



## Chloride-induced corrosion resistance of high-strength stainless steels in simulated alkaline and carbonated concrete pore solutions

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### ARTICLE INFO

#### Article history:

Received 4 August 2011

Accepted 16 December 2011

Available online 27 December 2011

#### Keywords:

A. Stainless steel

A. Concrete

A. Steel reinforced concrete

B. Polarization

C. Pitting corrosion

C. Alkaline corrosion

### ABSTRACT

This paper presents the results of a study examining the  $\text{Cl}^-$  induced corrosion resistance of austenitic, duplex, and martensitic high-strength stainless steels (HSSs) and a pearlitic prestressing steel using cyclic potentiodynamic polarization (CPP) techniques in simulated alkaline and carbonated concrete solutions. CPP testing found that in alkaline solutions, all HSSs showed high corrosion resistance at  $\text{Cl}^-$  concentrations from zero to 0.25 M. When exposed to carbonated solutions, corrosion resistance was reduced and only duplex grades S32205 and S32304 exhibited high corrosion resistance. A strong correlation between microstructural defects (e.g., strain-induced martensite) and corrosion damage was observed in the cold-drawn HSSs.

Published by Elsevier Ltd.

### 1. Introduction

The corrosion of reinforcing and prestressing steels in concrete structures exposed to chlorides ( $\text{Cl}^-$ ) in marine environments and/or deicing chemicals is a problem of critical concern which, even after extensive research, continues to plague modern concrete infrastructure. One of the most effective methods of corrosion mitigation in reinforced concrete (RC) structures is the use of corrosion-resistant stainless steel reinforcing bars [1]. RC applications have focused primarily on widely available austenitic stainless steels (e.g., UNS S30400 and S31600) and more recently on austenitic–ferritic duplex and lean duplex stainless steels (e.g., S32205, S32101, and S32304) [2]. The replacement of mild carbon reinforcing steels with these corrosion-resistant stainless steels has been shown to decrease maintenance costs by upwards of 50% with projected service lives far greater than 100 years in even the most severe of environments [3].

In spite of the exceptional performance of stainless steels for corrosion mitigation in RC structures, basic and applied research

on stainless steels for corrosion mitigation in prestressed concrete (PSC) structures has been limited. When compared with RC, prestressing steels used in PSC require high tensile strengths (typically in excess of 1400 MPa) such that sufficient precompressive stresses can be developed within the concrete to limit cracking [4]. These high tensile strengths can be achieved in stainless steels by cold drawing to a reduction in cross-sectional area of approximately 60–70% [5]. Previous studies have shown that such heavy cold drawing results in the formation of strain-induced  $\alpha'$ -martensite in metastable austenitic stainless steels (e.g., S30400) [6,7] as well as in the austenite phase of duplex stainless steels [8,9]. The presence of  $\alpha'$ -martensite is known to lead to an apparent decrease in corrosion resistance when compared with the same alloy in the annealed condition [10,11]. As a result, the abundance of information available in the literature regarding the corrosion resistance of stainless steel reinforcing bars is not directly applicable to those same alloys when produced and tested in the cold drawn condition (i.e., as high-strength stainless steels (HSSs)).

The challenges associated with optimizing mechanical properties, materials production and processing techniques, resistance to corrosion and environmentally assisted cracking, and economic considerations have made research on HSSs for PSC a difficult task that few have pursued. Of the limited previous studies that examined HSSs for PSC, most have focused on widely available austenitic stainless steels (S30400 and S31600) [10,12], low-Ni/high-Mn N-charged austenitic stainless steels (Nitronic<sup>®</sup> alloys) [13], and workhorse duplex stainless steels (S32205) [14]. Investigations of

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HSSs in other industries (e.g., spring wire and aerospace) have focused primarily on mechanical behavior rather than corrosion resistance [15–17]. No previous studies have investigated the corrosion resistance of lean duplex and martensitic HSSs that are known to provide good corrosion resistance along with high tensile strengths.

In the present study, the corrosion resistance of austenitic, duplex, and precipitation-hardened martensitic HSSs, and a pearlitic high-C prestressing steel was evaluated using cyclic potentiodynamic polarization (CPP) techniques in simulated alkaline and carbonated concrete pore solutions.  $\text{Cl}^-$  was added to the simulated pore solutions at concentrations of up to 1.0 M to simulate marine exposures. Following testing, corrosion damage was characterized using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) to correlate damage with microstructural features. The primary goal of the study was to identify HSS alloys that showed the most promise for utilization as corrosion-resistant prestressing reinforcement in PSC structures exposed to marine environments.

## 2. Materials and methods

### 2.1. Materials

Candidate stainless steel alloys selected for the investigation included: austenitic grades S30400 and S31600; duplex grades S32101, S32205, and S32304; and a precipitation hardened martensitic grade S17700. HSSs were produced from annealed and pickled wire rod material which was cold drawn with the assistance of stainless steel spring wire manufacturers to increase tensile strength. A target final wire diameter similar to that typically used for prestressing reinforcement (3–5 mm) was specified for the cold drawing operation along with a target tensile strength of approximately 1400 MPa. In order to achieve the desired tensile strength and wire size and initial wire rod size of approximately 9 mm was cold drawn until a reduction in cross-sectional area of approximately 70% was achieved. Additional details regarding the production of HSSs are provided in Ref. [5]. A G10800 pearlitic prestressing steel also was included as a control in the electrochemical testing. The center “king” wire of a 15.2 mm diameter seven-wire ASTM A416 [18] prestressing strand served as the G10800 material. Measured chemical compositions and basic mechanical properties of the as-received materials are provided in Table 1. The chemical composition of all HSSs was within the limits specified in ASTM A276 [19] with the exception of austenitic grade S31600 that exhibited a sulfur content equal to the specified limit of 0.030%. A brief summary of mechanical properties of all alloys investigated is provided in Table 2.

Fig. 1 shows electron and optical micrographs of the etched microstructures of the G10800 prestressing steel, typical austenitic HSS (retained austenite etched bright and  $\alpha'$ -martensite etched dark), typical duplex HSS (austenite etched bright and ferrite etched dark), and the precipitation hardened martensitic HSS

**Table 2**

Mechanical properties of alloys investigated. For additional details on mechanical properties see [5].

Alloy (UNS No.)	0.2% $\sigma_y$ (MPa)	$\sigma_{ult}$ (MPa)	$\epsilon_{ult}$ (%)	$E$ (GPa)
G10800	1750	1963	7.5	202
S30400	1173	1461	5.5	164
S31600	1185	1401	2.7	160
S32101	1101	1433	8.0	172
S32205	1026	1349	5.7	169
S32304	1035	1247	8.7	151
S17700	1226	1556	3.8	176

S17700. The pearlitic prestressing steel was wet-etched in a 2% nitral solution (2%  $\text{HNO}_3$  in ethanol ( $\text{C}_2\text{H}_5\text{OH}$ )). Austenitic and martensitic grades were wet-etched in a dilute aqua regia solution of equal parts  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ , and  $\text{HCl}$ . Duplex grades were electroetched in a 20%  $\text{NaOH}$  solution with an applied potential of 4 V. Significant longitudinal grain alignment and elongation which was axisymmetric with the drawing direction was observed as a result of the heavy cold drawing. Duplex HSSs exhibited an approximately 50/50 proportion of austenite and ferrite (measured using quantitative image analysis). Strain-induced  $\alpha'$ -martensite was evident in austenitic S30400 and S31600 HSSs. X-ray diffraction studies also indicated the presence of  $\alpha'$ -martensite in the austenite phase of all duplex HSSs examined (see [5]). Distributed Al-bearing intermetallic precipitates were observed in S17700 as a result of the precipitation hardening heat treatment. Distributed precipitates were also observed in the etched microstructures of S31600, S32101, and S32304.

In practice, prestressing reinforcement in concrete will not be polished, sand-blasted, or thoroughly cleaned prior to use. Therefore, the as-received surface condition of the materials was characterized as it may influence corrosion initiation and propagation. Fig. 2a depicts the typical surface observed on austenitic and martensitic HSSs. Fig. 2b depicts the typical surface observed on duplex HSSs. Details on the Zn phosphate ( $\text{ZnPO}_4$ ) film present on the surface of G10800 prestressing steels are presented in [20]. In all HSSs studied, a highly deformed and heterogeneous surface morphology was observed, with the amplitude of the deformations being less in duplex HSSs due to their smaller grain size. In many cases, the interstitial space between adjacent deformed grains at the surface was filled with Ca-containing compounds (see bright regions in Fig. 2a, confirmed by EDX) which likely corresponded to the remnants of stearate drawing lubricants.

### 2.2. Test specimens

All corrosion test specimens were sectioned directly from cold drawn HSS wires and prepared using the techniques presented in Ref. [20] in order to isolate a well defined surface area to be exposed to the testing solution and to prevent unintended crevice corrosion from occurring. Each specimen was produced with a standard exposed length of 2.15 cm. However, because each HSS

**Table 1**

Chemical composition of alloys investigated expressed in terms of wt.%.

Alloy (UNS No.)	Composition (wt.%) – Fe balance											
	C	Mn	P	S	Si	Ni	Cr	Mo	Cu	V	N	Al
G10800	0.81	0.73	0.009	0.005	0.24	0.06	0.04	0.01	0.11	0.08	–	–
S30400	0.07	1.02	0.028	0.001	0.33	8.3	17.8	0.33	0.47	0.10	0.09	–
S31600	0.03	1.67	0.030	0.030	0.21	10.8	16.4	2.23	0.46	0.16	0.05	–
S32101	0.027	5.0	0.018	<0.001	0.71	1.56	20.9	0.16	0.25	0.12	0.29	–
S32205	0.004	0.82	0.023	<0.001	0.51	5.1	22.1	3.2	0.21	0.12	0.22	–
S32304	0.018	0.87	0.011	0.001	0.43	4.8	22.3	0.31	0.23	0.07	0.14	–
S17700	0.07	0.82	0.023	0.001	0.23	7.83	16.1	0.19	0.30	0.15	0.02	0.81

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