steady state has been reached. The potential after stabilization was called corrosion potential, E_{corr} . Polarization was carried out using a EG&G PARC 273A Potentiostat. The potential range was from -100 mV (vs. E_{corr}) to 1600 mV (vs. SCE), and the scan rate was 0.8 mV/s. EIS measurements were accomplished with a 1255 Solartron frequency response analyzer coupled to a EG&G 273A Potentiostat. All EIS measurements were performed in potentiostatic mode at the corrosion potential, E_{corr} .

Results and Discussion

Fig. 1 shows the PIM steels, 17-4PH and 316L, after 2600 hours of cyclic salt spray testing in the concentrated acid rain solution.

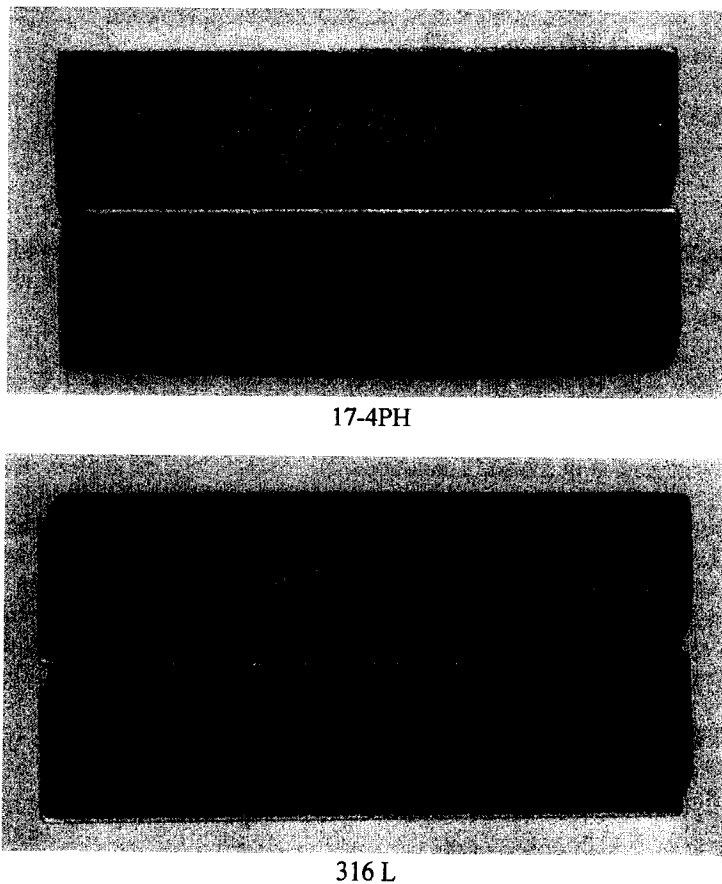


Fig. 1. 17-4PH and 316L PIM steels after 2600 hours of cyclic salt spray test using a concentrated artificial acid rain solution

At the end of test, the specimens were still metallic bright, and corrosion products were not seen on their surfaces. This result indicates that both PIM steels tested show high corrosion resistance in acid rain atmospheres.

Previous study suggested that the same steels also present favorable corrosion resistance to marine atmospheres. This evidence was found by the exposure of specimens of the same steels to a salt spray test that simulates the effects of marine atmospheres (ASTM B117). After 700 hours of test, all the specimens only showed slight staining of their surfaces [12].

The potentiodynamic polarization curves of 316L and 17-4 PH PIM steels in concentrated acid rain solution, are shown in Fig. 2. The two steels exhibit similar electrochemical behavior in this solution. E_{corr} values of both steels are around -280 mV (SCE) and they show very low corrosion rates, of the order of 10^{-7} A cm^{-2} , in the artificial acid rain solution used. A behavior typical of active materials followed by an active-passive transition at potentials of approximately 100 mV (SCE), was obtained for both steels. The passive range, from 100 mV to 500 mV, and the passive current densities, $3 \cdot 10^{-6}$ A cm^{-2} were similar for the two steels. The current densities of both steels started to increase at potentials of 500 mV (SCE), indicating a transpassivation that could have been caused by at least partial dissolution/breakage of the oxide passive film on these steels. A secondary passivation was indicated by the decrease in current observed at 850 mV (SCE), but the repassivation of the steels occurred at larger potentials. Current densities after the secondary passivation were approximately $7 \cdot 10^{-6}$ A cm^{-2} for both steels, indicating that this passive film is less protective than that due to the primary passivation. At potentials above 1200 mV (SCE), a second transpassivation, likely due to the oxygen evolution reaction, occurred.

Wendt and Chin [13] also observed two transpassivation processes for AISI 304 steel in solutions with pH ranging from 2 to 5. The first transpassivation was reported at potentials of 800 mV (SCE), and was attributed to metal dissolution. The second transpassivation process was reported at about 1400 mV (SCE), and was attributed to the oxygen evolution reaction.

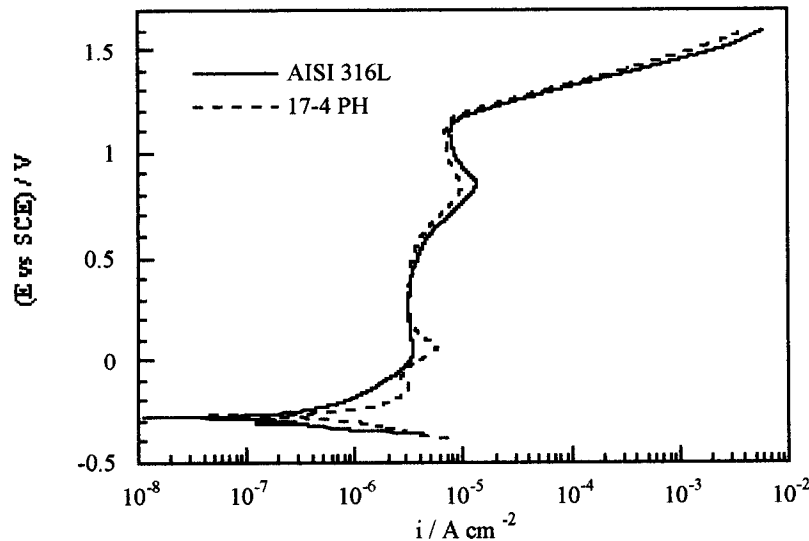


Fig. 2. Polarization curves of AISI 316L and 17-4 PH steels in concentrated acid rain solution.

No pitting potential was indicated in the polarization curves of both steels in the concentrated acid rain solution, even though it contains sodium chloride in its composition. Besides, pits were not seen on these steels after prolonged periods of immersion in solution of similar composition. These results show that both steels do not have a tendency to pitting in this kind of environment. The chloride concentration in the concentrated acid rain solution used (8.7 mM) was apparently not enough to cause the breakage of the passive layer on the steel surfaces.

Polarization curves of 17-4PH and 316L PIM steels obtained in 3% NaCl solution in the same range of polarization have shown tendency to pitting of both the steels in sodium chloride solution. Pits were in fact observed on the surfaces of specimens of both steels after cyclic polarization in 3% NaCl solution.

EIS results of 316L PIM steel after 1 day of immersion in the concentrated acid rain solution are shown in Fig. 3. Similar results were obtained for 17-4PH steel specimens.

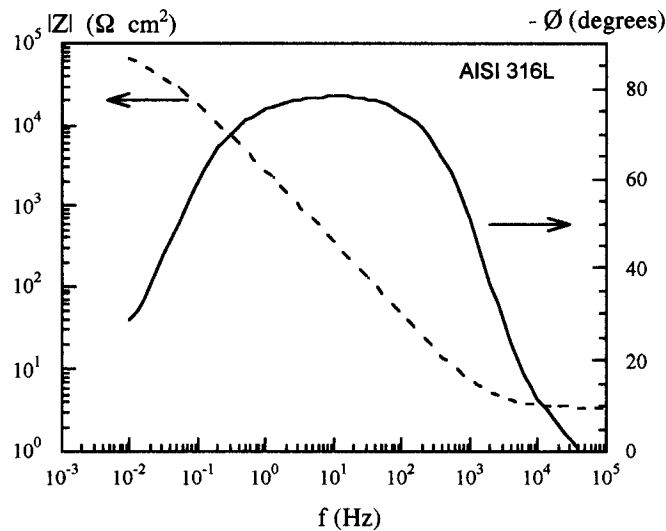


Fig. 3. Bode plots of AISI 316L PIM steel in concentrated acid rain solution.

EIS spectra exhibit a near capacitive response over a wide frequency range illustrated by a phase angle close to -90 degrees indicating fairly compact passive film. It can be observed that Bode $|Z|$ impedance plots showed linear portions at intermediate frequencies. The $|Z|$ values at low frequencies in the order of $10^4 \Omega \text{ cm}^2$, also support the high corrosion resistance of these steels in this environment.

Conclusions

The corrosion behaviour of powder injection moulded, AISI 316L and 17-4 PH, steels in acid rain simulated environments revealed that these steels have high corrosion resistance under such atmosphere. The results of polarization and EIS tests confirmed the results obtained by the cyclic salt spray test using a solution simulating the acid rain of Sao Paulo city, and indicated that both PIM steels are potential candidates for use in acid rain environments. Behaviour typical of passive materials and absence of pitting corrosion was related to the PIM steels tested.

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