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ORIGINAL PAPER

Restoration of cultural heritage: evaluation of the compatibility between metals and sealing products

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Abstract When restoring historical monuments, it is often verified that reinforcements, mostly made of ferrous alloys, are in quite a bad state and must be partially or totally replaced to prevent further degradation or accidents. Modern alloys such as stainless steels are increasingly used for such purpose, which raises the open question concerning their compatibility with the new types of sealing products available on the market. Even though it is not possible to use accelerated tests to give a livelong guarantee of adequacy of materials combination, electrochemical tests of metals in an aqueous extract of the sealing products could be used as screening to rapidly identify situations that would conduce to the premature corrosion of the metal.

Keywords Stainless steel · Metallic reinforcement · Sealing agent · Restoration · Polarization plot

Introduction

The motivation for this work stems from a practical problem encountered during routine restoration of historical monuments. It concerns metallic structural parts of buildings and statues, mostly in iron, which were originally intended to give mechanical stability and sustain the construction. After decades or even centuries of exposure to all kinds of weather conditions, they are often in a quite bad state of conservation, causing fissures in the stone due to the higher volume occupied by corrosion products (Fig. 1).

In such cases, ethical principles of restoration [1] recommending the conservation of all original parts cannot be applied, since reinforcing elements play an important role in the stability of a building or a statue. Among the materials already used for such replacements, stainless steel is being increasingly applied due to its good corrosion resistance [2, 3].

However, the question of its compatibility with the many different products available on the market for fixing armature inside the stone during the intervention remains open. Since the chemical composition of such sealing products is generally unknown, specific tests should be performed before use, in order to verify that the association of sealing products and metallic alloys is safe. This task is however not practically achievable due to the long period of time necessary to obtain reliable results when conducing aging tests and also to the difficulty in interpreting them. Aiming to overcome this inconvenience, the present paper investigates the adequacy of an electrochemical technique to assess the compatibility between different materials in an easy and quick way.

Experimental

The experimental procedure consisted in comparing the performance of given combinations of alloys and mortars when tested under different conditions. Regarding materials, two types of metallic alloys provided by Arcelor have been used. One was stainless steel (AISI 301 L) and the other was iron-nickel alloy (Invar 36% Ni). As sealing

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Fig. 1 Cracks in the stone sculpture due to corrosion of iron armature. "Prophète tendu vers le Christ qui monte aux Cieux". Saint-Pierre cathedral, Angoulême, France

products, commercial plaster and polyester resin have been employed, prepared, and applied following the supplier's recommendations.

Samples submitted to aging tests have been prepared simulating an actual situation of restoration. Therefore, metallic alloys in the as-received surface condition were cut to a uniform size (3×20 cm), and their extremities were bent and fixed with sealing products in previously open cavities in stone 'bricks'. Each combination metal/mortar was prepared in triplicate, in order to keep one sample as reference and let the other two age under natural and accelerated conditions. For atmospheric aging, samples were placed at the top of Langres Cathedral, in eastern France, where extreme variations of temperature are recorded. In the case of artificial aging tests, cycles of −10°C to 60°C have been applied three times a

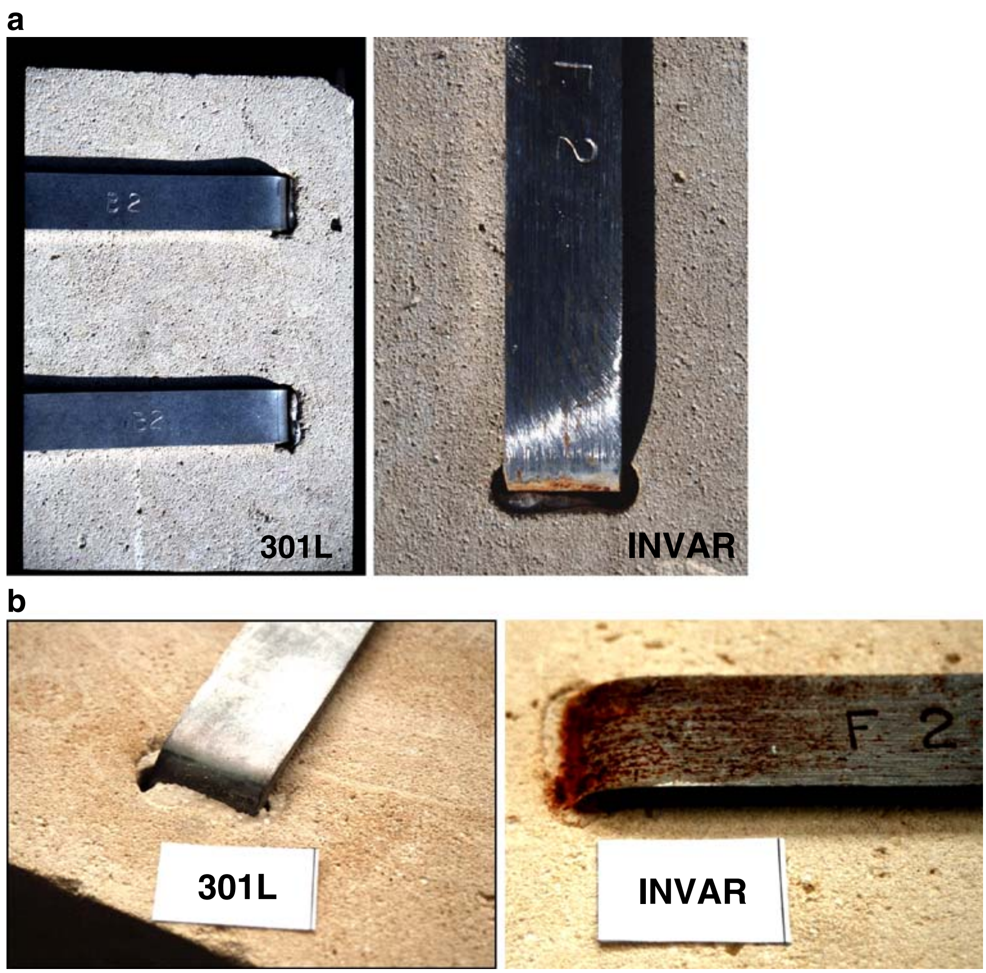

Fig. 2 Hooks sealed with plaster, after 8 months of exposure at Langres Cathedral (**a**) and 5 months in a climatic chamber (**b**)

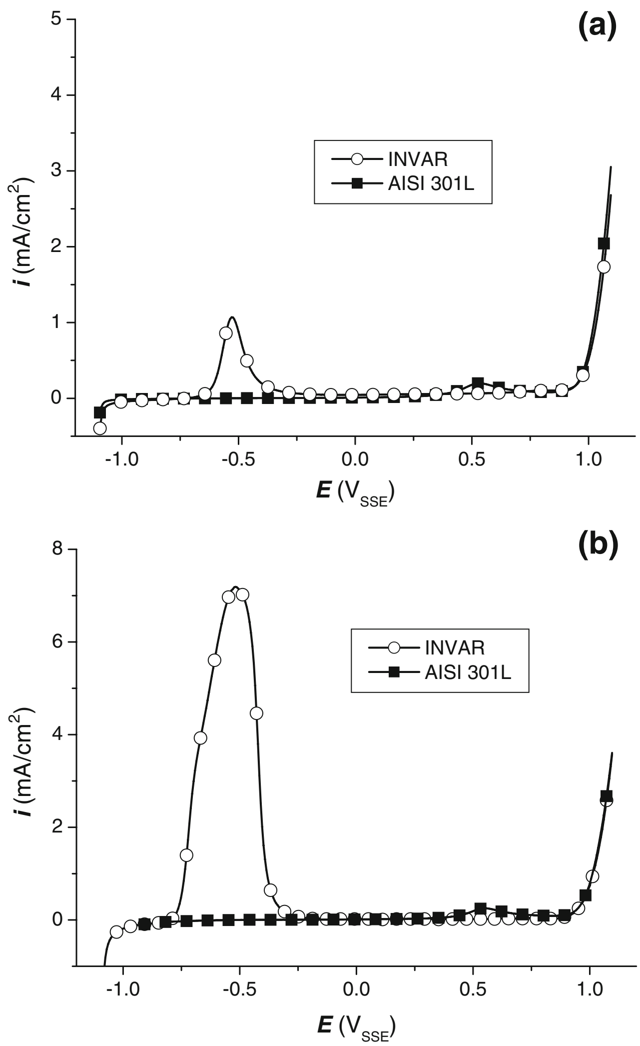

Fig. 3 Polarization plots for stainless steel and iron-nickel alloys in extracts of polyester resin (**a**) and plaster (**b**)

day in a climatic chamber. Periodical visual inspection recorded alterations in the aspect of the samples.

Electrochemical tests have been performed with a Voltalab 21 (Radiometer analytical) using the same metallic alloys, a Pt counter-electrode, and a saturated sulfate electrode as reference electrode. The area of the working electrode (1 cm^2) was limited with varnish. The electrolyte was an aqueous extract of each sealing product, to which has been added a support solution (0.1 M Na_2SO_4) [4]. Starting from open circuit, the electrode potential was scanned into positive values at 10 mV/s.

Results

A significant difference in the corrosion behavior of the two metallic alloys could be observed after exposure periods of 8 months in atmospheric conditions and 5 months in climatic chamber. While the stainless steel clamps seem not altered, the invar samples show already visual signs of corrosion, more evident in the regions in close contact with plaster (Fig. 2).

Voltammograms obtained in extracts of mortars confirm the above-described trend. As shown in Fig. 3, anodic polarization of stainless steel (black squares) do not lead to current flow in either media, except at potentials more positive than 1 V. In the case of invar (white circles), one observes a peak of current (at ca. −0.5 V), the amplitude of which depends on the composition of the extract. The peak is more prominent in the plaster extract than in the polyester extract. This region of potential is very close to the open circuit condition (−0.7 V), attesting the susceptibility of that alloy under natural conditions.

Conclusion

Electrochemical tests using aqueous extract of sealing products have been shown to allow the evaluation of their inadequacy to be used with certain metallic alloys. The good agreement between polarization curves and the visual inspection of samples after long duration tests suggests that electrochemical tests could be used as a fast screening trial, valuable to promptly discard some combination possibilities that would be dangerous on the long term for the conservation of the monument.

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