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Mechanical Characterization and Adherence of Iron Carbonate on an X65 Steel

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ABSTRACT

Formation of iron carbonate layers on mild steel is an important factor in CO_2 corrosion as they provide a protective barrier that can help preserve pipeline integrity. However, the protectiveness conferred by such layers can be compromised due to their mechanical removal.The main objective of this work was to evaluate the mechanical integrity of an iron carbonate layer, grown on an API 5L X65 steel, by nanoindentation and scratch test methods. Berkovich and Vickers-type indenters were used to determine the hardness of an iron carbonate layer and its X65 steel substrate. A scratch tester with a conical indenter, 120° cone angle and 20 µm diameter, was used to determine the critical force to remove the iron carbonate layer. Nanoindentation results indicated that the hardness of the iron carbonate layer was 11.6 ± 3.5 GPa and the hardness of the steel was 2.4 ± 0.2 GPa. According to the failure map (hardness of the substrate *vs.* hardness of the layer), the failure mode of the iron carbonate on steel (whose hardness is 5 times higher than the substrate) is by chipping. In order to corroborate this postulate, scratch testing was used to determine the minimal normal force to detect superficial removal and total delamination of the iron carbonate layer from the steel. The required forces were determined to be of the order of 40 mN and 400 mN, respectively. The presence of chevron-type cracking patterns confirmed cohesive failure of the layer at low applied forces, while the chipping pattern at higher forces was indicative of the adhesive failure mode. These results were further corroborated by profilometry and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) analyses. Finally, the shear stresses associated with the partial and total removal of iron carbonate were determined. The results indicate that the shear stresses required for partial and total delamination are of the order of 300 MPa and 2 GPa, respectively.

INTRODUCTION

Iron carbonate is a corrosion product layer that may play an important role in CO_2 corrosion mitigation[1]. Such layers can act as a barrier and protect pipeline from internal corrosion[1]. However, their protectiveness can be challenged by mechanical removal[2]; a phenomenon that has previously been explored[2–5].

Another way to assess the persistency of the iron carbonate layer is to use techniques developed in tribology science to determine the adherence forces between a layer and a substrate[6–8]. Tribology science techniques have been used to evaluate the persistency of vapor deposited and precipitated layers on substrates such as glass and steels[6–8]. Specifically for steels, there are several studies on the adherence of precipitated carbides on tool machinable steels[9–11]. Herein, we have a parallel situation for such layers and the formation of iron carbonate on X65 steel. Before taking this parallelism further, one needs to be sure that the assumptions and lessons derived from the experimental conditions in these works are indeed applicable to corrosion product layers. Consequently, the assumptions made in tribology science are discussed in more detail below.

Most of the current research performed on the assessment of the adherence of layers precipitated and deposited on substrates are based on the work of Bull, *et al.*[12]*.* In that work, a qualitative assessment is proposed to evaluate the applicability and validity of particular methodologies to determine the substrate/layer adherence characteristics. For instance, the extensively used method proposed by Burnett and Rickerby[6] consists of performing Vickers indentation on a deposited/precipitated layer on a substrate and of measuring of the indentation imprints. By using a mathematical model, it is possible to determine important mechanical properties of the layers; such as fracture toughness, hardness, and even elastic modulus[6,13]. However, recognition of fundamental limitations is usually omitted in the discussion of the acquired data. Specifically, assumptions relating to plastic deformation of the substrate and the low fracture toughness of the layer are often not considered. If the behavior of the layer and the substrate changes (*e.g.*, the substrate does not deform plastically and/or if the layer has a high fracture toughness value), the model will not be valid, and the analysis will be incorrect. Consequently, the research herein primarily focuses on identifying the correct mathematical model that will enable the determination of a critical shear stress for iron carbonate removal. A failure map analysis[12] is used to carry out this task of selecting the most appropriate mathematical model, with the ultimate objective to determine the critical shear stress for iron carbonate detachment from a X65 pipeline steel.

EXPERIMENTAL PROCEDURE

The parameters listed in Table 1 were used in order to ensure the formation of a dense layer of iron carbonate, using a typical glass cell setup described elsewhere[14].

Table 1. Test conditions for formation of a uniform iron carbonate layer on a X65 steel

Parameter	Value
Temperature of solution	80 °C
Sparge gas	CO_2
Substrate material	API 5L X65 Steel (tempered martensitic microstructure)
Working solution	1 wt.% NaCl
pH	8.00 ±0.20
Fe^{2+} initial concentration	50 ppm
Test duration	3 days

After an iron carbonate layer was formed on the substrate surface, the parameters listed in Table 2 were used to determine the failure mode and the critical load for removal for the iron carbonate layer *via* the scratch test. A tribometer for micro scratch testing was utilized in this research‡. The indenter was a diamond 120-degree cone. Finally, constant load scratch testing was further used to corroborate the previously determined critical load of removal.

Table 2. Conditions for constant and progressive load scratch test

Parameter	Values
Type of Load	Progressive, Constant
Progressive Load (mN)	0.1 to 800
Constant Loads (mN)	100, 200, 250, 300, 350, 380, 390
Scratch Length (mm)	2
Scratching Speed (mm/min)	2
Indenter Geometry	120° Cone
Indenter Material	Diamond
Indenter tip Radius (µm)	20
Chemical and Optical Characterization	SEM, EDS, Optical Microscopy, Profilometry

RESULTS AND DISCUSSION

In order to determine the critical shear stress for iron carbonate removal, this research followed the methodology described by Bull, *et al.*[12], therefore, the following steps were followed for the overall assessment of the adherence of an iron carbonate layer on the X65 steel:

1. Determine the hardness of the layer and the substrate to have a qualitative understanding of the mode of failure of the layer by using the qualitative failure map reported by Bull, *et al.*[12]

2. Based on the previous results, perform a progressive load scratch test to find the mode of failure of the layer on the substrate.

3. Estimate the critical load force from the progressive load scratch test. (Figure 1).

‡ Nanovea™ Tribometer PB1000

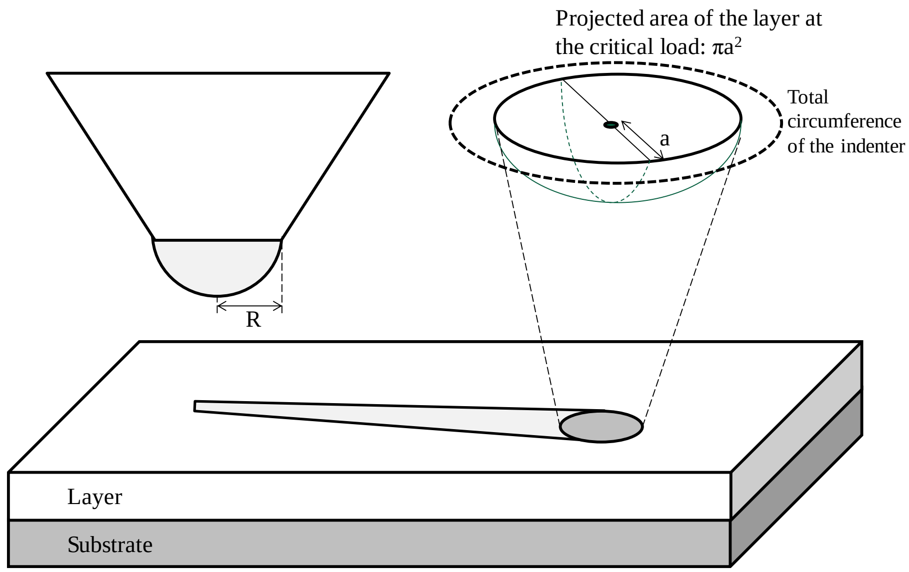

Figure 1. The principle of scratching to remove a layer (white) from a substrate (gray). The indenter cone has radius "R". After the scratch, the projected area for the layer removal (πa^2) has a radius "a". These geometrical parameters are used to calculate the critical shear stress[15].

4. By using the constant load scratch test, corroborate the previously estimated critical load.
5. Depending on the mode of failure, utilize the correct mathematical model to transform the critical load into the corresponding shear stress.

The steps are further discussed in the following sections.

Formation of Iron Carbonate Layer

Figure 2 shows an SEM image of the developed iron carbonate layer. The thickness and the chemical signature of iron carbonate were determined by cross-section analysis and EDS, respectively (Figure 3).

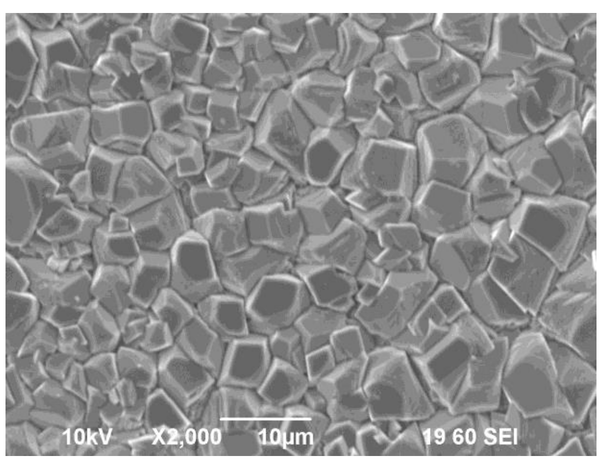

Figure 2. Iron carbonate layer formed.

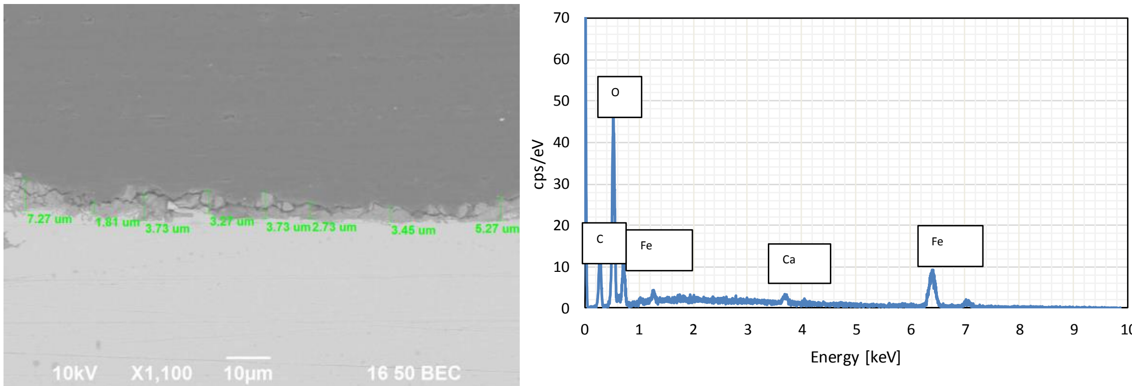

Figure 3. Cross-section area of the iron carbonate layer. EDS confirmed the formation of iron carbonate.

Characterization of the Substrate and Layer

The hardness of the substrate and the iron carbonate layer were determined *via* nanoindentation. The results are summarized in Table 3.

Table 3. Summary of hardness measurements

Material	Hardness / GPa
X65 steel	2.4 ± 0.21
Iron carbonate	11.63 ± 3.5

From the previous hardness values, and according to Ohring[16], the X65 steel can be considered a "medium hardness substrate" while the iron carbonate can be considered as a "hard film". Therefore, the mode of failure can be estimated with the map failure mode proposed by Bull *et al.*[12]. Figure 4 depicts the hypothesized failure mode. If the x-axis is set at the middle of the scale, and the hardness in a high point, then the expected mode of failure for the iron carbonate precipitated onto an X65 steel was buckling. It has to be noted that this map failure is for qualitative purposes and thereby, this postulate will be corroborated with the constant load scratch test.

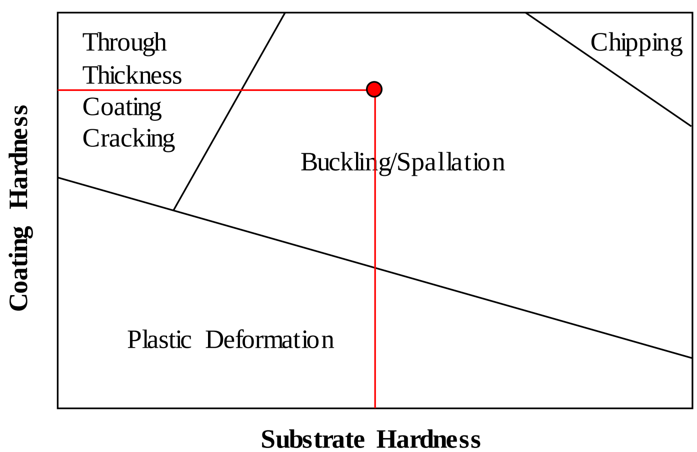

Figure 4. Failure map for iron carbonate precipitated on steel. Buckling is the most likely mode of failure for this system.

Proposed Mode of Failure

The corroboration of the previous postulate was done by a progressive load scratch test (from a load of 0.1 to 800 mN) and microscopy. Figure 5 shows the mode of failure at the critical load. Buckling was detected *via* microscopy (optical and SEM). Given the mode of failure of the layer, the adhesive properties can be estimated by the model proposed by Olivier & Matthews[15]. Such a model assumes that the scratch test is performed quasi-statically (very slow in order to avoid high values of friction). This model will be discussed in detail when the shear stress is determined. For now, attention will be focused on the determination of the critical load (an important parameter for the shear stress determination) *via* microscopy and EDS analysis.

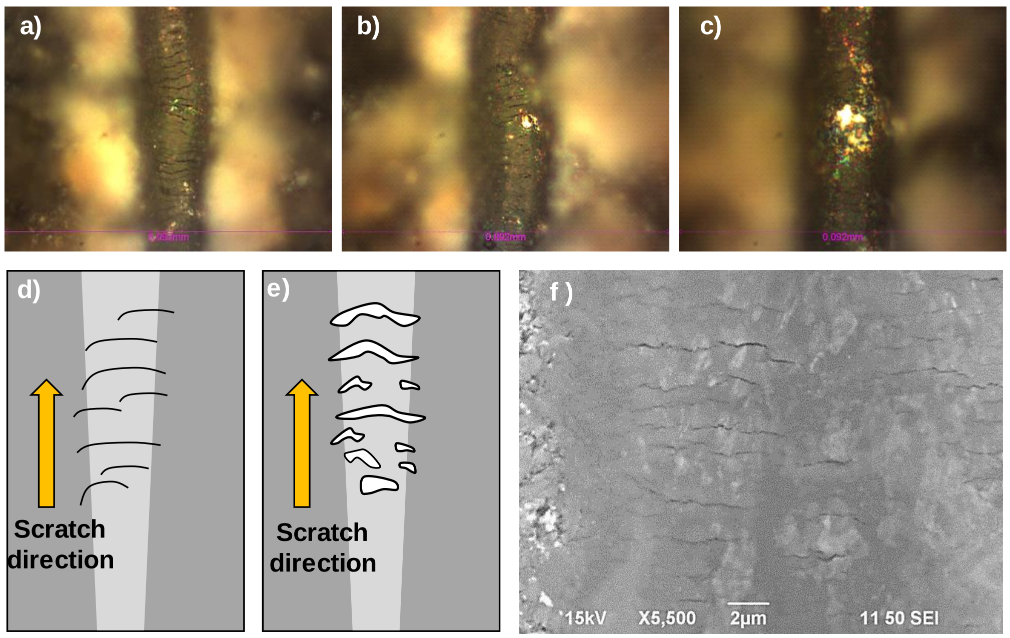

Figure 5. Buckling detection in the iron carbonate layer around the point of failure: a) optical microscope image prior to the failure; b) and c) failure point; d) and e) standard mapping for buckling failure[12,17]; f) buckling images of the iron carbonate layer with SEM.

Critical Load Determination

Progressive Load Scratch Test

A progressive load scratch test was performed as per parameters listed in Table 2 (from 0.1 to 800 mN load force). Figure 6 shows the result of the test.

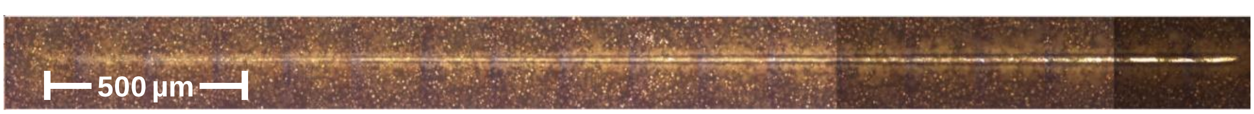

Figure 6. Progressive scratch test from 0.1 to 800 mN.

The analysis started by determining the minimum force to produce a noticeable damage to the iron carbonate layer at approximately 35 mN, as shown in Figure 7 a). As the load increased, more damage was noticed in the layer, until the detachment of the iron carbonate layer was observed at a load range of 405 ± 15 mN.

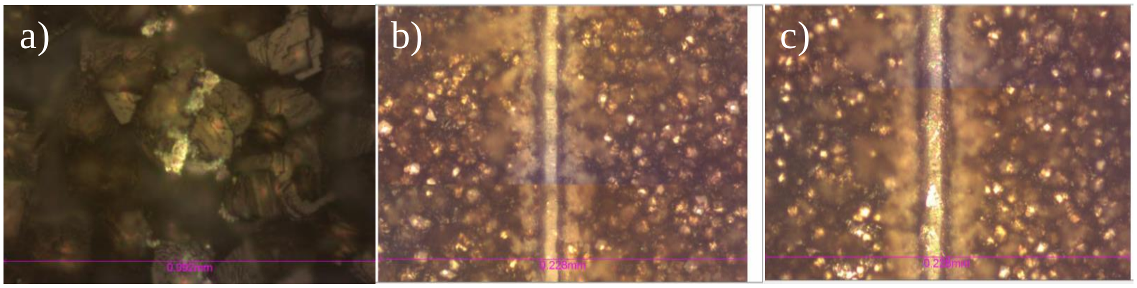

Figure 7. Progressive scratch test results from Figure 6: a) Minimum damage detected Force: 35 ± 5 mN; b) Damage of the layer with no detachment (approximately 365 mN); c) removal of the iron carbonate layer at a force of 405 ± 15 mN.

Constant load scratch tests around 400 mN of load were performed to corroborate this finding (force for detaching the iron carbonate layer).

Constant Load Scratch Test

Low Loads Scratch Tests

Constant load scratch tests were performed to corroborate that at low loads there was no detachment of the iron carbonate layer. Figure 8 shows the constant load test images for 10 and 30 mN,

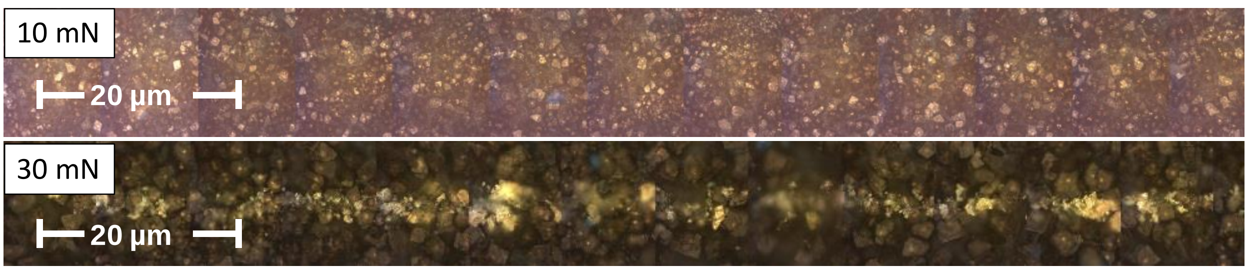

Figure 8. Constant load scratch test at low penetration forces.

It is noteworthy that there is no detachment of the layer at these loads, only superficial damages at 30 mN. Moreover, SEM images corroborated this finding, as shown in Figure 9.

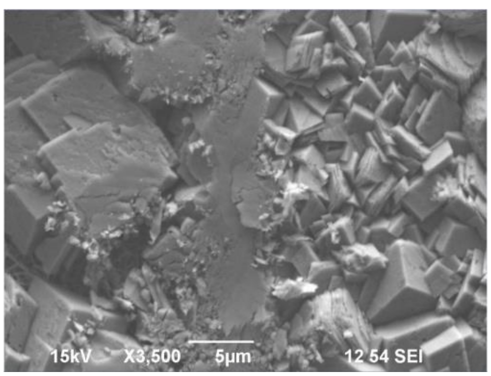

Figure 9. Constant load scratch test at 30 mN. There is superficial damage, but no detachment of the iron carbonate layer.

High Load Scratch Tests

Constant load forces for 400, 390, 380 and 370 mN were used to perform the constant load tests. Figure 10 shows the profilometry data for the test specimen and Figure 11 shows the depth analysis of the surface grooves left by the test.

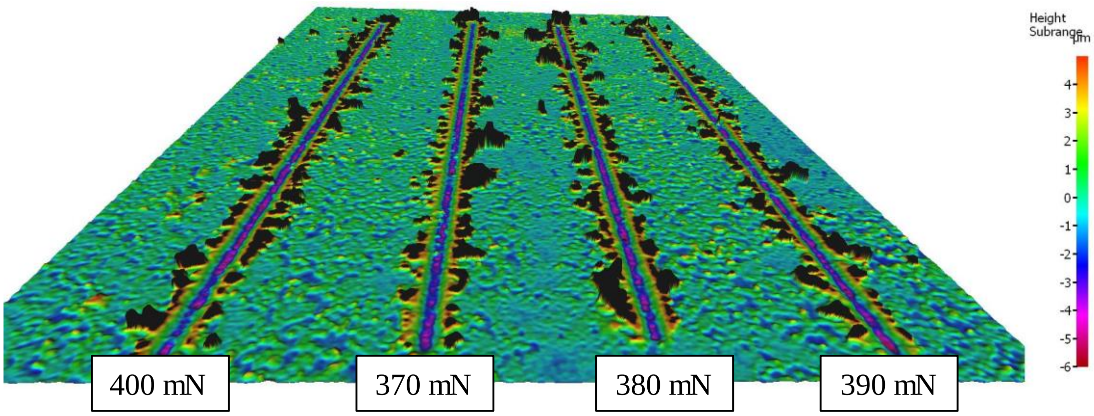

Figure 10. Profilometry data for different constant load scratch tests.

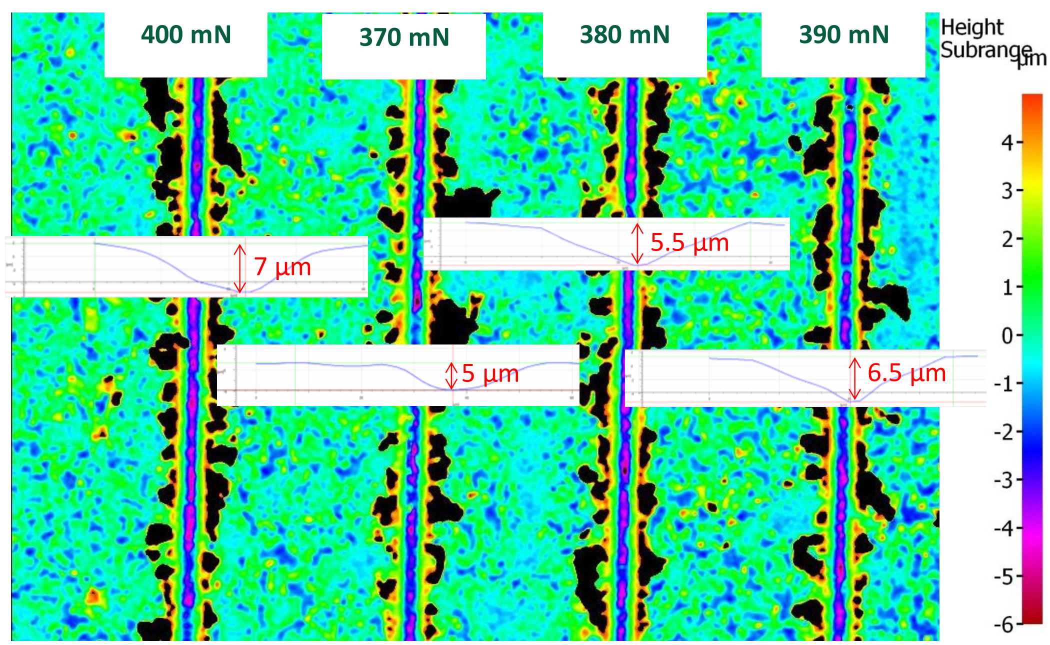

Figure 11. Depth analysis for different constant load scratch tests.

The thickness of the layer was of the order of 5 µm. However, the mark left by the load at 390 mN showed a depth larger than this value (a depth of 6.5 µm). This can be interpreted as the minimum force to completely penetrate the iron carbonate layer. However, the depth of the scratch being significantly larger than the average thickness of the layer is not a conclusive evidence of iron carbonate detachment, since the possibility of plastic deformation of the layer and the substrate can be present. Therefore, EDS was used as a complementary technique to assess such a detachment.

Constant Load Scratch Test EDS Analysis

In order to find the detachment force of the iron carbonate layer, EDS was utilized to establish the local chemical composition within the grooves. If the chemical signature shows a presence of Fe, C and O, then this would be a sign that the iron carbonate layer has not been fully removed. On the other hand, if the chemical composition shows a high content of iron (and minimal oxygen/carbon), then it can be assumed that the iron carbonate layer has been completely removed.

Three different loads were used to corroborate the detachment of the iron carbonate layer *via* EDS analysis. Figure 12 and Figure 13 show the three tests performed and the resulting scratch tracks. Results from optical microscopy suggest that the iron carbonate layer is partially removed at 250 mN and totally removed at 390 mN.

Figure 12. Constant load scratch tests at different forces.

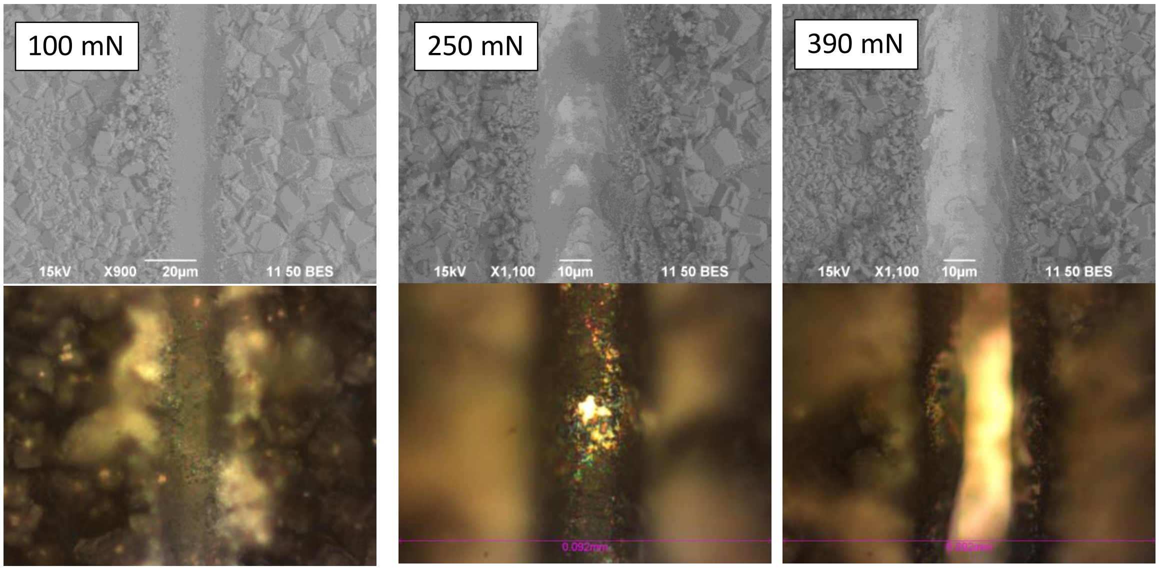

Figure 13. Zoomed images of constant load scratch tests at different forces.

The scratch tracks were then analyzed with EDS as shown in Figure 14. In the scratch test performed at a constant load of 100 mN, the local chemistry of the mark was very similar to its surroundings. This indicated that the iron carbonate layer had not been removed. When the force was increased to 250 mN, there was a partial removal of the layer, indicated by the pink pattern (representing the presence of iron). Finally, at 390 mN, the iron carbonate was totally removed as corroborated by the pink pattern in the mark of the scratch (representing the chemical signature of iron), which unequivocally proved that the steel surface was exposed.

Figure 14. EDS mapping analysis of constant load scratch tests at different forces.

Figure 15 shows the atomic mapping analysis for carbon, oxygen and iron in the grooves. Again, the chemical signatures are consistent with the previous claim of total removal of iron carbonate at 390 mN of load force in the scratch test.

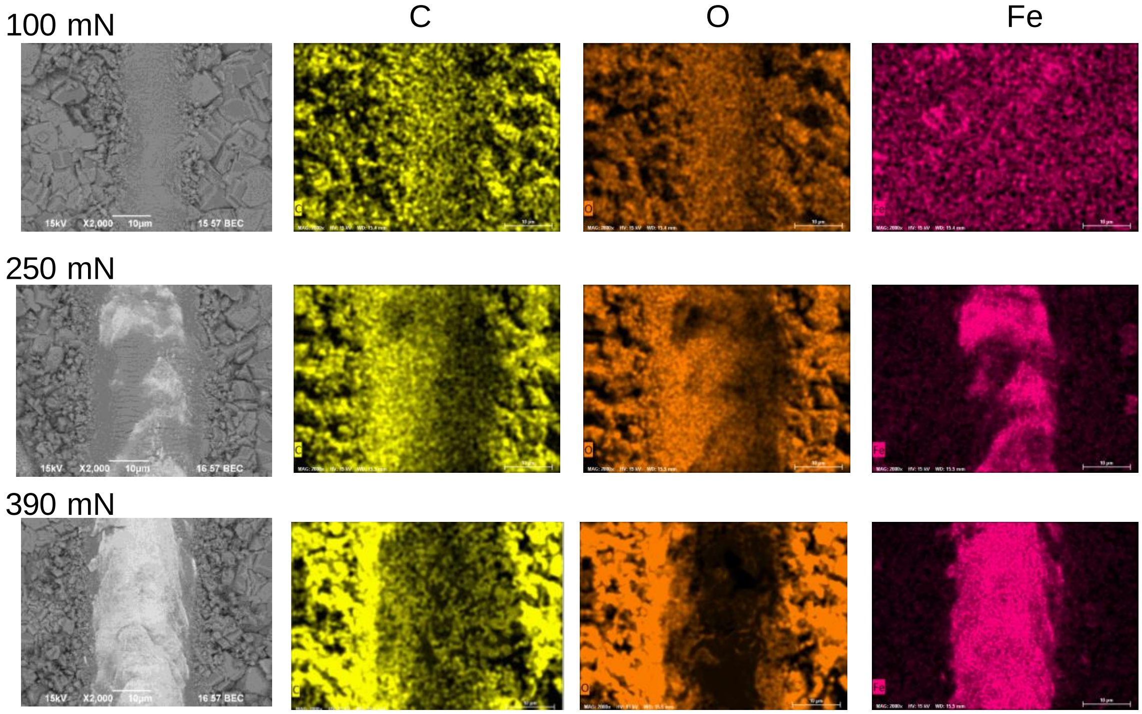

Figure 15. EDS analysis for constant load scratch tests at different forces.

Shear Stress Determination

As previously stated, the model of Olivier & Matthews was used to determine the shear stress for the delamination of the iron carbonate layer. The mathematical model is derived from Figure 16, based on the projected area of the layer at the critical load (Figure 1). The shear stress is determined based on the load measured at detachment and the area projected.

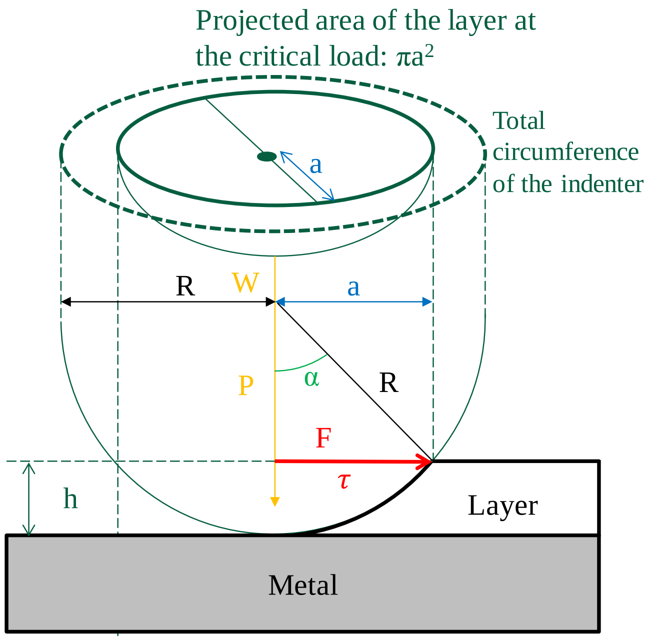

Figure 16. The principle of scratching to remove a layer (white) from a metal substrate (gray). Related physical magnitudes are colored-related. P is the vertical load of the indenter, related to the load (orange-colored). F is the tangential force and τ the shear stress (red-colored). R is the total radius of the indenter; a is the radius at the critical load (when the indenter reached the metal substrate); h is the thickness of the layer.

The mathematical development of the formula is based upon the combination of geometrical parameters and the previously-mentioned forces, as discussed elsewhere[15]. The result is a formula that transforms the critical load into shear stress:

$$\tau = \frac{L_c}{\pi a\sqrt{R^2 - a^2}} \qquad (1)$$

Where:
W - load, N
a - radius of the projected area, m
P - vertical load of indenter (Force/area), Pa
F - tangential force, N
R - indenter radius, m
L_c - critical load, N
τ – shear stress, Pa

A summary of the critical loads and shear stresses is given in Table 4.

Table 4. Summary of Critical Loads and Shear Stresses

Parameter	Load / mN	Shear Stress / MPa
Minimum force to create a noticeable damage	36 (cohesive failure)	235 ± 5
Load to partially remove the layer	250 (adhesive failure critical load)	396 ± 8
Load to totally remove the layer	390 (full delamination)	630 ± 15

Finally, those results were compared with data available in the open literature for the removal of iron carbonate layers from a steel substrate[2,18]. The comparison is given in Figure 17 which shows that the values obtained in this study are one order of magnitude higher than those obtained from the literature. One possible explanation for the disagreement can be the formation conditions of the layers: in the other studies, the mechanical integrity of an iron carbonate layer formed in a bulk pH of 6.6 was assessed. Consequently, different bulk chemical conditions might lead to different adherences forces of the layers. Therefore, at lower pH (*i.e.* 4-6) the unprotective nature of the corrosion product layers can be attributed to potentially low adhesion forces. Such speculation will be tested as part of the future research on this matter. However, as it relates to applications within the oil and gas industry where shear stresses generated by fluid flow are of the order of hundreds or thousands of Pa, the mechanical integrity of iron carbonate layer formed at high bulk pH cannot be easily challenged.

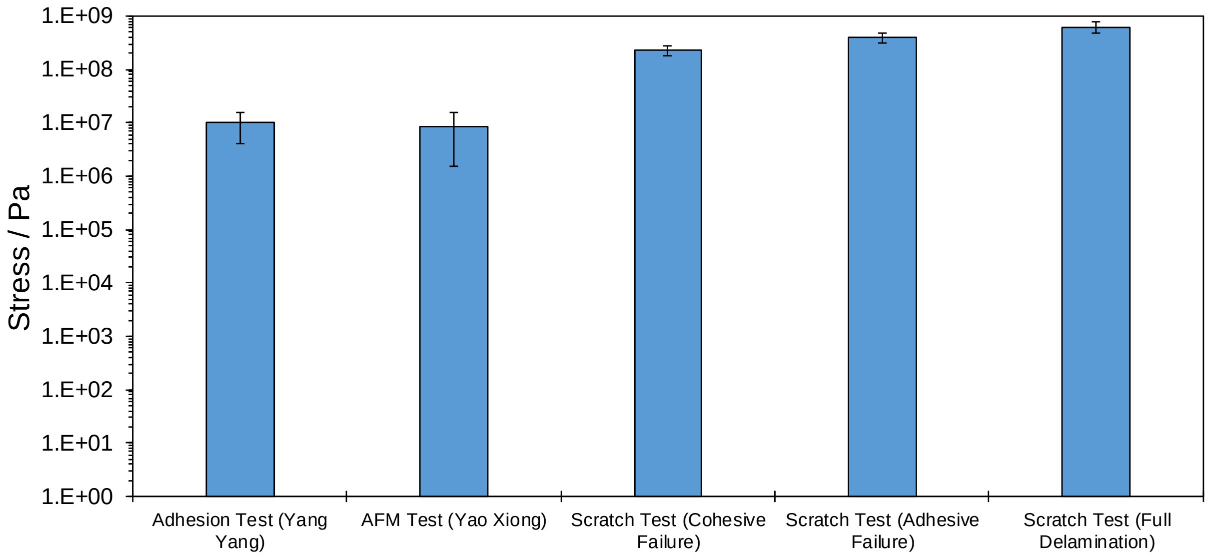

Figure 17. Comparison of shear stresses obtained by different techniques[2,18]. The estimated shear stress to produce cohesive and adhesive failure is of the order of 10^8 Pa.

CONCLUSIONS

- Scratch tests were successfully utilized to assess the mechanical integrity of an iron carbonate layer on mild steel.
- Critical shear stress to produce a partial damage to the iron carbonate layer was of the order of 200 MPa.
- Shear stress to reach the metal substrate (removing the iron carbonate layer) is of the order of 600 MPa.

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