CORROSION PRODUCT IDENTIFICATION BY MICRO-RAMAN AND MÖSSBAUER SPECTROSCOPY

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Micro-Raman spectrometry and Mössbauer spectroscopy have been used to identify the corrosion products on a steel coupon exposed in an industrial environment for 16 years. The Raman analysis was performed on a polished metallographic cross-section in order to map the oxides across the thickness of the coating. The spectra were recorded using a LabRam Micro-Raman spectrograph incorporating a 17 mW HeNe laser (attenuated to 1mW to prevent oxide transformation), focused to 1 µm spot size, and 1800 g/mm grating. The confocal line-scan imaging enabled 100 spectra to be recorded in one scan at 0.5 µm intervals across the thickness of the coating. The Mössbauer analysis was performed using in-situ scattering Mössbauer spectroscopy on the attached corrosion coating and transmission Mössbauer spectroscopy at 300K and 77K on the removed coating, to measure the fraction of each oxide present.

Micro-Raman spectrometry showed that the corrosion products had formed in distinct layers as shown in Figure 1. The main layers were labeled as (a) inner protective layer and (b) outer layer, from the Micro-Raman spectra which identified the type “a” layers as pure goethite (α-FeOOH), Figure 2(a), and the type “b” layer as a mixture of lepidocrocite (γ-FeOOH) and goethite, Figure 2(b), with the former being most abundant.1 Within the inner protective layer closer to the steel substrate, small islands of magnetite (Fe₃O₄), Figure 2(c), and maghemite (γ-Fe₂O₃), Figure 2(d) were identified. Mössbauer spectroscopy identified goethite as the most abundant oxide (79%), and lepidocrocite (16%). A very small fraction of maghemite (5%) was identified but no magnetite, most likely because of the small fraction (<1%) present. Figure 3 shows the large change in the Mössbauer spectra recorded at 300 K and 77K. This is due to the presence of very small particle (<15nm) goethite which exhibited superparamagnetic relaxation which collapsed the room temperature spectra, Figures 3(a) and 3(b).2 At 77K the Mössbauer spectrum, Figure 3(c), shows most of the goethite to be magnetically ordered with only 8% still being superparamagnetic due to particle size less than 8 nm.3

The identification of the goethite close to the steel substrate by Micro-Raman spectrometry and the analysis by Mössbauer spectroscopy showing that 75% of the goethite had particle size less than 15nm, explains why the corrosion products on many steels are adherent protective layers. Goethite is a very stable oxide and after 16 years exposure of the steel, the corrosion products are expected to be stable. The small particle goethite packs densely at the surface of the steel substrate, reduces the porosity of the corrosion coating and prevents moisture, air and pollutants from reaching the steel, thereby reducing further corrosion.

FIG. 1. Oxide layers formed in the corrosion coating of steel exposed for 16 years in an industrial environment and showing regions, a: inner layers, b: outer layer, and island clusters identified as c: magnetite and d: maghemite.

FIG. 2. Micro-Raman spectra of the layered corrosion products recorded at: (a) inner layers, (b) outer layer and islands of (c) magnetite and (d) maghemite within the inner layer.

FIG. 3. Scattering and transmission Mössbauer spectra, recorded at 300K and 77K, of the corrosion products formed on the atmospherically exposed steel, showing goethite, lepidocrocite and maghemite.