Applied Surface Science 256 (2010) 6139–6143

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Review

Low-nickel stainless steel passive film in simulated concrete pore solution: A SIMS study

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ARTICLE INFO

Article history:
Received 9 February 2010
Received in revised form 23 March 2010
Accepted 29 March 2010
Available online 4 April 2010

Keywords:
SIMS
Passive film
Low-nickel stainless steel
Concrete pore solution
Depth profile

ABSTRACT

Low-nickel and AISI 304 austenitic stainless steel (SS) passive films were studied using secondary ion mass spectrometry (SIMS). An alkaline $Ca(OH)_2$ saturated test solution containing different chloride additions was used at room temperature. The passive film formed consists mainly of an inner chromium-rich oxide layer and an outer iron-rich oxide layer. The chemistry of the passive film depends strongly on the chloride content in the alkaline solution. Under these exposure conditions nickel was detected in the outer part of the oxide, whereas chloride ions were *not* found in the passive film for either the low-nickel or AISI 304 SS alloys.

Contents

1. Introduction

Steel rebar embedded in concrete is protected from corrosion by a thin oxide layer that is formed and maintained on their surfaces because of the highly alkaline environment of the surrounding concrete, with a pH usually in the range 12–13 [1]. However, with time, severe corrosion may occur in reinforced concrete structures (RCS). Corrosion is most frequently induced by the entry of chloride ions, leading to localised corrosion activity. Chloride ions are commonly found in construction materials and may originate from contamination of the water used in concrete production, from contaminated aggregates, or even from the external environment, as in the case of marine environments or de-icing salts [2].

Austenitic stainless steels (SSs) are alloys of great interest in technological applications where materials with high corrosion resistance are required. The stability of the surface oxide (i.e. passive film) formed on an austenitic SS depends mainly on the alloy composition, temperature, passivation time and working environment. These passive oxide films are of the order of only 1–4 nm thick and their analysis is therefore challenging [3].

The solid-state properties of passive films formed on SS have been widely studied using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and X-ray absorption spectroscopy (XAS) techniques [4–8]. Secondary ion mass spectrometry (SIMS) is well suited for the study of surface oxidation phenomena related to sample transfer because it allows the detection of isotopes at very low concentration levels [9,10]. Previous studies have revealed that passive films formed on austenitic SS exposed

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doi:10.1016/j.apsusc.2010.03.140

Table 1
Chemical composition (% by weight[a]) of the tested low-nickel austenitic SS and AISI 304 austenitic SS.

Material	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N
Low-nickel	0.082	0.48	7.26	0.027	0.001	16.56	4.32	0.07	0.13	0.075
AISI 304	0.049	0.32	1.75	0.028	0.001	18.20	8.13	0.22	0.21	0.050

[a] The balance was Fe.

to aqueous solutions are a mixture of iron and chromium oxides, with hydroxide and water-containing compounds concentrated in the outermost region of the film and chromium oxide enrichment at the metal/film interface [11].

In the literature it has been proposed that during the anodic dissolution of SS materials the alloying elements chromium, molybdenum and nickel are enriched at the metal/oxide interface in their metallic states and that nickel decreases the current in the passive state, hence enhancing the passivation of the alloy [12,13].

The SS offers exceptional advantages for certain applications in construction, combining intrinsic durability with aesthetics, strength, ductility and formability. However, their use as rebar has been limited due to the prohibitively high cost of SS compared to carbon steel. For this reason, new SSs, in which the nickel content has been lowered by replacement with other elements [14,15] (nickel is subject to considerable price fluctuations due to stock market factors), are being evaluated as possible alternatives to conventional carbon steel [16–18].

Low-nickel austenitic SSs exhibit attractive properties comparable to those of traditional austenitic SSs, such as good corrosion resistance, high levels of strength and ductility and reduced tendency of grain sensitisation [19]. These low-nickel SSs should be highly nitrogen alloyed and have a well-balanced two-phase structure: 40% ferrite (α)–60% austenite (γ) up to 60% α–40% γ. The production of these low-nickel steels is made possible by the addition of manganese that increases the nitrogen solubility in the melt and significantly retards the tendency of nitride precipitation (such as chromium nitride, Cr_2N).

It has been reported that the oxide film breakdown occurs non-uniformly over the surface, starting from a number of activated sites which reaction products formed consist of voluminous non-protective hydroxide [20]. Several authors have reported on the effect of manganese on corrosion resistance, for instance, manganese decreases the pitting resistance of 18% chromium, 5% nickel, 10% manganese and 0.07–0.35% nitrogen alloy [21,22]. The decrease of nickel, essentially a γ-stabiliser increasing pitting corrosion resistance [23], is compensated with an increase in nitrogen content. Manganese is an important γ-stabiliser and it also contributes to improved nitrogen solubility [14]. It is well known that manganese and nickel promote austenitic microstructures which are more corrosion resistant in chloride media than the ferritic microstructure [23].

The different models proposed to describe the events leading to breakdown of the passive film can be classified into two groups attributing specific role to the chloride ion: adsorption of the chloride ions on the passive film, and ion migration or penetration of the chloride ions through the passive film to the metal surface [24–26].

The aim of this paper was to investigate the influence of chloride content in a simulated concrete pore solution on a low-nickel SS generated passive film using the SIMS technique. A conventional AISI 304 SS was also studied for comparative purposes. Special attention was paid to study the presence of chloride ion within the passive film.

2. Experimental

Low-nickel and AISI 304 austenitic SSs (from ACERINOX SA Company, Palmones, Cádiz, Spain) plates of 0.5 cm × 0.5 cm were used. Table 1 shows the chemical composition of the two materials, provided by the manufacturer. Specimens were polished using a series of silicon carbide (SiC) emery papers down to grade 1200, and afterwards, using diamond paste of 1 μm, and then ultrasonically cleaned with ethanol and rinsed with water.

The simulated concrete pore (SCP) solution was a calcium hydroxide ($Ca(OH)_2$) saturated solution with a pH ~12–13, with different amounts of sodium chloride (NaCl): 0, 0.4, 1.0, 2.0, 3.0 and 5.0% by weight. Specimens were immediately immersed in the solutions after the surface preparation. The total immersion time was 20 days. After that period of time, specimens were cleaned with isopropanol, ethanol and water and dried in N_2 in order to remove any surface contamination before analysis.

An Atomika 6500 was used for SIMS measurements. A primary ion beam of N_2^+ was used, with a beam energy of 500 eV and in normal incidence. The beam current was 50 nA. All craters were ~500 μm in diameter.

3. Results and discussion

Fig. 1 shows chromium depth profile for AISI 304 SS (Fig. 1a) and for low-nickel SS (Fig. 1b) specimens after 20 days immersion in the SCP solution with different NaCl contents. Analysis was performed for 1200 s; however no changes were observed after 600 s, suggesting that the bulk alloy was reached within that period of time. For

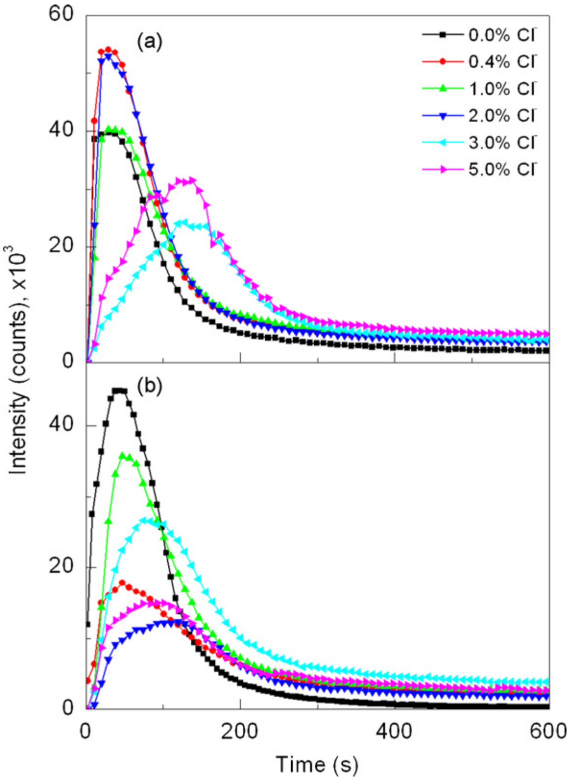

Fig. 1. Depth profiles for (a) AISI 304 SS and (b) low-nickel SS specimens immersed in a simulated concrete pore solution with different concentrations of NaCl, showing chromium content of the oxide layer. N_2^+ primary beam, 500 eV, 50 nA. Crater size of 500 μm.