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Corrosion behaviour in concrete of three differently galvanized steel bars

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Abstract

The increasing use of galvanized steel reinforcements in concrete structures submitted to aggressive environments induces research into innovative zinc coatings with higher corrosion resistance. In this work, several cylindrical concrete specimens were manufactured with two cements of different alkalinity and reinforced with different hot-dip galvanized bars obtained from the "traditional" Zn–Pb bath and from two "modified baths": Zn–Ni–Bi and Zn–Ni–Sn–Bi. The corrosion rate and corrosion potential of the bars were monitored during the air curing period and during wet–dry exposure both in tap water and in a 5% sodium chloride solution. The results showed that the coatings obtained from Zn–Ni–Sn–Bi bath have the highest corrosion rates, when the aggressiveness of the concrete matrix is determined mainly by its alkalinity. On the contrary, when the corrosion process is determined mainly by the penetration of chlorides (concrete manufactured with cement having a low alkali content) Zn–Ni–Sn–Bi was attacked only when the chloride concentration at the concrete cover depth reached the threshold of 4.02% (by weight of cement), which is higher than those necessary for the attack of the other coatings studied (1.36% for Zn–Ni–Bi, 1.73% for Zn–Pb).

Keywords: Galvanized steel; Alloying elements; Corrosion in concrete; Chlorides exposure

1. Introduction

The production of zinc coatings with a good "quality-cost" ratio [1] means a low zinc consumption during the process and the obtainment of coatings with controlled thickness and good corrosion resistance. Coating quality and zinc consumption in hot-dip galvanizing strongly depend on the zinc–iron reactivity and on the drainage of zinc from workpieces during their withdrawal. The zinc–iron reactivity is mainly influenced by the silicon and phosphorus steel content [2]; zinc drainage, instead, is influenced by bath fluidity [3]. Therefore, some alloying elements are added to the molten zinc bath in order to limit the zinc–iron reactivity and to improve the bath fluidity. In particular, lead additions (usually, about 1%) were extensively used because it gives a more fluid molten zinc bath; however, this metal is considered hazardous to the environment, so new baths with different alloying elements have been proposed, such as Zn–Ni–Bi [1] or Zn–Ni–Sn–Bi. Nickel additions to the molten bath reduces zinc–iron reactivity while maintaining the specification minima for coating thickness [4]. Tin also reduces zinc–iron reactivity and is commonly used in combination with nickel [5]. All these "modified baths" with respect to the Zn–Pb "traditional bath" have been mainly developed in order to decrease zinc–iron reactivity and to reduce the coating thickness. Furthermore, the corrosion resistance in the concrete matrix of the coatings obtained with these baths is gaining interest [4] because the initial cost for galvanizing could be lower than that of restoring during the service life [6]. In Italy, the use of galvanized steel is becoming important because a recent technical normative on constructions recommends the use of these reinforcements in particularly aggressive environments, as in the presence of chloride contamination, especially when the concrete cover is cracked. The interaction between galvanized steel and various alkaline solutions, with and without $Ca(OH)_2$ has been widely studied [7–11]; the interaction between galvanized bars

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and concrete matrixes obtained with different cements has been studied in the past by other researchers [4,12] and by the present authors [13,14].

The aim of this work was to study the corrosion resistance of reinforcements galvanized with Zn–Ni–Bi and with Zn–Ni–Sn–Bi "modified baths", with respect to reinforcements galvanized with the Zn–Pb "traditional bath" and to a pure zinc rod, where the effect of the alloying elements and of the zinc–iron alloys, typical of the galvanized coatings is absent. Cylindrical concrete specimens were manufactured and reinforced with galvanized bars and with a pure zinc rod; two cements with a different alkali content were used to study the effect of alkalinity of the concrete matrix on the behaviour of the reinforcements. After the air curing period, the concrete specimens were submitted to wet–dry exposure both in tap water and in a 5% sodium chloride solution. The corrosion rate and the corrosion potential of the bars were monitored during the air curing period and during the wet–dry exposure.

2. Experimental details

Several cylindrical specimens ($\phi = 16$ cm; height = 12.5 cm) (Fig. 1) similar to those used in a previous work [15] were manufactured. Two 52.5 R Portland cements (Table 1) were used: the first one, labelled "L", develops less alkalinity than the second one, labelled "P", in the concrete matrix in wet conditions. Both for L and P cement the mix design reported in Table 2 was used.

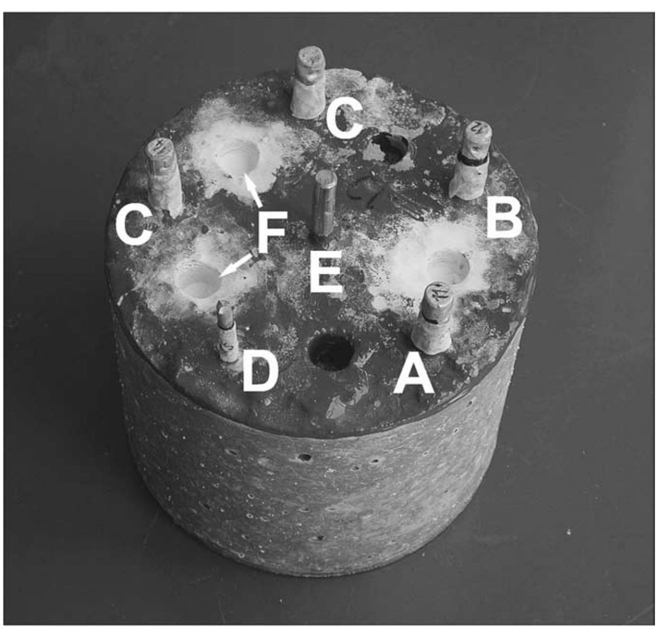

Fig. 1. Concrete reinforced specimen: (A) bar galvanized in the Zn–Pb bath; (B) bar galvanized in the Zn–Ni–Bi bath; (C) bars galvanized in the Zn–Ni–Sn–Bi bath; (D) pure Zn rod; (E) counter electrode; (F) pits for placing the reference electrode.

Table 2
Mix design relative to 1 m^3 of concrete (water–cement ratio = 0.55)

Water	3.02 kg
Cement	5.48 kg
Sand ($D_{max} = 4$ mm)	7.88 kg
Gravel ($D_{max} = 8$ mm)	11.81 kg

Table 3
Composition of the baths used for hot-dip galvanizing of the bars

Bath	Label	Pb (%)	Bi (%)	Sn (%)	Ni (%)	Al (%)
Zn–Pb	A	1 (Saturated)	–	–	–	–
Zn–Ni–Bi	B	–	0.15	–	0.05	0.004
Zn–Ni–Sn–Bi	C	–	0.1	1.1	0.05	0.007

Each specimen was reinforced with four galvanized ribbed steel bars ($\phi = 10$ mm; length = 12 cm) and one pure zinc rod ($\phi = 5$ mm; length = 12 cm), used for comparison (Fig. 1). Considering the silicon and the phosphorous content of the steel used, which was respectively 0.14% and 0.0015 wt%, it can be classified as a "hyper-Sandelin" steel [2]: its reactivity with respect to molten zinc during the hot-dip galvanizing may be considered high. Before hot-dip galvanizing, each bar sample was pretreated as described previously [1]. After the pretreatments, the bars were galvanized ($T = 444 \pm 1$ °C, time = 6 min, air cooling) in three different baths having the composition reported in Table 3. For all the bars and the zinc rods, the concrete cover was 1.5 cm. In the centre of each concrete specimen, a stainless steel rod was embedded and used as counter electrode during polarization resistance measurements. The pits visible in Fig. 1 on the top of the concrete specimens were produced for placing the saturated calomel electrode (SCE) used as reference electrode. An epoxy resin was applied on the top and on the bottom of the concrete cylinders (Fig. 1) to limit the penetration of aqueous solutions from the only lateral surface. The epoxy resin was not applied on the pits described above in order to keep the electric contact for the reference electrode during the electrochemical measurements free. During wetting tests, the solution level was maintained slightly under the top of the concrete specimen to avoid the penetration of the solution in the pits. Each bar sample, before embedding in the concrete specimen, was suitably shielded with an epoxy

Table 1
Chemical composition of the cements used

Cement type	Loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Insoluble residue	Free lime	C_3A	C_4AF
L	1.80	21.90	3.30	5.10	62.50	2.70	2.10	0.30	0.40	0.90	1.40	0.20	15.50
P	3.26	21.83	3.41	0.23	65.41	1.67	2.70	0.69	0.37	0.54	1.01	8.64	0.70