Micro-Mechanical Analysis of Corrosion Products Formed During Long-Term Carbonation Induced Corrosion of Steel

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ABSTRACT

During corrosion distinct types of corrosion products form, composed of different ratios of ferrous ions and oxide, hydroxides. Corrosion products have different physical and mechanical properties, mainly density, resistivity, volume and modulus of elasticity compared to iron. Knowing properties of corrosion products is indispensable for service life modelling of structures and can give valuable insight into the long-term corrosion propagation process.

In this study micro-indentation method was used to evaluate mechanical properties of different layers formed during long-term carbonation induced corrosion of steel in concrete. Investigation was performed on three sets of reinforced concrete samples, that underwent corrosion during 50, 60 and 70 years. Raman microspectroscopy was performed locally to determine and locate the constitutive phases of the corrosion system and to correlate them to the results of micro-indentation. Using grid technique, spatial distribution of phases with different mechanical properties was obtained for samples of different age. Comparison of values of mechanical properties for the same phases obtained on different samples, allowed hypothesis on their long-term behaviour.

Keywords: micro-indentation, Raman microspectroscopy, carbonation, corrosion, reinforced concrete.

1.0 INTRODUCTION

At the micro-scale level a typical corrosion pattern is composed of four successive layers: the uncorroded metal, the corrosion layer or dense product layer DPL (or inner corrosion product layer), the transformed medium containing phases originating from both the DPL and the binder (or the outer corrosion product layer) and the binder (Chitty *et al.*, 2005; Dehoux *et al.*, 2012; Milard and L'Hostis, 2012). During corrosion different types of corrosion products form, composed of different ratios of ferrous ions and oxide, hydroxides. Different products have different physical and mechanical properties, mainly density, resistivity, volume and modulus of elasticity compared to iron. Knowing properties of each of these levels is indispensable for service life modelling and durability management of structures. One of the methods that can be employed for evaluating micro-mechanical properties of corrosion products is micro or nano-indentation. Micro-indentation has been a widely-used method to interpret the local elastic properties and hardness of different materials at the micro-scale. Method was previously used to study micromechanical properties of naturally and accelerated occurring corrosion layers (Zhao *et al.*, 2012), and on thicker layers of products found on archaeological analogues (Dehoux *et al.*, 2012; Reguer *et al.,* 2007; Zhao *et al.*, 2012). More recently nano-indentation was used to study mechanical properties of cement hydration products [7]–[9]. Micro-indentation and nano-indentation tests performed on corrosion layers reveal that local elastic modulus values are in the range of 50 and 200 GPa (Dehoux *et al.*, 2012). Other results indicate several magnitudes lower values, obtaining modulus of elasticity as low as 0.1 GPa (Care *et al.,* 2008; Zhao *et al.,* 2012a*)*.

In the present literature there is still a lack of distinction between the mechanical properties of different layers of corrosion products, and there is still a high discrepancy between the values obtained depending on the methods used (nano, micro-indentation) and sample preparation (pure corrosion

products, cross section). Considering the importance of this parameter in the predictions of time to cracking of concrete, it is evident that further efforts should be focused at evaluating this parameter with higher precision.

Additionally, it is not only the type of products that influence the stresses formed in the concrete during corrosion, it is their position compared to the surface of the steel. The spatial distribution of products formed during long-term corrosion can reveal history of their consecutive formation, dissolution of one and formation of the other phase. Since the mechanical properties are different, hypothesis is that the information on their mechanical properties can be used for differentiating them and analysing their spatial distribution.

The aim of the present research is to perform micro-indentation analysis to distinguish distinct phases of corrosion products formed during long-term corrosion.

2.0 MATERIALS AND METHODS

To perform the analysis of corrosion products, it is necessary to have thicker products available. Products can be formed artificially, using electrochemical or environmental acceleration (Care *et al.,*2008; Zhao *et al.,* 2012b). Other strategy is to use samples of archaeological analogues (Monnier *et al.,* 2012) or samples from old concrete structures (Dehoux *et al.,* 2012), which went through the natural long-term process of corrosion of steel. In the present research corrosion samples were taken from three different old buildings: 1 - sample from Maison du Bresil, Cite Universitaire (1957 - 1959), approximately 50 years old corrosion sample, 2 - sample from ONERA wind tunnel, Meudon (1950), approximately 60 years corrosion sample, and 3) sample from Bourse du travail in Bordeaux (1938), approximately 70 years old corrosion sample. Samples were previously mounted in epoxy resin and cut to obtain thinner cross sections. They were grinded with SiC papers and then polished with a 3 μm diamond paste under ethanol. On all of the samples used in this research there are available information that can be found elsewhere (Chitty *et al.,* 2005; Demoulin *et al.,* 2010; L'Hostis *et al.,* 2009).

Micro-mechanical properties of corrosion products were obtained using a depth sensing Micro Indenter (MHT) of CSM Instruments. Indentation tests were carried out under constant room temperature of 20 °C. Quasi-static loadings comprised between 0.03 and 30 N was applied by means of a Vickers diamond indenter/probe, with a load resolution of 0.3 mN and a resolution in displacement of 1 nm, and a microscope magnification of 5x or 50x. The load and depth (or relative displacement of the indenter), were continuously monitored during a programmed

micro-indentation load cycling through differential capacitive sensors, resulting in a typical load-indenter displacement curve (Oliver and Pharr, 1992). Under increasing loading, the impression produced consists of permanent or plastic deformations, and elastic deformations recoverable under unloading. Determination of the elastic recovery by analysing the unloading data according to a model for the elastic contact problem leads to a solution for calculation of elastic or Young's modulus and also micro-hardness of the test area, according to Oliver and Pharr's (1992) method (Dehoux *et al.,* 2012)

Raman microspectroscopy was carried out locally to determine and locate precisely the constitutive phases of the corrosion system and to correlate them to the results of micro-indentation. Raman microspectroscopy is often used for determination of different iron phases formed as corrosion products (Fari *et al.*1997; Colomban, 2011; Antunes *et al.,* 2003; Joiret *et al.,* 2002) Raman spectra were obtained using spectrometer Jobin Yvon Horiba with a Laser at 532 nm. The laser power is filtered under 100 mW in order not to transform under laser heat the corrosion phase during measurements. The diameter of analysed area under the 100x objective is of about 3 μm. Acquisition and analysis of data was performed using software Labspec 5. The acquisition time ranged from 10 to 40 s.

3.0 RESULTS

The first analysed sample was the sample from Maison du Brésil (Paris, France), which is a sample of 50 years old corroded reinforcing steel in concrete, Fig. 1 a). Corrosion products in the case of 50 year old sample are formed on one side of the sample. All around the steel a 40 μm thin rim of dense corrosion products was evident, probably original mill scale. On part of the cracked rim there is a thicker layer of corrosion products forming between the steel and the mill scale, forming inner layer of corrosion products. On other parts, there are both inner and outer corrosion products evident, formed beyond the mill scale, Fig. 1 b).
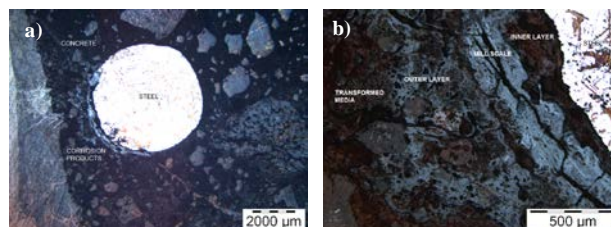

Fig. 1. a) Cross section of sample with reinforcing steel, b) concrete and layer of corrosion products

Figure 2 a) shows optical image and Fig. 2 b) obtained micro-indentation results on the corresponding locations. Figure 2 c) shows Raman microspectroscopy results obtained on the same

locations. After the steel (185 GPa), there is a layer of dense corrosion products, probably mill scale, composed of wüstite and magnetite and with modulus of elasticity of 120 GPa. On locations where mill scale was cracked there is an inner layer of corrosion products formed mostly of goethite, with elastic modulus of 40 to 60 GPa. After the dense layer, there is a layer of transformed media with modulus of elasticity around 40 GPa, composed mostly of goethite. Concrete has values of modulus of elasticity around 20 GPa.
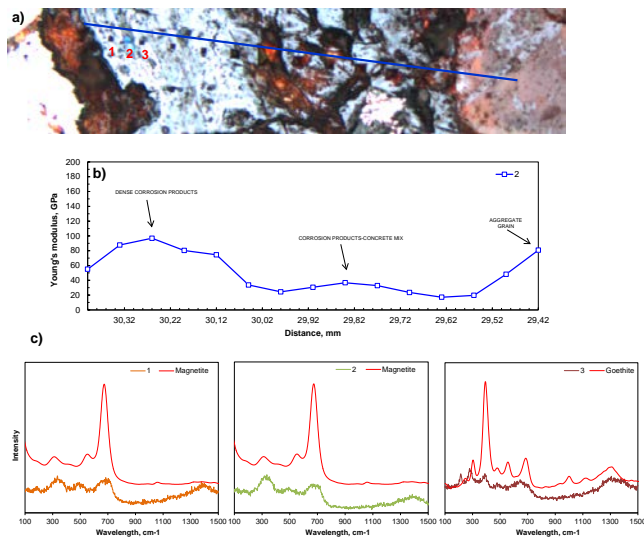
Fig. 2. a) Optical image, b) micro-indentation and c) Raman spectra results on corresponding locations

The second sample was from ONERA building, a sample of 60 years old corroded reinforcing steel in concrete. In the case of this sample there is no continuous mill scale visible, however, on some points around the surface of the steel there is leftover mill scale visible, mixed with inner and outer corrosion products.
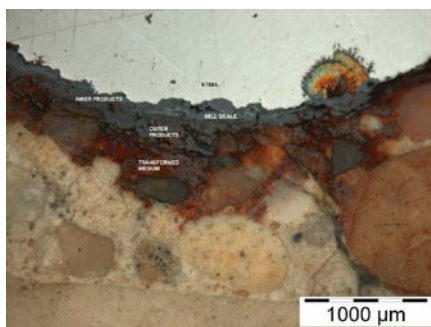

Fig. 3. Layers of corrosion products: inner layer, leftover mill scale, outer layer and transformed media

Location with all visible layers was chosen and both micro-indentation and Raman microspectroscopy were performed. Map on Fig. 4 was obtained by performing automatic micro-indentation on a matrix with 25 points in x direction, with 50 μm distance,

and 25 points in y direction, with 50 μm distance, comprising a total area of 1200 μm x 1200 μm. Map shows layer of steel, inner corrosion products, part of the leftover mill scale and outer corrosion products. On the upper right of the grid there is an aggregate visible. Layers can also be distinguished on the map of micro-indentation. Steel has a modulus of elasticity of around 220 GPa. Inner corrosion layer had modulus between 60 and 80 GPa, mill scale between 90 and 120 GPa, and outer corrosion layer between 40 and 60 GPa.
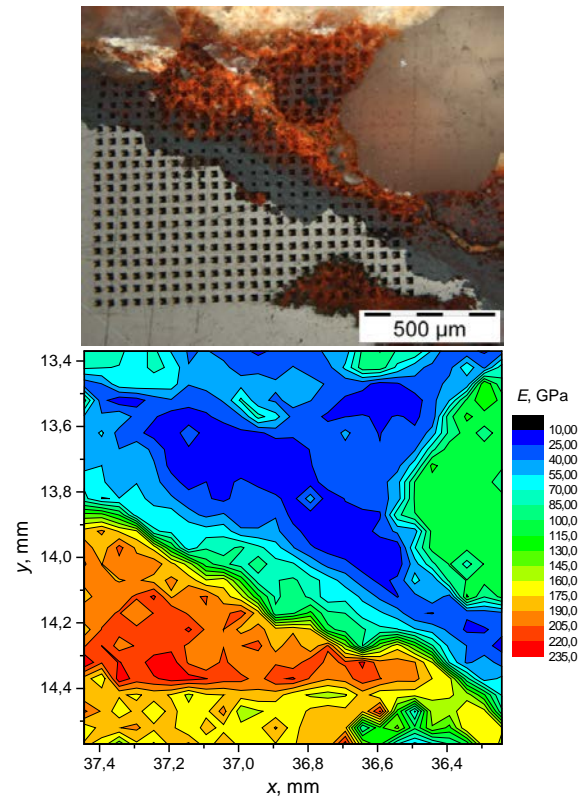

Fig. 4 Optical microscope image after micro-indentation and map of values of modulus of elasticity

Raman microspectroscopy performed on the same location, Fig. 5., revealed that the inner layer of products, products that are formed between mill scale and steel (points 1, 6 and 11), and outer layer, products that are formed after the mill scale (point 10), are mostly composed of goethite. Marblings of leftover mill scale are mostly composed of maghemite and magnetite.

The last analysed sample was the sample from Bourse du Travail de Bordeaux (France), which is a sample of 80 years old corroded reinforcing steel in concrete. In the case of this sample, all around the steel a 30 μm thin layer of corrosion products was evident, original mill scale, Fig 6 a). The same as in the case of 50 year old sample, at a certain point there is a layer of corrosion products forming between the steel and the mill scale and evident penetration of corrosion products further outside the mill scale, Fig 6 b). Map on Fig. 7 was obtained by

performing automatic micro-indentation on a matrix with 15 points in x direction, with 50 μm distance, and 15 points in y direction, with 50 μm distance. Map shows layer of steel, inner corrosion products, mill scale and outer corrosion products.
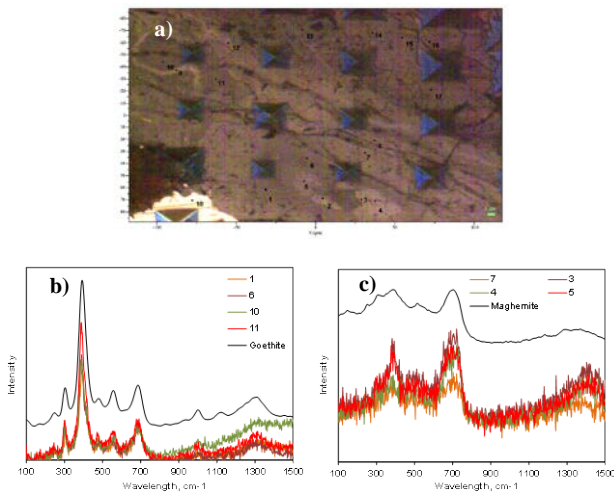

Fig. 5. a) Optical image with indicated locations of Raman microspectroscopy, b) Raman spectra obtained on inner and outer layer of corrosion products; b) Raman spectra obtained on mill scale
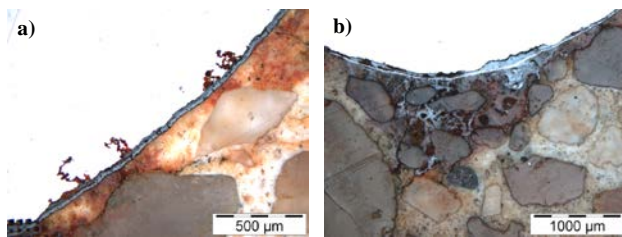

Fig. 6 a) Mill scale layer around the steel; b) Inner and outer corrosion products

For this sample it can be concluded that the modulus of elasticity od steel is between 150 – 200 GPa, with modulus of elasticity between 40 and 60 GPa, mill scale with modulus of elasticity between 70 and 90 GPa and outer layer of corrosion products with modulus of elasticity between 20 and 40 GPa.

Raman microspectroscopy revealed that goethite is the main phase forming between the mill scale and the steel (points 1, 2, 3 on Fig. 8 a), while magnetite is the main phase of the mill scale (points 5-1, 5-2 on Fig. 8 b). Goethite closer to the surface of the steel has modulus of elasticity of around 50 GPa, while magnetite in the mill scale has modulus of 80 GPa. Outer layer (away from the mill scale) is composed from goethite and has modulus of around 50 GPa, which is decreasing with the increase of distance from the steel, due to the mixing of corrosion products layer with cement matrix. Beside the goethite, hematite is observed.
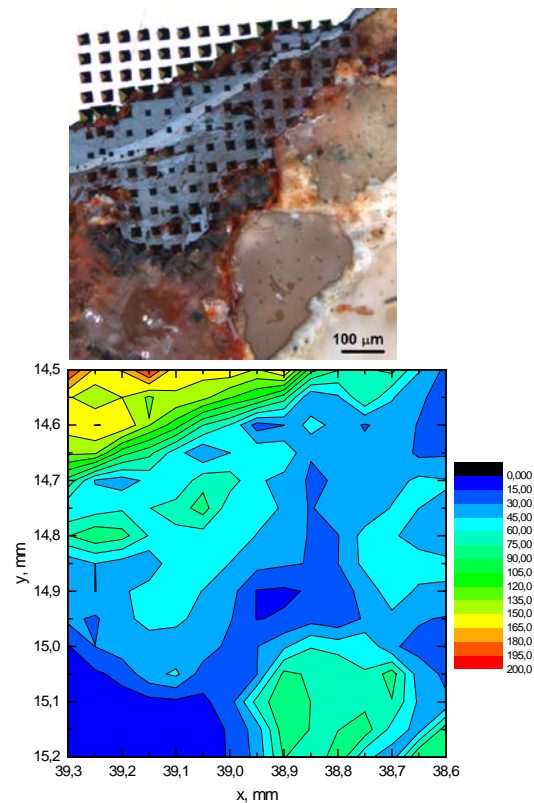

Fig. 7 Optical microscope image after micro-indentation and map of values of modulus of elasticity
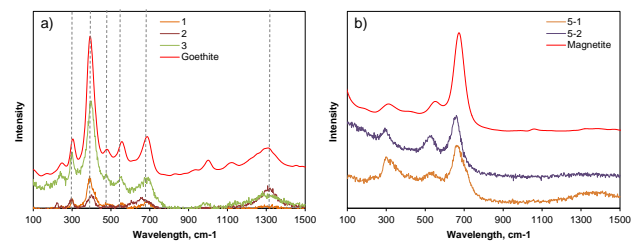

Fig. 8 a) Raman spectra obtained on inner layer; b) mill scale

4.0   CONCLUSIONS

In the present study it was confirmed on three different samples that transition zone between the steel and concrete during corrosion is composed of several consecutive layers: i) inner layer of corrosion products that form between the surface of the steel and the original mill scale, ii) original mill scale, iii) outer corrosion products, iv) transformed medium.

The inner corrosion layer is mostly composed of goethite and had modulus of elasticity between 50 to 70 GPa for 80 years old sample and 40 GPa for 50 years old sample. The layer of original mill scale is evident in the case of all tested samples, around the whole surface of the steel, in a thick layer of 55 μm

for 50 years old sample and of 20 μm for 80 years old concrete. For both tested samples it was observed that the layer is mostly composed of magnetite and wüstite and has modulus of elasticity around 115 GPa for younger concrete sample and around 70 - 90 GPa for older one. The presence of remains of former mill scales made of wüstite, magnetite and hematite formed during the manufacturing process is usually found on old samples Demann et al., 2010; Zhao et al., 2012c), [20]. This layer can be visible next to the surface of the steel, or away of the surface, depending how far corrosion has propagated. It usually has higher values of modulus of elasticity compared to other corrosion products, between 90 and 130 GPa (Zhao et al., 2012c), and is denser (light in colour, higher iron amount). It is reported in the literature that this layer has lower values of modulus of elasticity in the case of older samples, since it had time to additionally oxidize (Zhao et al., 2012c), which is further confirmed with this study.

Previous studies also showed that the mill scale provides some protection of the steel from further corrosion (Palacios and Shadley, 1991). However, if defects exist inside the scale, such as a crack, any mechanical load will lead to the crack propagating inside the scale, resulting in the scale spalling. Additionally, if the interface between the scale and steel includes voids or cracks, the expansion of these defects will cause the delamination of the scale from steel (Gao et al., 2008). Both the cracks and delamination voids connected by pore solution by micro-cracks serve as pathways for concrete pore solution to reach the steel surface, hence allowing ion movement between the pore solution and the crevices (Ghods et al. 2011). As is usual for crevice corrosion, the chemical composition of the pore solution within the crevices begins to differ from that of the bulk solution and favourable conditions for corrosion occur. Therefore, through the porous, cracked or delaminated mill scale oxygen dissolved in pore water reaches the metal/oxide interface and formation of inner corrosion products starts. These inner layers of goethite are evident both in the case of 50 years old concrete, Fig. 1 and in the case of 80 years old concrete, Fig. 6. Also, because of the difference between steel and mill scale, galvanic corrosion can occur. It is evident that there are layers of different corrosion products, which have different density and different electrical resistivity. It is possible then that due to the favourable conditions for the corrosion, corrosion products transform from one phase to the other due to the galvanic corrosion. In the case of younger sample hematite is also observed in the inner layer, while in the case of older maghemite.

Outer corrosion products are also formed of goethite, being less dense and more mixed with concrete matrix, further from the surface. The modulus of elasticity of this layer was found to be around 30 – 40 GPa for younger concrete and

around 50 GPa for older concrete. It is spread into around 800 μm and 1150 μm layer for younger and older concrete sample, respectively.

Present study is contributing to a more detailed micromechanical and microstructural analysis of layer formed during long-term corrosion of steel in concrete, which provides valuable information for more precise prediction of time-to-cracking of reinforced concrete due to corrosion.

Acknowledgement

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