



Anelastic spectroscopy study of iron carbonate scales from CO₂ corrosion of steel

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ABSTRACT

In the present work we report an anelastic spectroscopy study of pure FeCO₃ (siderite) and of carbon steel samples covered by siderite films. Uncovered steel samples have also been investigated for reference. The siderite shows two relaxation processes below room temperature, at about 220 K and 140 K, while the covered steel sample displays only the peak at lower temperature. The presence of such a relaxation can be used to monitor the deposition of siderite.

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1. Introduction

Although there have been many developments in corrosion resistant alloys, steel corrosion is a great concern in the gas and oil industry, as mild steel still constitutes one of the most employed materials. The work-over of pipelines is generally not caused by uniform corrosion but by localized phenomena such as flow-induced local corrosion [1]. The understanding of the mechanism of the localized corrosion process is fundamental for the formulation of appropriate mitigation methods. In this process, the precipitation of iron carbonate (FeCO₃) from carbon dioxide wet corrosion plays a major role, since the formation of FeCO₃ scales on the surface of mild steels reduces their corrosion and prevents further damage [1–3]. Indeed, it has been reported that localized corrosion starts at sites where the local spalling of scales was not followed by re-formation of protective layers, due to locally changed fluid flow conditions.

The knowledge of the mechanical properties and of the fracture conditions of scales [3] is therefore fundamental in the elaboration of prevention mechanisms.

2. Experimental

We report preliminary results of anelastic spectroscopy in steels subjected to corrosion produced by the flow of hydrocarbons. In the

present case, the corrosion was simulated by immersing, at 80 °C for several days, steel bars in a solution of deionized and CO₂ saturated water containing 1 wt% NaCl (pH 6.6). Controlled quantities of a solution of FeCl₂ in deionized water are added in order to provide Fe²⁺ ions. Under those conditions, an iron carbonate (FeCO₃) film (with a thickness ranging between 5 and 20 μm) is formed on the samples surface, while part of FeCO₃ precipitates on the bottom of the reactor. After the film deposition the steel samples are dried in flowing nitrogen, while the precipitated siderite is filtered and in some cases heated to be dried. A typical Scanning Electron Microscope (SEM) image of the steel bar covered by FeCO₃ is reported in Fig. 1. X-Ray Diffraction (XRD) analysis revealed that the film is composed of pure siderite (see Fig. 2), while the precipitated powder in some cases contained small traces of NaCl.

The samples studied in the present work were rectangular bars of three different types:

- sample 1; carbon steel bars (type API 5L X52) of 50.0 mm × 5.0 mm × 1.3 mm, covered by FeCO₃ films having thickness of about 5 μm;
- sample 2; compacted samples of FeCO₃ powders, obtained from the precipitate phase;
- sample 3; carbon steel (type API 5L X52), uncovered for reference (50.0 mm × 5.0 mm × 1.3 mm).

The manipulation of scales introduces some difficulties, to be overcome, arising from their fragility and the need to keep their stability. The measurement on scales pulled out directly from pipelines is a major task.

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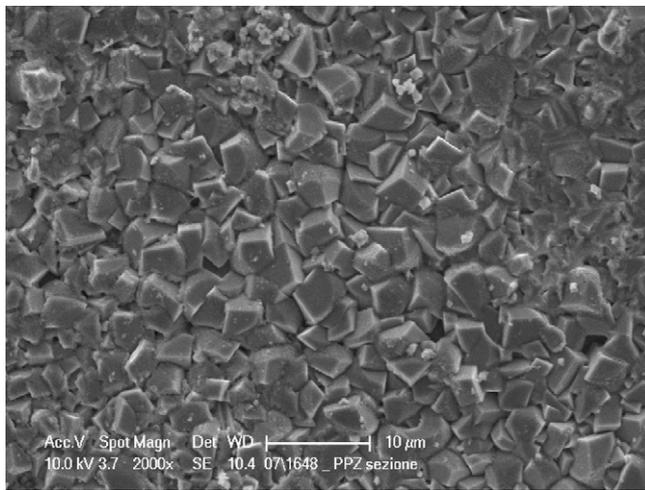


Fig. 1. Typical SEM image of carbon steel covered by FeCO_3 scales.

The samples of FeCO_3 were consolidated by pressing the powder in a die (25.0 mm \times 5.0 mm \times 0.7 mm), following a new procedure recently introduced at the Laboratory of the University “La Sapienza” of Rome [4,5].

Anelastic spectroscopy measurements (elastic modulus and energy dissipation) are conducted suspending the samples on thin wires located at the nodal lines of flexural vibration modes and electrostatically exciting their corresponding mechanical resonances. At the temperature at which the relaxation rate τ^{-1} of the mobile species is equal to the angular vibration frequency ω ($\omega\tau = 1$) the stimulated atomic migration is able to follow, by thermal activation, the sample vibration, and the coefficient of elastic energy dissipation Q^{-1} reaches its maximum value. The energy dissipation (or reciprocal of the mechanical quality factor Q) is measured from the decay of the free oscillations or from the width of the resonance peak. The measurement of the dynamic Young modulus E' is simultaneously obtained from the angular vibration frequency $\omega^2 = kE'/\rho$, where ρ is the mass density, and k a numerical factor depending on the sample geometry. The independent and concomitant measurements of Q^{-1} and E' allow the complex modulus $E = E' + iE''$ to be derived, being $Q^{-1} = E''/E'$. For a single relaxation time, τ , Q^{-1} is given [6] by:

$$Q^{-1} = gv_0(\lambda_1 - \lambda_2)^2 \frac{cn_1n_2}{kT} E' \frac{(\omega\tau)^\alpha}{1 + (\omega\tau)^{2\alpha}} \quad (1)$$

where c is the molar concentration of the jumping atoms and n_1 and n_2 their equilibrium fractions in sites 1 and 2; λ_1 and λ_2 are the main components of the λ tensor of the elastic dipoles of the defects in their two configurations; g is a factor of the order of 1/2 depending on the geometry of the jump and the type of sample vibration, v_0 the unit cell volume, α a parameter equal to 1 for a single-time Debye process, and k the Boltzmann constant. For classical processes the relaxation time follows the Arrhenius law $\tau = \tau_0 e^{W/kT}$, W being the activation energy. As τ is temperature dependent for thermally activated processes, the relaxation condition ($\omega\tau = 1$) is satisfied at low temperatures for fast processes and at high temperatures for slow processes. In many cases the experimental peaks are broader than a single Debye peak and they can be described by means of a Fuoss–Kirkwood model, according to which the parameter α in equation (1) is allowed to become lower than 1 [6].

3. Results and discussion

Fig. 3 shows the elastic energy loss (Q^{-1}) and the square of the vibration frequency (which is proportional to the dynamic Young modulus) measured between 290 and 65 K in sample 1. On decreasing temperature, the frequency increases, as expected, and Q^{-1} monotonically decreases until a very small peak appears around 150 K (Peak A, $f \sim 2.5$ kHz). This peak is not present in the anelastic spectrum measured in the uncovered carbon steel substrate (sample 3), also reported for comparison in Fig. 3; therefore, that peak should be ascribed to a relaxation process taking place in the FeCO_3 film. Strong confirmation of this attribution is given by the presence of a very pronounced dissipation peak (higher by two orders of magnitude) in the same temperature range (130–150 K) in the compacted FeCO_3 powder (sample 2). The higher peak intensity measured is congruent with the 100% FeCO_3 composition of this sample. The relaxation curve of sample 2 has been drawn in Fig. 3, on a scale compressed by a factor of 100; the curve also reveals the presence of a well-developed peak around 220 K (Peak B).

In order to gain further information on the nature of the two peaks, the anelastic spectrum of sample 2 was measured at two different vibration frequencies, and the result is reported in Fig. 4. It is seen that both Peak A and Peak B shift to higher temperatures at the higher frequency, indicating that the peaks are caused by thermally activated relaxation processes. This means that the FeCO_3 phase contains mobile species, and that those entities are able to relax with rates of the order of the kHz below room temperature.

The two peaks of pure FeCO_3 could not be fitted by single Debye curves or Fuoss–Kirkwood process. A satisfactory fit (continuous lines in Fig. 4) was obtained by summing two Debye relaxations, each one having a Gaussian distribution for both W and τ_0 . A back-

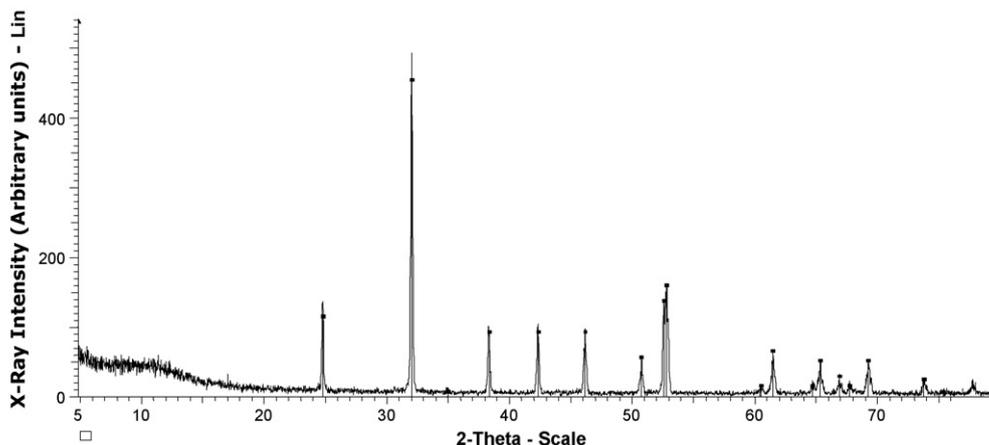


Fig. 2. XRD pattern (X-Ray Intensity versus 2 Theta) of the carbon steel bar covered by FeCO_3 (sample 1). All peaks can be attributed to siderite (lines).

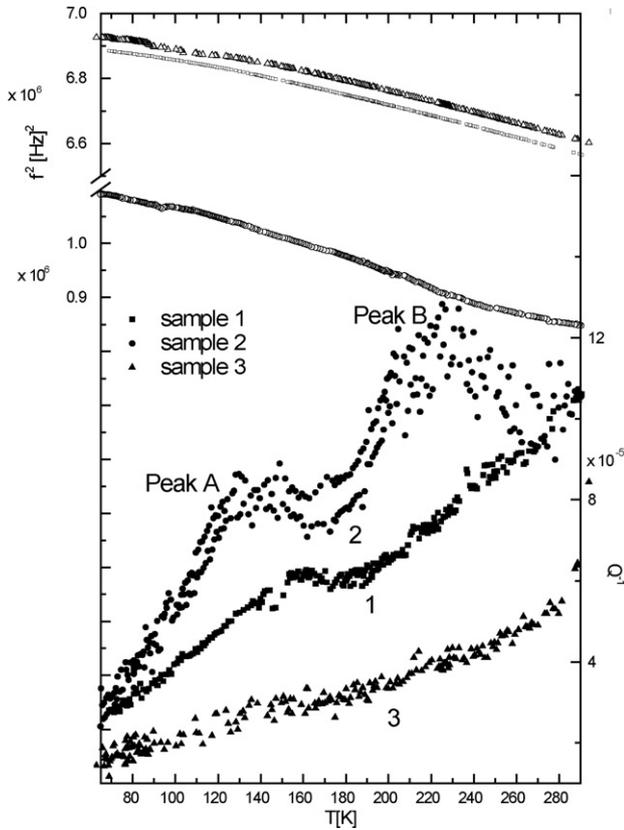


Fig. 3. Elastic energy dissipation (lower part) and square of the vibration frequency (upper part) of carbon steel covered by FeCO₃ (curve 1) and pure FeCO₃ (curve 2). In the latter case data have been divided by 100. Data of uncovered steel (curve 3) have been included for reference.

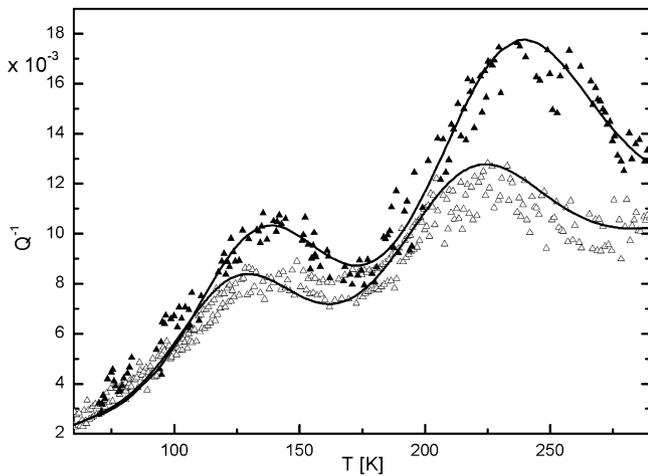


Fig. 4. Elastic energy dissipation of sample 2, pure FeCO₃ (Δ, *f*=1.0 kHz; ▲, *f*=4.1 kHz). Lines are best fit curves.

ground dissipation was taken into account by adding a polynomial curve. Accordingly the experimental points were fitted to the following formula:

$$Q^{-1} = c_0 + c_1T + c_2T^2 + \sum_{i=1}^2 a_i \int_0^\infty \frac{1}{T} \frac{\omega\tau_i}{1 + (\omega\tau_i)^2} g(W_i)g(\tau_{0i})dW_id\tau_{0i} \quad (2)$$

where the first three terms represent a polynomial background, *a_i* are constants and *g* is the normalized Gaussian distribution func-

Table 1
Best fit parameters for the relaxation processes of pure FeCO₃.

	Pure FeCO ₃
Peak A	
<i>W</i> ₁ (eV)	0.227
$\sigma(W_1)$ (eV)	0.039
τ_{01} (s)	6×10^{-14}
$\sigma(\tau_{01})$ (s)	2×10^{-15}
Peak B	
<i>W</i> ₂ (eV)	0.405
$\sigma(W_2)$ (eV)	0.043
τ_{02} (s)	6×10^{-14}
$\sigma(\tau_{02})$ (s)	2×10^{-15}

tion. In the model described above the fitting parameters are the factors *c_j* (*j*=0, 1, 2), *a_i*, the mean activation energy, *W_i*, the mean relaxation time, τ_{0i} , and the standard deviations of *W_i* and τ_{0i} of each peak. The values obtained for the best fit are reported in Table 1. A similar procedure in which only the activation energy was allowed to have a distribution function was successfully applied in the case of a flip-flop relaxation of H in calixarene [4]. The value of the mean relaxation time obtained ($\sim 10^{-14}$ s) is typical of point defect relaxation for both relaxations (peak A and B).

The anelastic spectrum of the steel bar covered by FeCO₃ was also measured at two different frequencies (results not shown) and the shift of peak A to higher temperatures at the higher frequency was confirmed. The values of the obtained parameters are compatible with those in Table 1.

Concerning the physical processes giving rise to the two anelastic peaks, some considerations can be done, even though, to our knowledge, the siderite minerals were poorly investigated in the literature and there are no reports about anelastic processes in them. Possible origins for relaxation might be the dynamics of oxygen vacancies around C atoms in the crystal structure. Moreover, considering that the samples studied in the present work are obtained by an immersion method that simulates corrosion, one can speculate that some unwanted impurities coming from the bath (i.e. Na or Cl) can be present in the crystals. In this case, also the relaxation of O around such impurities should be considered. Finally, the dynamics of the Fe-O octahedra constituting the siderite should not be excluded. Indeed, as the Fe-O₆ octahedra are all interconnected, the tilting of one of them would involve a collective and coordinated dynamics of the octahedra chains. This proposed model would be similar to what was observed for the Cu-O₆ octahedra motion in LaCuO₄ giving rise to an anelastic peak with an activation energy of 0.23 eV [7]. However, the prefactor of the relaxation time we presently obtained is not typical of the dynamics of extended defects ($\sim 10^{-12}$ s).

Further analysis and experiments are required to attain a better knowledge of the physical mechanisms occurring during progression of corrosion, which would be useful from an industrial point of view. The reasons for the absence of peak B in the FeCO₃ layer covering the carbon steel bar should be matter of investigation, too. At present it can be concluded that the presence and the features of relaxations in steels subjected to corrosion may be used to monitor the FeCO₃ layer formation.

4. Conclusions

The presence of two anelastic relaxation peaks in pure siderite obtained during the corrosion of a steel sample by means of CO₂ is reported. The activation energy and relaxation time of the processes were obtained by an original fitting procedure in which a Gaussian distribution of both parameters was considered. The siderite deposited on the steel bar shows only the peak centered at lower temperature. The occurrence of such a peak

may be used to monitor the FeCO_3 layer formation during corrosion.

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