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Effect of temperature on the corrosion behaviour of low-nickel duplex stainless steel bars in concrete

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ABSTRACT

Stainless steel reinforcing bars can be a means for prolonging the service life of reinforced concrete structures exposed to tropical climates. To select a suitable grade of stainless steel according to exposure conditions and design service life, the definition of the chloride threshold for pitting corrosion initiation is required. This paper investigates the effect of temperature in the range 20–60 °C on the resistance to chloride-induced corrosion of low-nickel duplex stainless steel rebars and, for comparison, of traditional austenitic stainless steel rebars. Tests in concrete and in solutions simulating the concrete pore liquid were performed and an attempt to evaluate the chloride threshold levels for corrosion initiation was carried out. Results showed lower corrosion resistance and higher sensitivity to increase in temperature for low-nickel duplex stainless steel bars compared to traditional austenitic stainless steels.

1. Introduction

The aggressive nature of tropical marine environments determines great problems of durability for reinforced concrete structures (e.g. bridges and marine piers), due to chloride-induced corrosion of embedded steel bars [1]. The concrete cover itself may not succeed to guarantee long-term corrosion protection of usual carbon steel bars, even if good quality concrete and high cover thickness are considered, and preventative measures are necessary even for a service life of less than 100 years [1–3]. The use of stainless steel bars can provide a durable and maintenance-free solution to corrosion problems in the most critical parts of marine concrete structures, typically the splash, spray or tidal zones [4–6]. To achieve this goal, a correct selection of the grade of stainless steel that can be used on the basis of environmental aggressiveness is needed. As a matter of fact, even though stainless steels offer a corrosion resistance higher than carbon steel, the different grades of stainless steel bars available on the market have different corrosion performances [4,7,8]. To make a proper choice of the stainless steel grade, data on chloride threshold for corrosion initiation are required as a function of the exposure condition (i.e. moisture conditions and temperature of concrete). If the chloride threshold levels for available types of stainless steels are known, the design for durability of reinforced concrete elements can be carried out by selecting a suitable and cost-effective combination of concrete composition, concrete cover thickness and grade of stainless steel, e.g. using deterministic or probabilistic methods [3,9].

Similarly as for conventional carbon steel bars (for which indicative value in the range of 0.4–1% by mass of cement is usually considered under atmospheric exposure [1]), the chloride threshold level of stainless steel bars depends on the temperature and relative humidity of the environment (that influence the temperature and moisture content of the concrete in contact with the steel). This threshold, however, is also remarkably affected by other important factors such as chemical composition, microstructure and surface finish of the steel, steel potential, pH of the concrete pore solution, and presence of voids at the steel/concrete interface [10–14]. Taking also into account that pitting corrosion induced by chlorides is a stochastic phenomenon, the chloride threshold should be defined not by a single value, but by a probability distribution.

The task of defining the chloride threshold is rather difficult. Unfortunately, simple indices, such as the pitting resistance equivalent number (PREN) that is often utilised to rank the corrosion resistance of stainless steels in near-neutral environments, are not reliable in predicting the corrosion performance of steels in alkaline environments [15,16].

Tests in solution are often used to evaluate the corrosion resistance of stainless steel rebars; these tests, however, cannot be used to estimate the chloride threshold in concrete and may even fail in ranking of the corrosion resistance of stainless steels in concrete [16].

To estimate the chloride threshold for pitting corrosion initiation a large number of tests should be carried out in conditions that are representative of the actual steel–concrete interface of real structures [12,13]. Beyond the fact that the actual condition of bars embedded in real structures are rather difficult to reproduce in the laboratory, tests in concrete are in any case time consuming [17].

As a consequence only few data based on tests in concrete are reported in the literature for stainless steel bars embedded in concrete.

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Moreover data are generally limited to traditional austenitic stainless steel grades with about 18%Cr and 10% Ni (e.g. grades 1.4307 or 1.4311 according to EN 10088 standard; 304L or 304LN according to ASTM standard) and possibly 2–3%Mo (e.g. 1.4404, 1.4406 or 1.4436; AISI 316L or 316LN), and to exposure to mild temperatures of 20–25 °C [18–24].

Nevertheless stainless steel bars are often used to increase the service life of reinforced concrete structures exposed to marine tropical climates [25] where the aggressiveness of the environment is increased by temperatures that may exceed daily average values of 40 °C with much higher peak values [26]. In these environments, even though concrete has a low thermal conductivity, high temperature may be reached at the depth of the steel bars, leading to a remarkable decrease in the chloride resistance, i.e. on the chloride threshold.

Only few data on other stainless steel grades [27–30] and in hot environments are available [6,31,32]. Particularly, few data are available on different grades of stainless steels with duplex austeno-ferritic microstructure which have been proposed as rebars for concrete [15,27–30]. Initially duplex stainless steel 1.4462, with about 22% Cr, 5%Ni and 3%Mo, was studied and this showed a corrosion resistance in chloride-contaminated concrete even higher than that of austenitic stainless steels [32]. In recent years, the increase in the cost of alloying elements has led to the use of low-nickel and low-molybdenum duplex stainless steels as reinforcing bars, such as 1.4362 (about 23%Cr and 4% Ni) and 1.4162 (about 21%Cr, 1% Ni and 4% Mn). At temperatures of about 20 °C, duplex 1.4362 stainless steel was shown to suffer pitting corrosion in concrete with 3% chloride by cement mass [16]; a lower corrosion resistance in chloride contaminated concrete was observed on 1.4162 [16,28,29]. As far as the effect of high temperature is concerned, results of potentiodynamic polarisation tests at 50 °C in alkaline solutions (pH = 12) with 21 g/L of sodium chloride showed that neither duplex stainless steels (1.4362 and 1.4462) nor traditional austenitic stainless steels (1.4301 and 1.4404) exhibited pitting corrosion initiation [33]. However, no data on the corrosion resistance of these stainless steel grades embedded in concrete exposed to high temperature are available. So the corrosion behaviour in tropical environments of low-nickel duplex stainless steel reinforcing bars still needs to be evaluated.

This paper reports the results of an investigation on the effect of temperature on the corrosion resistance of rebars of low-nickel duplex stainless steels and traditional austenitic stainless steels. Tests in concrete and in solution were carried out in the presence of different concentrations of chloride ions. A detailed description of the results of the tests performed at 20 °C is reported in reference [16], in which different test procedures to estimate the critical chloride content for corrosion initiation in solution and in concrete are compared. This paper describes results of tests at temperatures in the range 20–60 °C and focuses on the effect of increasing temperature on the chloride threshold.

2. Experimental procedure

Tests were carried out on commercial rebars of two grades of low-nickel duplex stainless steels (1.4162 and 1.4362) and, for comparison, two grades of austenitic stainless steels (1.4311 and 1.4406). Table 1 shows the chemical composition and mechanical properties of the steel bars. The surface of the bars was subjected to ordinary commercial pickling; in order to remove all the potential contamination on the steel surface, the bars received in the lab were further pickled and degreased with acetone. Microstructure of the stainless steels were analysed and results are reported in Ref. [16].

Table 2
Mix proportions of concrete.

Water/cement ratio (w/c)	Cement[a] (kg/m^3)	Water (kg/m^3)	Aggregate[b] (kg/m^3)	Chloride (%)[c]
0.65	300	195	1830	0, 3, 5 and 8
0.5	350	175	1840	5 and 8

[a] Type: CEM II/B-L 32.5R (EN 197-1 standard).
[b] Crushed limestone aggregate, maximum size 9 mm.
[c] By mass of cement, added to the mixing water as calcium chloride.

2.1. Tests in concrete

Bars were embedded in concrete with water/cement ratio of 0.5 and 0.65 and limestone–portland cement (CEM II/B-L 32.5R; EN 197-1 standard) was utilised (Table 2). Concrete with different chloride contents (0, 3%, 5% and 8% by mass of cement added as $CaCl_2$) was cast with a *w/c* ratio 0.65 (two replicate specimens were prepared for each chloride contamination). In order to study the possible role of the water/cement ratio on the chloride threshold concrete with *w/c* ratio 0.5 was also cast with 5% and 8% of mixed-in chloride by mass of cement. Each specimen embedded a bar of each grade of stainless steel. The bars had a concrete cover thickness of 10 mm at the side of casting.

A mixed-metal oxide activated titanium (MMO) wire was fixed near each bar, to be used as reference electrode for measurements of corrosion potential, and a mesh of MMO was embedded in each specimen, to be used as a counter-electrode for electrochemical tests. Concrete specimens without mixed-in chloride were subjected to chloride penetration in order to promote chloride penetration through the concrete cover, reproducing condition of ingress of chloride similar to those expected in real structures. Chloride penetration was carried out by means of ponding with a solution of 35 g/L of sodium chloride for about five months; during this period the chloride content in the concrete at depth of 10–20 mm, representative of the position of the steel bars, reached a value of about 2.5% by cement mass, as described in Ref. [16]. Specimens with both mixed-in and penetrated chlorides were placed in a climatic chamber at 20 °C and 90% R.H. for at least three weeks. Afterwards the temperature was increased to 40 °C, 50 °C and 60 °C and then it was returned to 20 °C. Each step of temperature was maintained for at least one week. Corrosion potential and corrosion current density of the bars were monitored. Corrosion potential was measured versus activated titanium electrodes embedded close to the surface of each bar as well as versus an external calomel reference electrode. Corrosion current density was estimated by means of the polarisation resistance technique. The polarisation resistance was measured by imposing potential steps of ±10 mV versus the free corrosion potential and measuring the current density circulating after 30 s of polarisation. The corrosion current density was calculated as: $i_{corr} = R_p/B$, and a value of 26 mV was considered for the parameter B [34].

Table 1
Chemical composition and mechanical properties of stainless steel bars.

Designation		Alloy elements (% by mass)										Y.S	U.S.
EN 10088-1	ASTM/UNS	C	Si	Cr	Ni	Mo	Mn	N	P	S	Cu	(MPa)	(MPa)
1.4406	361LN	0.017	0.58	17.53	11.26	2.56	1.11	0.14	0.033	0.001	–	558	783
1.4311	304LN	0.017	0.42	18.71	8.58	–	1.22	0.16	0.028	0.001	–	790	882
1.4362	S32304	0.024	0.49	23.13	4.49	0.25	1.46	0.137	0.025	0.001	0.14	633	774
1.4162	S32101	0.048	0.8	22.07	1.18	0.02	4.14	0.212	0.024	0.001	–	513	761