

Corrosion of stainless steels in sulfuric acid environments: influence of chloride content and temperature

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ABSTRACT

Stainless steel is a common material in reactors, tanks, pipes, mixers, filters and valves in process industry. The selection of a suitable stainless steel grade for a specific industrial application is conducted based on the characteristics of the environment, but often limited by the foreseen lifecycle costs. For applications in raw material sector, the main challenge is that corrosion performance data for several stainless steel grades for, e.g., hydrometallurgical processes is lacking. Corrosion rate of the materials may remain low when general corrosion is the primary corrosion form, but material losses across wall thickness may become high if localized corrosion is present. Therefore, in order to make material choices that enable a continuous and safe operation of the process, it is important to define such operation conditions that cause the corrosion mechanism change.

In this research, altogether six austenitic and duplex stainless steel grades with a varying Pitting Resistance Equivalent Number (PREN) were studied in test environments which varied with respect to their H₂SO₄ and chloride concentrations, while temperature ranged from room temperature up to 90 °C. The results from potentiodynamic polarization measurements are presented and discussed. The electrochemical measurements are complemented with immersion tests conducted in environments with chlorides.

Key words: Stainless steels, Sulfuric acid, Chloride concentration, Temperature.

INTRODUCTION

Corrosion is the most important material failure mechanism in industry and annually responsible for costs amounting approximately to 2 trillion US dollars worldwide.¹ In raw materials industry, like in hydrometallurgy, construction materials for the harsh operating conditions are expensive and, if deteriorated by corrosion, cause significant losses in production and high maintenance costs. Reliability and cost-effectiveness of processes in raw materials sector, such as those in hydrometallurgical industry, rely heavily on the performance of process equipment and constructions like reactors, tanks, pipes, mixers, filters and valves.² Process equipment is usually made from stainless steels, but the alloying depends on the corrosiveness of the environment. The selection of a proper stainless steel grade is crucial for the designed lifetime of the equipment. The operating conditions in the hydrometallurgical industry can be very demanding: elevated

temperatures up to 105 °C, sulphuric acid concentrations up to 10 % in weight, high concentrations of halide ions, including chlorides and fluorides, and the presence of oxidizing ions, like cupric and ferric cations.

There are mainly two main groups of factors that affect corrosion properties of stainless steels: metallurgical factors and environmental factors. The metallurgical factors include the alloy composition and microstructure while the environmental factors are, for example, the chloride ion concentration, pH, oxidising species, oxygen content and temperature. The corrosion resistance of stainless steels is associated with the thin protective layer, the passive film. The passive films may vary with respect to thickness, composition and electronic structure, depending on alloying elements, microstructure and the media where they were formed and the oxidizing capacity of the environment.³⁻⁷ The presence of aggressive ions, particularly halides, in the environment can be detrimental to passive films and affect film stability and pit initiation.^{9,10} On the other hand, some ions, such as sulfate ions, are known for inhibiting pitting corrosion in chloride-containing media.¹¹

Chromium is the most important element for giving passivity to stainless steel. A sufficient chromium level, typically 10.5 %, is required to introduce passivity and thus prevent chemical dissolution at the interface between the metal and the solution.³⁻⁷ The direct effect of an increased nickel content on corrosion properties is that it reduces the corrosion rates in the active state in acid environments.¹² Molybdenum lowers the critical current for passivation and also increases the resistance to pitting corrosion. Molybdenum stabilizes the passive film and contributes to the interaction between chloride ion and the passive film¹³; this interaction between Mo and Cl is believed to have an important role in the improved pitting corrosion resistance of Mo-bearing stainless steels.^{14,15} Nitrogen also has a strong influence on the localised corrosion of stainless steels, especially in combination with molybdenum. It has been shown that molybdenum and nitrogen act together and enhance the pitting characteristics in acid to neutral conditions.

The alloying levels and pitting resistance are correlated in the concept of the Pitting Resistance Equivalent Number ($PREN = \%Cr + 3.3x\%Mo + 16x\%N$). PREN has proved to be a good predictor for the relative resistance of localized corrosion in chloride environments. Therefore, it is convenient to use the PREN as a way of ranking different stainless steel grades in this study.

The main aim of present paper is to study the effect of sulfuric acid (1 and 10%wt), chloride ion (0-5000 mg/L NaCl) and temperature (22, 50 and 90 °C) on the corrosion properties of six stainless steel grades. The obtained data will be then used to develop a material selection software tool, in the form of a "virtual expert". Therefore, extensive testing has been performed with a combination of short term cyclic potentiodynamic measurements and long-term immersion experiments. Results are discussed in the terms of alloys composition (PREN) together with the environment conditions (chloride content and temperature) in order to determine the critical levels of key parameters concerning the corrosion behavior of stainless steels.

EXPERIMENTAL PROCEDURE

Tested stainless steel grades and sample preparation

Stainless steel grades of austenitic and duplex microstructures with varying corrosion resistance were selected for tests. The test materials were supplied by Outokumpu Stainless Steel[†], Sweden. All steels had normal microstructures with very low levels of non-metallic inclusions. Typical chemical compositions, UNS and EN designations, PREN numbers of the tested grades, density and types of microstructures are given in Table 1. Before the tests, all exposed surfaces were abraded with P320 emery paper and degreased by ultrasonic cleaning in acetone for 3 min.

[†] Trade name, company name

Table 1: Chemical analyses, UNS and EN designations, PREN values and microstructure of the tested stainless steels.

Designation		Thickness (mm)	PREN *	Density g/cm ³	Cr	Ni	Mo	N	others	C	Microstructure
UNS	EN										
S31603	1.4432	3.0	25	8.0	16.9	10.7	2.6	-		0.02	Austenitic
S31655	1.4420	3.0	26	7.9	20.3	8.6	0.7	0.19		0.02	Austenitic
S82441	1.4662	3.0	34	7.7	24.0	3.6	1.6	0.27	3Mn, Cu	0.02	Duplex
N08904	1.4539	3.0	34	8.0	19.8	24.2	4.3	-	1.4Cu	0.01	Austenitic
S32750	1.4410	0.5	42	7.8	25.0	7.0	4.0	0.27		0.02	Duplex
S31254	1.4547	3.0	43	8.0	20.0	18.0	6.1	0.2	Cu	0.01	Austenitic

PREN numbers = %Cr+3.3x%Mo+16x%N

Microstructural examination

Cross-section of the polished samples were etched in sodium hydroxide (NaOH) solution for duplex grades and in mix acid solution (V2A) containing hydrochloric acid (HCl) and nitric acid (HNO₃) for austenitic grade. Specific etching parameters are shown in Table 2.

Table 2: Etching parameters used.

Etching parameters					
Etch solution	Type of etch	Mixture	Applied Voltage (V)	Temperature (°C)	Time (s)
NaOH	Electrolytic	40g NaOH + 100 ml distilled water	2	RT	1-10
V2A	-	50 ml HCl+ 5 ml HNO ₃ +50 ml distill water	-	50	5-20

Electrochemical measurements

Experiments were performed in 1 % and 10 % sulfuric acid with various concentrations of NaCl, namely 0, 500, 1000, 2000, and 5000 mg/L at three temperatures: room temperature (22 °C), 50 °C and 90 °C.

Electrochemical measurements up to 90°C were carried out in a three-electrode corrosion cell with double walls, with an approximate volume of 350 cm³. Before and during the measurement the solution was purged with N₂. Higher temperatures of testing solutions were provided by an external heating unit. The counter electrode was glassy carbon and the reference electrode was Ag/AgCl electrode in saturated KCl solution. All measurements are reported vs Ag/AgCl reference electrode potential $E = 0.197$ V vs. standard hydrogen electrode (SHE) at 22 °C.

The electrochemical tests were initiated with at least 1-hour stabilization at open circuit potential (OCP).¹⁶ After them, the cyclic potentiodynamic polarization measurements were performed starting from -0.25 V vs. OCP and progressing in the anodic direction up to +1.4 V at a scan rate of 0.167 mV/s (0.6 V/h). The reverse potential was set at a current density of 0.1 mA/cm². Especially in the cases of detected pitting corrosion, additional measurements were done. At least 2 parallel samples were measured in such cases in order to provide reliable electrochemical results.¹⁷

The following parameters were extracted from electrochemical experiments: corrosion potential E_{corr} , corrosion current density j_{corr} , passivation potential E_{pass} , critical passivation current density j_{cp} , passive current density j_{pass} , breakdown potential E_{b} and repassivation potential E_{rep} .¹⁸

The most variable parameter in cyclic potentiodynamic (CPP) curves in this study was found to be critical passivation current density j_{cp} , a pronounced current peak in anodic region of CPP curve at active-passive transition zone.^{18, 19}

Immersion tests

Electrochemical results have been complemented with immersion tests (28 days) in stagnant 1 % sulfuric acid containing different amounts of NaCl at 90 °C in accordance with modified ISO 18069.²⁰

The samples were cut in a machinery shop by laser procedure into 2 cm × 5 cm, for each test condition, two samples were immersed into a flask. All the samples were ground to 280 (ANSI)/ P320 (FEPA) SiC papers for resemblance of an as-received surface finish. The edges of the samples were rounded. All samples were passivated for 18 h in air. The samples were ultrasonically cleaned for 3 minutes in acetone solution.

The samples were immersed in 1 % H₂SO₄ solution containing 5000 mg/L of NaCl.

RESULTS AND DISCUSSION

1. Microstructural features

All steels had normal microstructures with very low levels of non-metallic inclusions, see microstructures in Figure 1. The micrographs were taken close to the mid-thickness.

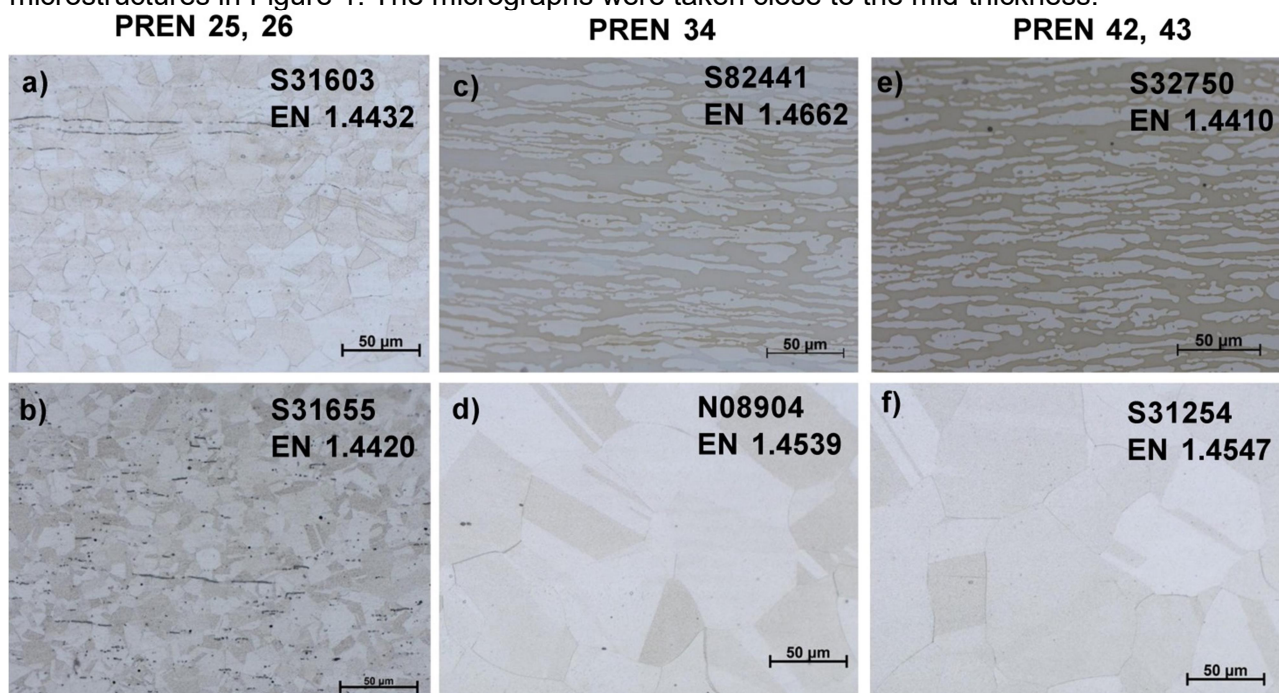


Figure 1: Metallographic images of the investigated steels with different PREN numbers: a) S31603 (PREN25), b) S31655 (PREN26), c) S82441 (PREN 34), d) N08904 (PREN34) e) S32750 (PREN 42) and f) S31254 (PREN 43).

2. Electrochemical tests

Open circuit potential measurements and cyclic potentiodynamic polarization measurements were conducted for six different stainless steels at 1 % and 10 % sulfuric acid with 0 mg/L, 500 mg/L, 1000 mg/L, 2000 mg/L and 5000 mg/L of NaCl at room temperature (22 °C), 50 °C and 90 °C. In the following, the influence of variables: chloride ion content, temperature and sulfuric acid content is presented through illustrative examples.

In Figure 2, effect of chloride concentration in 10 % sulfuric acid at 90 °C for S31603 (EN 1.4432, PREN 25) is shown. In Table 3, electrochemical parameters extracted from cyclic potentiodynamic polarization (CPP) curves are summarized. It can be observed that open circuit potential (OCP) decreased with increasing chloride content (Figure 2), while corrosion current density, j_{corr} , increased slightly with rising NaCl concentration (Table 3). The critical passivation current density,