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Adhesion of Corrosion Product Layers Formed in Dewing Conditions

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ABSTRACT

Engineers in the oil and gas industry frequently rely on the formation of protective corrosion product layers to mitigate internal pipeline corrosion. However, their protectiveness can be compromised if such layers, iron carbonate formed during CO₂ corrosion for example, are mechanically removed from the metal. Partial loss of a corrosion product layer has the potential to result in localized attack and loss of containment. In sour environments, this partial loss can lead to particulate (black powder in case of commercial gas pipelines) entrainment, which can cause multiple problems downstream in the pipeline. Consequently, the study of adhesion forces between iron carbonate, iron oxide or iron sulfide layers and their associated metal substrate is essential to the industry. In the current work, adherence characteristics of iron carbonate layers grown in dewing conditions (condensing water conditions) were mechanically characterized *via* scratch testing by measuring the critical force to produce a removal of the layer. With the use of critical frictional forces (tangential forces parallel to the surface that produce the removal of the corrosion product) and the projected area of the indenter, the shear stress associated with the removal of the layer was calculated. This mechanical assessment was extended to layers grown in bulk aqueous conditions for comparative purposes. The results indicated that the critical shear stress for the removal of iron carbonate in dewing conditions was 3 orders of magnitude lower than for iron carbonate grown in aqueous environments. Finally, the critical shear stress for iron sulfide produced in dewing conditions indicated that the layer was significantly more adherent than the iron carbonate layer grown in similar conditions. In addition to understanding corrosion phenomena, this work has significance relating to black powder formation and resultant erosion.

INTRODUCTION

The oil and gas industry produces a large variety of products essential to everyday life, such as gasoline, diesel, and natural gas as fuels as well as petrochemical feedstocks used to make a

wide range of products. To transport refined products as liquids or gases to customers, the oil and gas industry frequently uses transmission pipelines. One of the operational problems associated with gas transmission pipelines is the formation of black powder¹. As its name suggests, black powder is blackish dust that can impact the performance of transportation pipelines due to its accumulation, even resulting in pipelines potentially becoming blocked^{1,2}. This blockage affects the flow of gas, thereby reducing the amount that is delivered to the end user. In terms of pipeline integrity, black powder causes erosion of the internal pipe wall, compromises the functioning of critical components (e.g., sensors, valves), and induces pressure drop due to the variation of internal diameter³. Gas turbine blades are also susceptible to damage caused by black powder accumulation due to excessive wear and erosion³. Therefore, understanding mechanisms of spallation are essential so that conditions at which corrosion products form black powder can be avoided, predicted, or mitigated.

Consequently, if the proposed research determines the tendency of corrosion products on steel to undergo spallation related to evolving stresses with loss of adherence, then this knowledge can potentially be applied for the development of black powder prevention strategies. Also, the proposed research has the potential to add to the understanding of localized corrosion mechanisms associated with local detachment of iron carbonate and iron sulfide layer. Before proceeding to the experimental procedure, the critical points of the theory behind the tribology techniques to assess the mechanical integrity of thin films are discussed.

Cohesive Failures of Thin Layers

Cohesive failure of thin layers can be defined as the partial delamination that can occur within the same layer^{4,5}. This failure usually happens at the gas-layer interface^{4,5}. The most commonly reported forms of cohesive failures are buckling and spallation⁶. Buckling is the cracking and lifting of part of the layer⁶; spallation is the partial removal of small parts of the layer⁶. Partial delamination is generally caused by external agents such as shear stress exerted by a fluid, the internal stresses within the layer, or thermal expansion stresses⁷. Internal stresses refer to the stresses generated within a crystalline layer at deposition or growing due to mismatching of crystals, impingement during their growth, and bonds between crystals⁷.

Adhesive Failures of Thin Layers

This type of failure refers to the total detachment of a thin layer from the substrate⁸. Such a condition is reported to be produced by external mechanical forces such as shear stresses generated with industrial cutting tools^{4,5}. The forces required to produce this type of failure are generally higher than the forces to produce a cohesive failure⁶. The bonding between the film and the substrate plays a governing role in this type of failure, as well as other internal stresses within the layer⁹. Bull, *et al.*, have discussed the contribution of the abovementioned internal stresses in their practical assessment of adhesion of thin layers¹⁰. Regarding studies of corrosion product layers, in past research conducted on the forces required to remove iron carbonate product layers, Yang, *et al.*, used tensile strength testing to determine the layer removal forces from a mild steel surface. They reported values in the order of MPa to remove an iron carbonate layer¹¹. Xiong, *et al.*, reported similar values for the removal of a single crystal of iron carbonate with atomic force microscopy (AFM)¹².

Scratch Adhesion Testing Theory

Scratch testing is a tribological technique widely utilized, among other applications, in the determination of adhesive forces between a substrate and thin layers^{10,13,14}. This technique is considered a robust method to obtain information about the adhesion of a film to a substrate^{10,15}. The method can capture the three primary contributing parameters that govern the adhesion phenomena between a thin film/coating/layer and a substrate: internal stresses within the film, the adhesive friction between the stylus and the contacted surface, and the plowing contribution of the indenter.

Burnett, Rickerby, and Bull utilized the fundamental approach followed by Laugier¹⁶ (energy balance approach) to identify three main forces contributing to the layer detachment: elastic-plastic indentation stress, internal stresses, and tangential frictional stress as shown in Figure 1¹⁰.

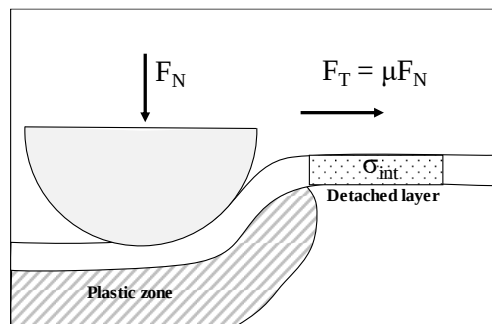


Figure 1. Three main contributors for the detachment of layers on a substrate: plowing component (a function of F_N), internal stress component (σ_{int}), and tangential force (F_T). μ is the friction coefficient of the layer. Adapted from Burnett, *et al.*¹⁷

Bull, *et al.*, also proposed that the friction forces measured by the scratch adhesion test can be represented as the sum of the three contributors (elastic-plastic indentation, internal stresses and frictional stress) under the premise that the indentation term produces a tangential force as a function of the friction coefficient, and the internal stresses add an extra resistance tangential force¹⁰. Moreover, Bull, *et al.*, also distinguished the adhesive failures produced by tensile forces and failures produced by compressive forces⁶. This type of failure depends on the nature of interaction of the layer and the substrate and can be detected by microscopy^{6,14}. Therefore, a microscopic inspection must be performed before choosing the model equation to obtain the critical shear stress for failures. If the failure is governed by compressive stresses, the shear stress is given by:

$$\tau_c = \frac{F_T}{A} \quad (1)$$

Where τ_c is the critical shear stress to produce failure, F_T is the tangential force of plowing, as defined in Figure 1, and A is the area where the tangential force was acting on the layer.

Whereas if the tensile stress is causing the detachment of the layer, the model equation for the critical shear stress (τ_t) is given by:

$$\tau_t = \frac{\nu_l F_T}{A} \quad (2)$$

Where ν_l is the Poisson ratio of the layer.

The Case for Flexible Substrates and Brittle Coatings

Ollivier and Matthews (O&M) simplified the energy criterion proposed by Bull and developed a mathematical model for hard thin films deposited on a flexible substrate¹⁸. Although simple, this model is in good agreement with the experimental observations of Laugier, Perry, and Weaver^{19–21}. They argued that the forces during a scratch test can be modeled by a quasi-static approach as depicted by Figure 2. Figure 2 shows the geometrical parameters and forces involved in the determination of the tangential force to transform it into a shear stress value. Under this assumption, the layers experience adhesive failure when a normal load (P : orange vector in Figure 2) in conjunction with its associated tangential force (the red vector in Figure 2, F) is reached. Such a normal load is called the critical load. Moreover, the authors assumed that, at the critical load, the plastic deformation of the substrate is negligible for flexible substrates. A flexible substrate can be defined as a substrate that exhibit elastic strain recovery in the range of working forces with a minimum of plastic deformation¹⁸. There are also two implicit assumptions: internal stresses are negligible, and the scratch testing process is performed quasi-statically. In other words, the process occurs so slowly that the static analysis of the forces is valid. Consequently, the tangential force is a linear function of the normal force, independent from the substrate.

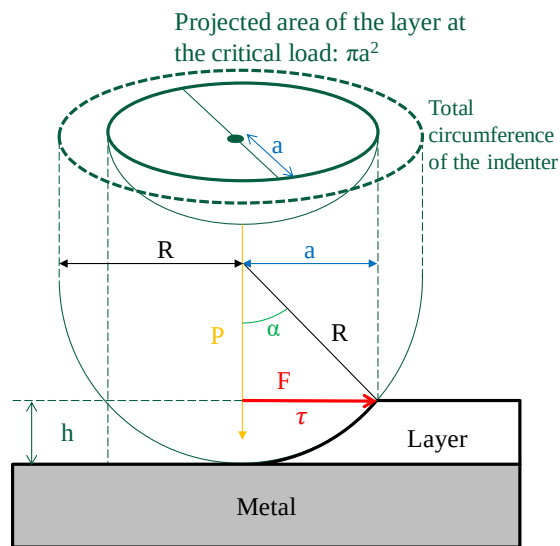


Figure 2. The principle of scratching to remove a layer (white) from a metal substrate (gray). Related physical magnitudes are colored-related. P is the vertical load of the indenter, related to the load (orange-colored). F is the tangential force and τ the shear stress (red). R is the total radius of 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 elsewhere¹⁸. The result is a formula that transforms the critical load into tangential forces and shear stress:

$$F_T = F_N \frac{a}{\sqrt{R^2 - a^2}} \quad (3)$$

At the critical load, $F_N = L_C$, thereby:

$$\tau = \frac{L_c}{\pi a \sqrt{R^2 - a^2}} \quad (4)$$

EXPERIMENTAL PROCEDURE

Table 1 shows the experimental conditions at which the iron carbonate layers were formed.

Table 1. Test Matrix for Iron Carbonate Formation

Parameter	Value	
Temperature of solution / °C	80	
Sparge gas	CO ₂	
Working solution	1 wt.% NaCl	
Material	X65	
pH	8.0 ± 0.2	6.6
Fe ²⁺ initial concentration / ppm	50	100
Test duration	3 days	

Formation of Layers in Dewing Conditions

Table 2 shows the parameters to obtain iron carbonate layers in dewing conditions, and Table 3 shows the experimental conditions to form an iron sulfide in dewing conditions.

Table 2. Test Matrix for Iron Carbonate Formation in Dewing Conditions

Parameter	Value
Steel substrate	X65
Temperature of steel / °C	60
Temperature of the gas / °C	75
Sparge gas	0.62 bar CO ₂ (0.38 bar H ₂ O vapor pressure balance)
Working solution	Condensate water (calculated bulk pH ≈ 4.0)
Test duration	3 days

Table 3. Test Matrix for Iron Sulfide in Dewing Conditions

Parameter	Value
Steel substrate	X65
Temperature of steel / °C	30
Temperature of the gas / °C	35
Sparge gas	H ₂ S/N ₂ mixed gas (100 ppm _v H ₂ S)
Working solution	Condensate water (calculated bulk pH ≈ 6.0)
Test duration	3 days

The gas and solution temperature were chosen based upon the work published by Colahan, *et al*²², since iron carbonate and iron sulfide layers were successfully developed at such conditions. X-ray diffraction (XRD) was used to corroborate corrosion product formation. The test apparatus