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Micromechanical and microstructural investigation of steel corrosion layers of variable age developed under impressed current method, atmospheric or saline conditions

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ABSTRACT

In this paper, we have gathered the conclusions of an experimental campaign dedicated to the microstructural characterization and the determination of the local elastic properties of various natural and artificial corrosion product layers. The results of micro-indentation testing and Raman spectroscopy coupled with a semi-quantitative analysis have been presented for the whole set of investigated materials, from early-age (2 weeks) corrosion products to 660 years-old massive corroded samples. An interpretation of the local Young's modulus and hardness values has been proposed by relying on a Gaussian mixture model. The relation between the observed morphologies of the corrosion products layers, their composition and the distribution of elastic modulus and indentation hardness has finally been discussed.

1. Introduction

The long-term isolation of radioactive waste in deep repositories relies on a multi-barrier concept in order to guarantee that no significant environmental releases occur over a long period after disposal. The immobilized or compacted waste packages are sealed inside reinforced concrete canisters and surrounded with bentonite clay before being located deep underground in a stable rock structure. In this multi-barrier concept, the reinforced concrete canisters are aimed to contribute to the mechanical stability of the storage, as well as to limit the mass transfer between the waste and the biosphere [1]. Consequently, it seems essential to understand the hydro-mechanical behaviour of all the materials involved and the possibly evolving interfaces between the various materials appear as a key aspect in the assessment of their long term performance.

Owing to the lack of available data concerning the mechanical properties of iron oxides at the mesoscopic scale of corrosion layers, the presence of evolving corrosion product layers at the interface between the concrete and the rebar cannot be explicitly taken into account in multiphase or multiscale models. For such a reason, our project has been dedicated to the mechanical characterization of corrosion layers formed within carbonated reinforced concrete [2,3]. As our work is mainly concerned with natural corrosion layers developed over the long term, such corrosion products have been sampled from old constructions, whose steel is completely corroded [4–7]. However, in order to compare our findings with the data available in the published literature, which deal generally with artificially created corrosion, our study also encompasses corrosion samples developed in the laboratory under an imposed electric current (accelerated corrosion) [8,9] or under a saline environment [10–13].

The Dense Product Layer (DPL) of iron oxides that develop at the interface between the remaining reinforcement and the concrete presents a complex, highly heterogeneous structure. At the micrometer scale, different phases are encountered in varying proportions. A small porosity (around 10 %) is also present, consisting mostly of cracks of finite extension approximately oriented along the initial rebar [2,14–17]. Depending on the kind of corrosion – natural or synthetized, the environmental conditions of corrosion and the age of the samples, the estimated modulus of the DPL at the mesoscopic scale is comprised between 0.1 GPa and 200 GPa [2,9,13,18]. Apart from the heterogeneous microstructure, the great dispersion of the published data is also due to the identification procedure. The lowest values of Young's modulus, of the order of 0.1 GPa, are found in [8,13,9,19,20], and may not be viewed as intrinsic values of the elasticity modulus. In those references, macroscopic experiments on composite samples comprising the concrete and the rebar corroded under impressed current, are numerically simulated in order to reproduce the time for cover-crack initiation. The latter approach requires the

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back-calculation of the elastic properties of corrosion layers using Finite Element computations based on an analogy with thermo-elasticity, the thermal expansion coefficient representing the expansion ratio of the corrosion products. Such an analogy has proved convenient to express some effects of the corrosion development on the damage of the cover concrete, and requires very low values of Young modulus for corrosion products as an input data in order to obtain realistic predictions. In other studies [21–23], the mechanical properties have been measured on macroscopic samples of rust particles reduced to powder, using oedometer tests. The resulting moduli are comprised between 0.3 and 5 GPa, this may be explained by the fact that the initial structure of the corrosion products has been completely destroyed, the investigated samples behave consequently as granular materials instead of the initial layered structure with strong cohesion between the different corrosion layers. In [21], the exploitation of oedometer test results using Hertz theory of contacting spheres leads in contrast to very high values of elasticity modulus, comprised between 307 and 477 GPa. The latter values are close to Young's moduli measured by [24,25] on mono or poly-crystals of magnetite. In recent studies, depth sensing nano-indentation [18,26] or micro-indentation [3] have been employed in order to identify the local elasticity modulus and Vickers hardness of corrosion layers at the micrometer scale of the heterogeneous corrosion layers. The resulting values measured on natural [18,3] or artificial [26] corrosion products are comprised between 51 and 158 GPa.

Owing to the great dispersion of the mechanical properties identified for iron oxides, and to their complex microstructure, it appears therefore necessary to study the porous DPL at the level of its components, with an aim to characterize the mechanical behaviour of corrosion layers at the mesoscopic scale in relation with typical microstructural features. In the continuity of a preceding work [3], Raman micro-spectrometry coupled with semi-quantitative interpretation using CorATmos software [4,27], and depth sensing micro-indentation have been employed on a variety of corrosion samples. For all the investigated materials, the results of more than 440 micro-indentation points and 1500 Raman spectra are summarized and discussed in the present paper. Whenever possible, the indentation test results have been interpreted using a Gaussian mixture model [28] which allows differentiating between groups characterized by statistically distinguishable mechanical properties (hardness and local elasticity modulus). The interpretation of microstructural and micromechanical data has enabled us then to identify a number of representative constituents and microstructural arrangements for each sample depending on the kind of corrosion (natural or artificial) and its age, as well as average mechanical properties for each representative groups of constituents.

2. Experimental

2.1. Materials

The study has been conducted on different types of corrosion products, from early-age corrosion synthetized in the laboratory to on-site, massive corrosion layers sampled on ancient buildings.

2.1.1. Corrosion products of reinforcing bars embedded in a concrete building

A specimen of reinforced concrete building, aged approximately 50 years, has been taken in the urban area of Paris (France), Fig. 1(a). This specimen is composed of ordinary concrete and the remaining part of a corroded rebar, and presents the advantage of maturation under the atmospheric cycles of the Parisian region. This sample allows to investigate atmospheric corrosion in a contemporary concrete under known carbonation conditions. From the test with phenolphthalein displayed in Fig. 1(a), we can notice that the upper surface of the mortar as well as a few localized areas around the corrosion layers are carbonated. However, the amount of corrosion products is limited (the maximum width of the corrosion layer is about 2 mm) and is not sufficient to conduct a complete experimental investigation.

2.1.2. Atmospheric corrosion of ferrous archeological artefacts

For this reason, and also because we are investigating long-term corrosion, we have chosen to focus our study on ancient ferrous artefacts embedded in aerial and hydraulic unsaturated binders exposed to atmospheric conditions. Such corroded samples

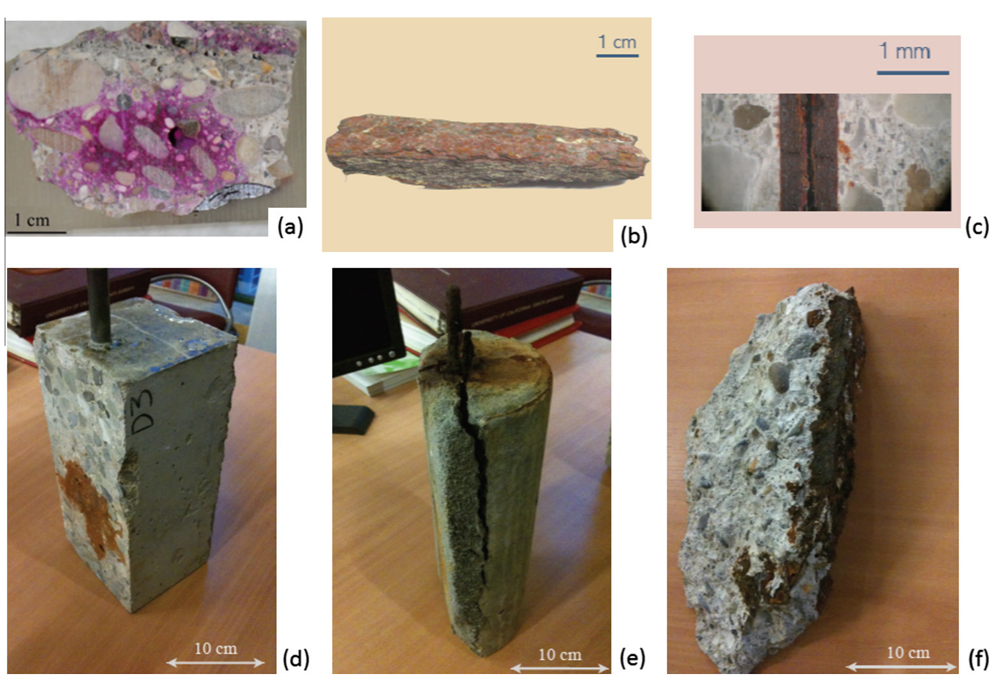

Fig. 1. Investigated samples. (a) Sample of reinforced concrete building aged 50 years; (b) ancient ferrous artefact aged 660 years; (c) corrosion synthetized under imposed current. Corrosion developed in the laboratory under controlled saline conditions; (d) 3 years-old sample; (e) 14 years-old sample; (f) 25 years-old sample.

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