Low-temperature Pack Aluminization Process on Pipeline Steel to Inhibit Asphaltene Deposition

DOI:
[10.1021/acsami.9b17430](https://doi.org/10.1021/acsami.9b17430)

Document Version
Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Shetty, P. P., Daryadel, S., Haire, B. T., Tucker, Z. R., Wu, T., Subramani, V., Morrison, J., Quayle, P., Yeates, S. G., Braun, P. V., & Krogstad, J. A. (2019). Low-temperature Pack Aluminization Process on Pipeline Steel to Inhibit Asphaltene Deposition. *ACS applied materials & interfaces*. <https://doi.org/10.1021/acsami.9b17430>

Published in:
ACS applied materials & interfaces

Citing this paper

Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights

Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy

If you believe that this document breaches copyright please refer to the University of Manchester's Takedown Procedures [<http://man.ac.uk/04Y6Bo>] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

Low-temperature Pack Aluminization Process on Pipeline Steel to Inhibit Asphaltene Deposition

Journal:	<i>ACS Applied Materials & Interfaces</i>
Manuscript ID	am-2019-17430t.R1
Manuscript Type:	Article
Date Submitted by the Author:	16-Nov-2019
Complete List of Authors:	Shetty, Pralav; University of Illinois at Urbana-Champaign, Materials Science and Engineering Daryadel, Soheil; University of Illinois at Urbana-Champaign, Materials Science and Engineering Haire, Barnaby; The University of Manchester, School of Chemistry Tucker, Zoë; University of Illinois at Urbana-Champaign, Materials Science and Engineering Wu, Tiffany; University of Illinois at Urbana-Champaign, Materials Science and Engineering Subramani, Velu; BP America Inc Naperville, Refining Technology Morrison, John; University of Manchester Quayle, Peter; University of Manchester, Chemistry Yeates, Stephen; University of Manchester, School of Chemistry Braun, Paul; University of Illinois at Urbana-Champaign, Materials Science and Engineering; University of Illinois at Urbana-Champaign, Materials Research Laboratory; University of Illinois at Urbana-Champaign, Beckman Institute for Advanced Science and Technology Krogstad, Jessica; University of Illinois at Urbana-Champaign, Department of Materials Science and Engineering; University of Illinois at Urbana-Champaign, Materials Research Laboratory

SCHOLARONE™
Manuscripts

Low-temperature Pack Aluminization Process on Pipeline Steel to Inhibit Asphaltene Deposition

Pralav P. Shetty^{†,‡,§}, Soheil Daryadel^{†,‡}, Barnaby T. Haire[¶], Zoë R. Tucker^{†,‡}, Tiffany Wu^{†,‡}, Velu Subramani^{||}, John J. Morrison[¶], Peter Quayle[¶], Stephen Yeates[¶], Paul V. Braun^{†,‡,§}, Jessica A. Krogstad^{†,‡,*}

[†]*Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 1304 W Green St, Urbana, IL 61801, USA*

[‡]*Materials Research Laboratory, University of Illinois at Urbana-Champaign, 104 S Goodwin Ave, Urbana, IL 61801, USA*

[§]*Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, 405 N Mathews Ave, Urbana, IL, 61801, USA*

[¶]*School of Chemistry, University of Manchester, Manchester, M13 9PL, UK*

^{||}*BP Products North America, Inc., Refining and Logistics Technology, Naperville, IL 60563, USA*

ABSTRACT

Asphaltene deposition in petroleum refineries is known to be problematic as it reduces efficiency and may lead to structural failure or production downtime. Though several successful approaches have been utilized to limit deposition through the addition of dispersants and inhibitors to petroleum, these methods require constant intervention and are often expensive. In this study, we demonstrate an innovative technique to engineer the surface chemistry of pipeline alloy steels to inhibit asphaltene deposition. Pack aluminization, a standard industrial-scale chemical vapor deposition process, is employed at a low temperature of 600 °C to aluminize API 5L X65 high strength pipe steel substrates. The results showed deposit free steel surfaces after high-pressure and high-temperature fouling experiments. The improvement is attributed to the formation of an aluminide intermetallic phase of Fe₂Al₅, which changes the native oxide chemistry to favor alumina over hematite. The continuous passivating oxide scale, acting as a protective barrier,

[†] These authors contributed equally to this work

^{*} Corresponding author: Jessica A. Krogstad, E-mail: jakrogst@illinois.edu

mitigates asphaltene deposition and sulfidic corrosion. Since this process is based on alloying the surface of the steel and is not a coating, it is not prone to delamination, and it can be reformed when damaged within the aluminized region. The combination of low-cost processing and improved anti-fouling characteristics makes surface chemistry modification of steel a promising preventative approach against asphaltene deposition.

Keywords: pack aluminization; pipeline alloy steels; asphaltene, fouling, surface modification

INTRODUCTION

Asphaltene deposition is a ubiquitous and undesirable phenomenon in the petroleum production chain.¹ In severe cases, flow from petroleum wells may completely cease within a matter of days because of arterial clogging from asphaltene deposition.² Asphaltenes that precipitate during the early stages of production may travel downstream and eventually deposit onto refining equipment. If not already precipitated, the change in operating conditions during refining may induce their precipitation and deposition.³ Such deposition is known to cause downtime and require remediation, which has steep economic implications for the oil and gas industry.⁴⁻⁵ In order to decrease the costs associated with this phenomenon, several approaches have been explored on the removal of deposited asphaltenes and prevention of asphaltene deposition.⁶

Amongst several preventative strategies, engineering the surface of components to inhibit asphaltene deposition is more desirable because it requires minimal intervention. However, given the massive scale of refining equipment and material cost restrictions, this approach is not commonly pursued. It is known that protective surface oxides like chromia and alumina can significantly improve the corrosion and fouling resistance of ferrous alloys.⁷⁻⁸ Though these oxides are more commonly used in their equilibrium corundum form, recent studies have shown their protective action even in a native amorphous form.⁹⁻¹¹ Such protective oxides can be introduced onto the surface of ferrous alloys by coating,¹²⁻¹⁴ alloying the surface,¹⁵ or changing the base composition of the alloy.¹⁶⁻¹⁷

In a previous study, it was shown that an atomic layer deposition (ALD) coating of alumina on steel surfaces significantly reduces asphaltene deposition at elevated temperatures from 150 °C to 350 °C.¹¹ The alumina surface chemistry, even in the amorphous form, was shown to alter the reaction pathway between the asphaltene and the surface from a corrosive sulfidation reaction to

1
2
3 a self-limiting chemisorption and oxidation process. For the alumina coating to serve as an
4
5 effective diffusion barrier against the inward diffusion of S at elevated temperatures, the coating
6
7 must be both continuous and greater than a critical thickness of 5 nm.¹¹ Despite the demonstrated
8
9 benefits of ALD to produce anti-fouling alumina coatings on steel, it is crucial to bear in mind that
10
11 typical film growth rates using ALD are very slow and, therefore intractable for most industrial-
12
13 scale applications.¹⁸
14
15

16
17 Additionally, the application of a distinct coating creates an interface, which can be easily
18
19 subjected to defects. The interfacial flaws can eventually lead to the delamination of the coating
20
21 during operation, which would leave the underlying alloy exposed. Although proper surface
22
23 preparation of the substrate before applying a coating can increase their longevity, the coating
24
25 failure leaves the substrate susceptible to environmental attack.¹⁹⁻²⁰ For instance, these flaws may
26
27 increase the risk of pitting corrosion mechanisms. Interestingly, some innovative self-healing
28
29 coatings provide further protection to the substrate if damaged or removed; however, most of these
30
31 coatings are polymer-based with limited thermal stability.²¹⁻²² Therefore, changing the base
32
33 composition of the alloy would be the best solution from a fundamental standpoint. However, this
34
35 method is not always economically practical. Thus, alloying the surface with a protective species
36
37 provides a good compromise between the two approaches as it can be applied with a low-cost
38
39 batch process and offers protection at the surface without the possibility of delamination.
40
41
42
43
44

45
46 Pack-based chemical vapor modification is an established alloying technique to introduce Al
47
48 (aluminization) and Cr (chromization) at the surface of alloys at large size scales. However, this
49
50 process is usually conducted at temperatures around 1000 °C, which is appropriate for nickel base
51
52 alloys, but not for ferrous alloys which are used more frequently in refineries.^{15, 23-24} Recently,
53
54 several studies have established low-temperature and high-activity packs that allow sufficiently
55
56
57
58
59
60

high deposition rates even at processing temperatures as low as 550 °C.²⁵⁻²⁷ The process allows for the surface chemistry modification of ferrous alloys without exceeding their tempering temperature, which in turn inhibits excessive grain growth and degradation of their mechanical properties.

In this study, low-temperature pack aluminization was used on ferrous alloys to change the native oxide to a protective alumina chemistry. High-temperature and high-pressure (HPHT) autoclave fouling with a model sulfur containing asphaltene was conducted on bare and aluminized steel surfaces. Complementary spectroscopy, mechanical testing, x-ray diffraction, and electron microscopy techniques were used to characterize the effect of aluminization on the chemistry, mechanical properties, and intermetallic formation. The change in corrosion resistance in an acidic HCl environment was also investigated. Collectively, these results suggest that using low-temperature pack aluminization may be a viable route to improve the fouling resistance of ferrous alloys with beneficial effects on other metrics like their mechanical properties and sulfidic corrosion resistance.

METHODS

Metallographic sample preparation

The ferrous alloy utilized for this study was API 5L X65 (Composition in atom percent: C - 0.16, S - 0.45, Mn - 1.65, P - 0.02, S - 0.01, V - 0.09, Nb - 0.05, Ti - 0.06, balance is Fe), a high strength pipe steel that is low in alloying elements. After being machined down to 5 mm × 5 mm × 0.5 mm size by electrical discharge machining (EDM), the coupons were brought to a level but stochastic finish (~20 nm RMS roughness) by grinding with silicon carbide papers up to 1200 grit followed by polishing with a 1 μm neutral alumina solution.

Low-temperature pack aluminization

The pack used for the aluminization process was comprised of three components: 82 wt. % inert Al_2O_3 powder [Baikowski/US Research Nanomaterials, 99.9 % pure], 3 wt. % NH_4Cl activator [Alfa Aesar, 99.999 % pure], and a 15 wt. % Raney-nickel aluminum source [Ni-50 wt. % Al, Acros, 99.99 % pure]. The relative amounts of the ingredients were based upon the need to ensure that the pack had a sufficiently high aluminum activity to work at the lower temperatures desired to minimize grain growth and preserve the base mechanical properties of the steel. After the components were combined, they were mixed with Al_2O_3 ball milling media for 48 hours to ensure homogeneous mixing. The samples were embedded in the pack, as shown in Figure 1a, and placed in an environmentally controlled furnace under 1 atmosphere of gettered argon (10^{-12} partial pressure of O_2) that was continuously purged at a flow rate of 1 L/min. In order to produce Al chloride vapors that reduce at the surface of the metal to leave behind Al metal, the embedded samples were heated to 600 °C at a ramp rate of 20 °C/min and held at this temperature for 6 hrs. The samples were then cooled under argon for an hour, followed by a nitrogen purge until they reached room temperature.

High-temperature fouling test

The model asphaltene used in this study is 1,6-bis(pyren-1-ylthio)hexane, referred to as BPH. The BPH was synthesized through a nucleophilic aromatic substitution reaction. The details of its synthesis have been provided in a previous manuscript.¹¹ A surrogate fuel was prepared using BPH and heptol (50:50 volume percent heptane to toluene). Since BPH is aromatic, it is soluble in toluene but not heptane. First, a solution of 0.22 wt. % BPH in toluene was prepared and sonicated for 30 minutes to ensure complete dissolution. Then, heptane was added to the mixture right before

the fouling test for a final composition of 0.125 wt. % of BPH in heptol. The heptane was used to destabilize the asphaltene in solution and accelerate its deposition onto the steel coupons.

For the HPHT fouling test, an autoclave [60 ml EZE Seal Pressure Vessel, Parker Hannifin] made from 316 stainless steel was used. The samples were supported in a mount of the same alloy, configured with three slits over a deeper groove. The groove allowed for the flow of the surrogate fuel around the samples and prevented the asphaltenes from concentrating around the bottom of the samples. The samples themselves were arranged vertically in the slits in order to avoid gravitational deposition of the asphaltene on the plan surfaces during the autoclave cooldown. The steel coupons were fully submerged in 5 mL of the model asphaltene solution before being air-sealed and then heated from room temperature at a rate of 10 °C/min. Once the furnace reached its final temperature of 350°C, the temperature was held for 1 hour and naturally cooled to room temperature. After the autoclave reached room temperature, the coupons were removed and rinsed with 1 mL of petroleum ether to remove loosely adhered deposits. The mass gain of the coupons was measured using a microbalance [XPE26, Mettler- Toledo] after the fouling test. Three samples were tested for each of the bare and aluminized cases.

Characterization of surfaces

Optical characterization of the coupons was conducted on a laser scanning confocal microscope [VK-X1000, Keyence Corporation]. This allowed for characterization of the surface morphology and roughness changes as a result of the aluminization and fouling processes over large areas of the steel coupons. Both scanning electron microscopy (SEM) [JEOL 7000F, JEOL Ltd.] and scanning transmission electron microscopy (STEM) [JEOL 2010F S(TEM), JEOL Ltd.] were used to characterize the morphology and chemical makeup of the aluminized X65 steel. Chemical

information about the Al and Fe composition within the steel was collected on both systems using energy dispersive x-ray spectroscopy (EDS) [SEM - Thermo Electron EDS, Thermo Fisher Scientific; STEM – Oxford INCA 30 mm ATW Detector, Oxford Instruments plc]. The STEM samples were prepared using focused ion beam (FIB) [Scios 2 DualBeam, Thermo Fisher Scientific] cross-section lift-out.

To complement the chemical information from EDS spectra and identify specific intermetallic Fe-Al phases present at the surface of aluminized samples, glancing incidence x-ray diffraction (GIXRD) [PANalytical X'Pert Diffractometer, Malvern Panalytical] was used. The radiation used was Cu K_{α} with a spot size of 1 mm x 3 mm and an incident angle of 5 °. The material attenuation coefficient was calculated to be 167.46 cm²/g, and the x-ray penetration depth was estimated to be ~ 5.04 μm using the software HighScore [Malvern Panalytical], considering a Fe-Al packing density of 0.6 and Fe₂Al₅ intermetallic chemistry. These parameters were optimized to achieve the highest signal from the intermetallic phase present within the aluminized region.

X-ray photoelectron spectroscopy (XPS) [Kratos Axis Ultra, Shimadzu Corporation] was used to identify the chemistry of the thin surface oxide that formed on the aluminized surfaces at three different conditions. The measurements were made on three separate samples, one immediately following the aluminization process (as-aluminized), another after a post-aluminization anneal in air at 350 °C for an hour (aluminized-annealed), and finally, after a post-aluminization HPHT fouling process also conducted at 350 °C for an hour (aluminized-fouled). A monochromatic Al K_{α} excitation was used with a spot size of 2 mm x 2 mm to generate photoelectrons from the aluminized surfaces. A pass energy of 40 eV was used with averaging over six scans of elemental regions. The XPS data were analyzed using the software package by CasaXPS. Peak fitting was conducted with a Shirley background subtraction for elemental regions of interest.

Mechanical characterization

The hardness of the aluminized coupons was measured along the depth of the cross-sectional samples using a nanoindentation system [Hysitron TI 950 TriboIndenter, Bruker Corporation] with a diamond Berkovich tip. All indentation tests were made to a maximum depth of 100 nm with a constant rate of 10 nm/s. The obtained load-displacement data were analyzed using the Oliver-Pharr method to calculate the hardness.²⁸ After indentation, the footprints were observed by atomic force microscopy (AFM) [Asylum Research MFP-3D, Oxford Instruments], and the true area was measured for the indents with pile-up.

Standard dog-bone tensile test specimens were sectioned from X65 coupons using an electrical discharge machine (EDM) according to ASTM E8/E8M.²⁹ The test specimens had a gauge section width, thickness, and length of 2, 0.5, and 8 mm, respectively. The sample surface was ground up to 1200 grit with silicon carbide papers and polished with a 1 μm neutral alumina solution before the annealing and aluminization process. Tensile tests were performed on bare annealed X65 and aluminized X65 test specimens using a 5 kN Instron universal testing machine under displacement-control mode with a crosshead speed of 0.01 mm/s measured by an extensometer. Six samples were tested in each condition. It is noteworthy that the bare samples were annealed at similar aluminization condition (600 °C for 6 hours in gettered Ar) to normalize the effect of the heat treatment in comparison of mechanical properties. Martensitic steels are usually tempered to improve ductility. While iron-carbon martensites are reported to progressively become more ductile upon annealing up to 700 °C, they tend to recrystallize above 600 °C, which can reduce their mechanical strength.³⁰ The temperature of 600 °C was chosen for the aluminization process (and annealing process for comparison) to inhibit the loss of mechanical properties like tensile and creep strength while achieving a high Al surface concentration.²⁷

RESULTS & DISCUSSION

Characterization of aluminized coupons

The pack aluminization process is schematically shown in Figure 1a. Several 5 mm × 5 mm × 0.5 mm X65 pipe steel coupons were aluminized in gettered Ar at 600 °C for 6 hours. An optical micrograph of the plan view of an aluminized X65 coupon is presented in Figure 1b. The as-aluminized surfaces have a light-grey metallic appearance. No pack particles were identified on the aluminized surface, showing that the coating was formed through inward Al diffusion. The Al deposition from the aluminization process is non-uniform because of the stochastic nature in which the aluminum chloride vapors are generated in the pack and reduced at the surface of the coupon. It is important to note that the aluminization process increases the original surface roughness of the polished X65 specimens (~180 nm RMS roughness). However, the benefits of reduced asphaltene fouling have been realized for passivated surfaces with average roughness on the order of several microns.¹¹

The cross-sectional SEM images of the deposition at two different magnifications are shown in Figures 1c and 1d. A continuous aluminide layer formed on the surface. As shown in Figure 1d, the aluminized region consisted of two distinct layers; a uniform single-layer structure followed by a transition layer to the base X65 alloy. The distinctive interfaces suggest the formation of an intermetallic compound. Also, it appears that because of the brittle nature of the aluminide surface, some cracks form in the outer layer during polishing. The results demonstrated a diffusion layer with variable thickness and significantly thicker deposition at the corners of the samples. The deposition thickness in the middle region of the coupons varied from ~2 to ~10 μm. It is noteworthy to mention that a more uniform deposition with the same composition and a higher thickness (up to 30 μm) was achieved at a similar temperature and time duration by using a pack with a different

activator, AlCl_3 , and a higher source Al content, 40 wt% NiAl (Figure S2). Previous detailed studies have demonstrated that the aluminization parameters, such as pack composition, deposition temperature, and time affects the coating thickness, without changing the surface phase and Al concentration.³¹⁻³² The feasibility of controlling the thickness of the aluminized layer in X65 pipeline steel using different pack compositions is discussed in supplementary information.

A more detailed view of the aluminized surface layer can be seen in the cross-sectional STEM micrograph of the aluminized coupon (Figure 1e). Surface pores on the order of tens of nanometers are observed in the diffusion layer; these pores are attributed to the coalescence of Kirkendall voids. The Kirkendall voids were formed in the diffusion layer to accommodate the fast, inward diffusion flux of Al. The aluminized surface enables the formation of a stable alumina native oxide through preferential Al oxidation in air. A higher magnification STEM micrograph of the surface of the aluminized sample shows a very thin native oxide layer (dark contrast at the surface). This native oxide most likely forms during the exposure of the aluminized coupon to air and not during the aluminization process that is conducted under an inert environment (Figure 1f).

Figure 1. (a) Schematic of the crucible nesting technique used in the low-temperature pack aluminization process. The X65 coupons are embedded in a high activity aluminizing pack prior to the thermal activation in an inert environment. (b) Optical plan view micrograph of an as-aluminized X65 coupon showing the typical surface morphology. (c) and (d) SEM images of the cross-section of the aluminized surface at two different magnifications. The distinctive layers suggest the formation of an intermetallic region. (e) and (f) Detailed cross-sectional STEM micrographs of the aluminized layer showing a very thin native oxide layer formed because of air exposure.

Figure 2b shows the Al and Fe concentration profiles measured by EDS along the depth starting at the top aluminized surface. The average atomic percentage of Al in the top layer is about ~70 at%. The Al concentration remains constant throughout the top layer with a thickness of 7.2 μm and shows a gradual drop afterward. The interdiffusion zone (IDZ) had a thickness of ~2.1 μm, in which the Al concentration gradually decreased to zero. The value of Al concentration along the entire depth suggests a high Al interdiffusivity in the X65 steel. Based on the measured constant Al concentration (and XRD data in Figure 2c), the intermetallic phase Fe_2Al_5 was identified in the

top diffusion layer. It is noteworthy that Fe_2Al_5 is the most stable compound among all Fe-Al binary compounds, one indication for this is its low formation enthalpy.³³

Figure 2c shows the GIXRD pattern of an aluminized sample. Fe_2Al_5 is the main phase detected by GIXRD at the surface, which confirms the diffusion of a significant amount of Al in the surface shown by EDS. The result from the aluminized sample reveals a strongly textured Fe_2Al_5 phase with a high intensity (002) peak. As expected, the Fe phase from the base X65 alloy was also detected by the GIXRD. Similar Fe peaks could be observed in the XRD patterns for the non-aluminized reference X65 specimens. However, no Fe or Al oxide peaks were detected using GIXRD, confirming that the native oxide formed is amorphous.

Nanoindentation tests were carried out on the cross-section of aluminized X65 steel. The SEM image of a representative array of indents can be observed in Figure 2a. The hardness of the aluminized top layer and the X65 substrate beneath was evaluated from the indentation load-depth curves. Figure 2d shows the typical load-depth curves for the indents made in the intermetallic surface layer and the base X65 alloy. The aluminized surface had a much higher maximum indentation load, thus higher hardness compared to the base X65. The high ratio of final indentation depth to the maximum indentation depth in the X65 base region suggested the possibility of pile-up during nanoindentation. AFM images of the indents' footprint confirmed the occurrence of the pile-up. Therefore, the predicted hardness values by the Oliver-Pharr method were overestimated due to the underestimation of the contact area. The true hardness value for the base X65 was recalculated with the area measured from AFM topography images.

The variation of hardness in the cross-section of the layers along the distance from the top surface is shown in Figure 2e. It is clear to see that the surface intermetallic layer is significantly harder than the base alloy subjected to the aluminization thermal treatment. The average hardness of the

aluminized surface is 8.77 ± 1.66 GPa, while it drops significantly to 3.22 ± 0.15 GPa in the base alloy region (Figure 2f). The depth with the higher hardness values correlated well with the measured thickness of the region with high Al concentration. Combined, these data confirm the formation of a surface Al-rich iron aluminide intermetallic layer. The high hardness in the aluminized region further corroborates the formation of Fe_2Al_5 , which is the hardest intermetallic phase formed among Fe-Al compounds. The attained hardness value approximates to the microhardness of Fe_2Al_5 compound formed by hot dip aluminization of carbon steel reported previously in the literature.³⁴

Figure 2. (a) SEM micrograph of the indentation on the cross-section of the aluminide surface and (b) EDS analyses of the Al and Fe concentration profiles constituting the aluminized area. The downward arrow indicates the approximate position of the EDS Linescan. The concentration of Al is ~ 70 at.% in the top region (blue) and gradually decreases to zero within the interdiffusion zone (green). (c) GIXRD patterns corresponding to the Fe_2Al_5 phase attained from the as-aluminized surface. (d) Typical Load-depth plot obtained from nanoindentation on the cross-section of the

aluminized and base X65. (e) Hardness distribution from the top surface to the base steel substrate. (f) The average hardness of aluminized and base X65 samples obtained from the nanoindentation test.

High-temperature fouling test

Fouling experiments were conducted on aluminized and bare X65 coupons at 350 °C, and the mass of the samples was measured before and immediately after fouling. The area normalized mass gain of the substrates is presented in Figure 3a. The average mass gain of the three measurements is reported along with the standard deviation. A point chart is used for a better demonstration of the negligible mass gain of the aluminized X65. The difference in mass gain between the aluminized and bare substrates was significant. The average amount of deposition at the bare X65 substrates was $2914 \pm 445 \text{ mg/m}^2$, while the mass gain for the aluminized X65 sample was not measurable ($0 \pm 35 \text{ mg/m}^2$) within the resolution limits of the microbalance.

The post-fouling optical images of the top surface of the bare and aluminized X65 coupons are shown in Figure 3b and 3c, respectively. The post-fouling micrograph of the top surface shows a drastic change in the polished bare X65 coupons that prior to fouling had a mirror polish. The deposits seen in the central part of this sample constitute a carbonaceous mat covering a bed of iron sulfide deposits. The yellow deposits seen along the edges of the coupon are also iron sulfides without a top carbonaceous mat which probably delaminated at the edges because of faster build-up. In comparison to this, almost no noticeable change was observed in the aluminized coupons post-fouling. No foulant build-up was measured or seen on the surface of the aluminized substrate which shows typical iron aluminide rich grey regions. The surface morphology of the exact as-aluminized X65 coupon before fouling is provided in Figure 1b. This anti-fouling behavior is similar to that achieved on ALD alumina coated X65 substrates. The results suggested that the aluminization process was successful in changing the surface oxide from hematite to alumina. The

deposit chemistry and reaction mechanism on the unpassivated X65 were explained in detail in the authors' previous work.¹¹

Figure 3. (a) Normalized mass gain of bare and aluminized X65 substrates after the high-temperature fouling test. No measurable mass gain was identified for the aluminized X65 coupon. The post-fouling optical micrographs of top surfaces show the drastic change in the (b) polished bare X65 coupons compared to almost no noticeable change in the (c) aluminized coupons. No foulant build-up was measured or seen on the surface of the aluminized substrate.

The surface of the aluminized sample before and after fouling was characterized thoroughly to confirm the formation of a passivating oxide layer during the fouling experiment and the mechanism leading to fouling resistance of the aluminized surface. XPS survey spectra were recorded for the samples as-aluminized, aluminized-annealed (350 °C for 1 hr in air), and aluminized-fouled (350 °C for 1 hr in air sealed autoclave). Detailed XPS spectra of Al 2p, corresponding to each condition are presented in Figure 4a-c. The results show that in all three cases, Al is present at the surface in both metallic (0) and oxide (+3) oxidation states. The relatively high Al oxide peak suggested the presence of a thin alumina oxide at the surface of three samples with photoelectrons from the underlying Al still reaching the detector. This is corroborated by the STEM micrographs of the as-aluminized sample in Figure 1f that showed a very thin oxide layer. However, the relative intensity of the metallic Al peaks is significantly decreased in annealed and fouled samples, corresponding to the growth of the alumina layer.

The peak area ratio between the oxidized and the metallic Al components can give an indication of the alumina thickness at different conditions. This ratio ($\frac{Al_{ox}}{Al_{met}}$) for as-aluminized, aluminized-annealed, and aluminized-fouled are 5.0, 11.4, and 9.7, respectively. This suggests that the surface alumina layer is thin in the as-aluminized state and grows in thickness after annealing at 350 °C in air and the fouling process at 350 °C in a surrogate fuel environment. Conceivably, the surface alumina layer, which grew during the fouling experiment, is slightly thinner compared to one formed during the annealing process in air. Figure 4d shows the S2p spectrum of the aluminized-fouled sample with a single peak at a binding energy of 169 eV, suggesting the formation of aluminum sulfate. The absence of the peak corresponding to sulfide (~161.5 eV) indicates that no metal sulfide is formed during the fouling experiment, similar to the previously studied ALD alumina passivated steel.¹¹ It is noteworthy that based on the XPS survey, the concentration of Fe on the top surface in all conditions is below 1 at. %, indicating enrichment of aluminum and the presence of an alumina passivating layer after aluminization.

A detailed cross-sectional STEM image of the aluminized X65 steel surfaces after fouling at two different magnifications is demonstrated in Figure 4e and 4f. The STEM data identified a dense and continuous film of Al₂O₃ with a thickness of ~10 nm (Figure 4f). In agreement with the XPS data, the results show that during the fouling experiment, the existing thin Al₂O₃ layer grew thicker. Previously bare X65 substrates were reported to form a significant amount of thiolate and sulfide deposits under identical fouling conditions. However, alumina coated X65 substrates were reported to limit the surface reactions to a thin layer of aluminum sulfate.¹¹ In contrast to the bare X65 substrates, the alumina layer formed on aluminized surfaces in this study also prevents the formation of thiolate and sulfides at the surface and instead forms a thin aluminum sulfate layer.

Therefore, the aluminized surface showed no significant mass gain from the fouling deposits compared to the bare X65 coupons.

Additionally, the corrosion behavior of aluminized X65 steel was studied in a solution of hydrochloric acid (Figure S1). This was done to evaluate the chloride corrosion behavior of the aluminized surfaces, as the available literature on aluminum alloys suggests some risk pitting corrosion, and localized dissolution of intermetallics in chloride solutions.³⁵⁻³⁶ The aluminized sample revealed a smaller mass loss compare to bare X65 for the first 12 days called Stage I (Figure S1a). However, the corrosion rate for both samples is relatively constant and similar after this stage. The presence of the thin aluminum oxide layer in as-aluminized specimens, which is confirmed by STEM and XPS data (Figures 1f and 4a), may explain the initially superior corrosion resistance of aluminized sample compared to bare X65 in preliminary room-temperature HCl immersion tests. The details of the corrosion test and reaction mechanisms on the bare and aluminized samples are presented in the supplementary information.

Figure 4. XPS spectra for Al 2p core levels from (a) an as-aluminized, (b) aluminized-annealed, and (c) aluminized-fouled X65 substrate. The Al oxide state is present in all conditions. The relative decrease of the peak intensity of the metallic Al in annealed and fouled samples reveals the growth of Al_2O_3 layer. (d) XPS spectrum of S 2p obtained from the aluminized-fouled sample. The peak at 169 eV signifies the presence of an aluminum sulfate deposit at the surface. No metal sulfide peak is identified after the fouling experiment. (e) and (f) Cross-sectional STEM micrographs of an aluminized-fouled X65 steel surface at two different magnifications showing a ~ 10 nm thick protective oxide layer formed during fouling tests. Other than a thicker oxide, the sample does not show any discernable deposit build-up at the top surface and resembles the as-aluminized samples.

It is crucial for the oxide to have the ability to reform, as even an amorphous, native aluminum oxide can grow in thickness (from prolonged exposure to elevated temperatures) and transform to a deleterious γ -alumina above a critical thickness susceptible to delamination.³⁷ In the aluminization process, unlike applied coatings, the aluminum diffuses into the steel and establishes an Al reservoir for the formation and healing of the passivating oxide. Therefore, the aluminum source in the substrate enables the reformation of the protective layer if there were any surface

1
2
3 damage. In order to examine the reformation of the passivating layer in aluminized samples, the
4
5 as-aluminized surface was first polished to remove the existing protective oxide layer and the top
6
7 surface of aluminized sample. A nanoindenter scratch test was performed along a 100 μm line with
8
9 a continuously increasing load from zero to a maximum load of 150 mN in order to determine the
10
11 desired depth of penetration. Accordingly, a scratch was made at a constant load of 50 mN and
12
13 depth of ~ 500 nm in order to deeply damage the surface while remaining in the aluminized region
14
15 considering the cross-sectional elemental analysis. Then, the sample was annealed in air at 350 $^{\circ}\text{C}$
16
17 for 1 hour (similar to the fouling experiment) for further analysis. The STEM cross-section image
18
19 of a representative scratch is shown in Figure 5a. The high magnification images confirm the
20
21 reformation of a ~ 10 and ~ 12 nm thick and uniform oxide layer both at the side and tip of the
22
23 scratch (Figure 5b and 5c). The results show that if the passivating oxide layer on the alloy steel is
24
25 damaged within the aluminized region, it can be reformed continuously from the Al reservoir.
26
27 Therefore, the reformation of the oxide layer is limited by the thickness of the aluminized region.
28
29 However, a benefit of the proposed aluminization process is that the thickness of the aluminized
30
31 region can be tuned by increasing the process time and temperature, or by increasing the aluminum
32
33 concentration in the pack.
34
35
36
37
38
39

40
41 It is noteworthy to mention that the XPS data for the aluminized-annealed and aluminized-fouled
42
43 samples (Figure 4b and 4c) confirms that the passivating aluminum oxide can grow in the air
44
45 within the scratch in a similar manner during the fouling tests. Additionally, considering less than
46
47 1 at. % Fe content at the surface of the aluminized coupon and assuming a pure Al surface, since
48
49 the autoclave for the fouling test is sealed in air, at 350 $^{\circ}\text{C}$ the standard free energy of the oxidation
50
51 reaction ($2/3 \text{ Al} + 1/2 \text{ O}_2 = 1/3 \text{ Al}_2\text{O}_3$) can be calculated as -483.2 kJ/mol .³⁸ Thus the oxygen partial
52
53 pressure for the oxidation reaction to be in equilibrium is 9.9×10^{-81} , which would be well
54
55
56
57
58
59
60

exceeded in the autoclave during the fouling experiments and thermodynamically favor oxidation to occur.

Figure 5. (a) Cross-sectional STEM image of an aluminized sample after scratching the protective layer followed by annealing. High magnification STEM image of (b) tip and (c) side of the scratch showing the reformation of a thick and dense protective oxide layer.

As mentioned earlier, Fe_2Al_5 is the most stable compound among all Fe-Al binary compounds, which is formed unavoidably during low-temperature aluminization process.³¹⁻³² Fe-Al intermetallics show different mechanical properties. For instance, Al-rich intermetallic phases, such as Fe_2Al_5 , exhibits lower toughness compared to FeAl and Fe_3Al . Therefore, the application of this brittle intermetallic phase is often limited. Thus, post-processing heat treatment can be employed to transform the Al-rich phase to more desirable phases with superior toughness. After 24 hours of heat treatment at 700 °C, the initial aluminide phase of Fe_2Al_5 in the as-aluminized sample transformed into a higher toughness FeAl phase (Figure S2). The results of fouling experiments on aluminized-annealed coupons showed that the FeAl surface has similar anti-fouling behavior to Al-rich Fe_2Al_5 intermetallic (Figure S3). The area normalized mass gain of the aluminized-annealed samples was not significant. The results of the post-processing heat treatment and fouling experiments are presented in the supplementary information.

The mechanical properties of bare and aluminized X65 were investigated using tensile experiments. Figure 6 reveals the comparison of the yield strength of the bare annealed and aluminized X65. The yield strength of the bare X65 ranged from 501.9 MPa to 579.0 MPa with an average of 548.7 ± 30.3 MPa, and the aluminized specimens demonstrated a range from 456.4 MPa to 602.0 MPa with an average strength of 543.0 ± 52.1 MPa. The results showed no significant difference between the mechanical properties of the bare and aluminized samples, and the yield strength of X65 remained constant after the aluminization process. Therefore, the results confirmed that the aluminized layer enables superior environmental compatibility without sacrificing mechanical properties. These findings are significant because if the aluminization process were conducted at a higher temperature, leading to massive grain growth, or resulting in poor surface properties to initiate flaws, the mechanical properties of the aluminized steel would have degraded compared to the bare steel, which is not desirable for real applications.

Considering the low temperature of the process, it is noteworthy that the as-machined X65 sample also revealed similar mechanical strength. The mechanical properties of the specimens are in good agreement with the previous literature data on X65 pipeline steel.³⁹⁻⁴¹ While the heat treatment conditions (temperature and time) is the major factor altering the mechanical properties of aluminized steel, previous studies showed that it is required to keep the thickness of the aluminized surface layer to a minimum value because of the brittle nature of aluminide layer and presence of pores.⁴² The surface layer failure results in the formation of cracks below the yield point of untreated steel, which lowers the strength of aluminized steel significantly. In this study, the thickness of the aluminized layer was about 10 μm , which did not reduce the mechanical strength of the specimen. Therefore, the aluminization process with a limited thickness of the aluminized layer does not affect the bulk tensile properties of X65 steel.

Figure 6. Comparison of tensile yield strength of the bare and aluminized X65 samples.

CONCLUSIONS

In conclusion, we demonstrated that low-temperature pack aluminization of low-carbon pipeline steel can be achieved without any detrimental effect on its mechanical properties. Surface aluminum enrichment enabled the formation of a stable intermetallic compound phase of Fe_2Al_5 , resulting in an enhanced hardness of the surface. The results showed that the aluminide intermetallic phase improves the resistance to asphaltene deposition because of the formation of a native Al_2O_3 oxide over hematite, which forms on the unmodified alloy. The uniform and continuous passivating Al_2O_3 oxide layer acts as a protective barrier to the reactive fouling environment, which mitigates the build-up of foulants and prohibits the outward diffusion of metal species from the steel. Since the aluminide layer is not a surface coating prone to delamination, and aluminum forms metallic bonds with the steel surface itself, it establishes a source for the formation and re-formation of the passivating oxide scale if damaged within the aluminized thickness. The results provide significant insight into the urgent and consequential problem of

asphaltene deposition by modifying established industrial processing techniques and using realistic fouling conditions. While the proposed technique can contribute to the development of a surface modification for large scale industrial components prone to fouling and sulfidic corrosion in downstream applications, the ideas presented in this manuscript may have applicability beyond this for other fouling and corrosion applications, as well as to improve the thermal stability and mechanical properties of nanostructured coatings.

ACKNOWLEDGEMENTS

The authors would like to thank the Seitz Materials Research Laboratory's (MRL) shared research facilities at the University of Illinois at Urbana-Champaign, most of the research was conducted here. The authors are also thankful for the microbalance in Prof. Shan J. Dillon's lab at the University of Illinois at Urbana-Champaign where the deposit mass gain measurements were conducted. Many thanks to Ernest P. Northern at the MRL Machine Shop for machining the custom autoclave sample mount. Most importantly, the authors would like to acknowledge the technical and financial support from BP through the BP International Centre for Advanced Materials (BP-ICAM).

ORCID

Pralav P. Shetty: 0000-0002-0583-5707

Soheil Daryadel: 0000-0001-7318-1963

Peter Quayle: 0000-0002-0002-1894

Stephen Yeates: 0000-0003-1190-2280

Paul V. Braun: 0000-0003-4079-8160

Jessica A. Krogstad: 0000-0003-0628-0501

REFERENCES

- (1) Thawer, R.; Nicoll, D. C. A.; Dick, G. Asphaltene Deposition in Production Facilities. *SPE-18473-PA* **1990**, 5 (04), 475-480, DOI: 10.2118/18473-pa.
- (2) Leontaritis, K. J.; Ali Mansoori, G. Asphaltene Deposition: A Survey of Field Experiences and Research Approaches. *Journal of Petroleum Science and Engineering* **1988**, 1 (3), 229-239, DOI: [https://doi.org/10.1016/0920-4105\(88\)90013-7](https://doi.org/10.1016/0920-4105(88)90013-7).
- (3) Buckley, J. S. Asphaltene Deposition. *Energy & Fuels* **2012**, 26 (7), 4086-4090, DOI: 10.1021/ef300268s.
- (4) Buenrostro-Gonzalez, E.; Lira-Galeana, C.; Gil-Villegas, A.; Wu, J. Asphaltene Precipitation in Crude Oils: Theory and Experiments. *AIChE Journal* **2004**, 50 (10), 2552-2570, DOI: 10.1002/aic.10243.
- (5) Kamran Akbarzadeh, A. H., Abdel Kharrat, Dan Zhang, Stephan Allenson, Jefferson Creek, Shah Kabir, A. (Jamal) Jamaluddin, Alan G. Marshall, Ryan P. Rodgers, Oliver C. Mullins, Trond Solbakken Asphaltenes — Problematic but Rich in Potential. *Oilfield Review* **2007**, 22-43.
- (6) Gharbi, K.; Benyounes, K.; Khodja, M. Removal and Prevention of Asphaltene Deposition During Oil Production: A Literature Review. *Journal of Petroleum Science and Engineering* **2017**, 158, 351-360, DOI: 10.1016/j.petrol.2017.08.062.
- (7) ChangMin Chun, M. A. G., Thomas Bruno, Ian A. Cody, Trikur A. Ramanarayanan Chromium-enriched Oxide Containing Material and Preoxidation Method of Making the Same to Mitigate Corrosion and Fouling Associated with Heat Transfer Components. US8037928B2, 2013.
- (8) Mark A. Greaney, T. B., Ashley E. Cooper, Ian A. Cody, ChangMin Chun, Corrosion Resistant Material for Reduced Fouling, A Heat Transfer Component Having Reduced Fouling and A Method for Reducing Fouling in A Refinery. US8201619B2, 2012.
- (9) Díaz, B.; Härkönen, E.; Światowska, J.; Maurice, V.; Seyeux, A.; Marcus, P.; Ritala, M. Low-temperature Atomic Layer Deposition of Al₂O₃ Thin Coatings for Corrosion Protection of Steel: Surface and Electrochemical Analysis. *Corrosion Science* **2011**, 53 (6), 2168-2175, DOI: 10.1016/j.corsci.2011.02.036.
- (10) Alboudwarej, H.; Pole, D.; Svrcek, W. Y.; Yarranton, H. W. Adsorption of Asphaltenes on Metals. *Industrial & Engineering Chemistry Research* **2005**, 44 (15), 5585-5592, DOI: 10.1021/ie048948f.
- (11) Shetty, P. P.; Zhang, R.; Haire, B. T.; Smith, C. S.; Kenny, L. M.; Wu, T.; Subramani, V.; Morrison, J. J.; Quayle, P.; Yeates, S.; Braun, P. V.; Krogstad, J. A. Effect of Surface Chemistry and Roughness on the High-Temperature Deposition of a Model Asphaltene. *Energy & Fuels* **2019**, 33 (5), 4104-4114, DOI: 10.1021/acs.energyfuels.9b00386.
- (12) Groner, M. D.; Fabreguette, F. H.; Elam, J. W.; George, S. M. Low-Temperature Al₂O₃ Atomic Layer Deposition. *Chemistry of Materials* **2004**, 16 (4), 639-645, DOI: 10.1021/cm0304546.
- (13) Angarita, G.; Palacio, C.; Trujillo, M.; Arroyave, M. Synthesis of Alumina Thin Films Using Reactive Magnetron Sputtering Method. *Journal of Physics: Conference Series* **2017**, 850, 012022, DOI: 10.1088/1742-6596/850/1/012022.
- (14) Niska, R. H.; Constant, A. P.; Witt, T.; Gregory, O. J. Chemical Vapor Deposition of Alpha Aluminum Oxide for High-temperature Aerospace Sensors. *Journal of Vacuum Science & Technology A* **2000**, 18 (4), 1653-1658, DOI: 10.1116/1.582401.
- (15) Wang, T. H.; Seigle, L. L. The Kinetics of Pack Aluminization of Iron from AlFe Alloy Packs. *Materials Science and Engineering: A* **1989**, 108, 253-263, DOI: [https://doi.org/10.1016/0921-5093\(89\)90428-0](https://doi.org/10.1016/0921-5093(89)90428-0).
- (16) Jedlinski, J. The Oxidation Behaviour of FeCrAl 'Alumina Forming' Alloys at High Temperatures. *Solid State Ionics* **1997**, 101-103, 1033-1040, DOI: [https://doi.org/10.1016/S0167-2738\(97\)00299-3](https://doi.org/10.1016/S0167-2738(97)00299-3).
- (17) Shetty, P. P.; Emigh, M. G.; Krogstad, J. A. Coupled Oxidation Resistance and Thermal Stability in Sputter Deposited Nanograined Alloys. *Journal of Materials Research* **2018**, 34 (1), 48-57, DOI: 10.1557/jmr.2018.403.

- (18) Johnson, R. W.; Hultqvist, A.; Bent, S. F. A Brief Review of Atomic Layer Deposition: from Fundamentals to Applications. *Materials Today* **2014**, *17* (5), 236-246, DOI: 10.1016/j.mattod.2014.04.026.
- (19) Wigren, J. Technical Note: Grit Blasting as Surface Preparation before Plasma Spraying. *Surface and Coatings Technology* **1988**, *34* (1), 101-108, DOI: [https://doi.org/10.1016/0257-8972\(88\)90093-X](https://doi.org/10.1016/0257-8972(88)90093-X).
- (20) Campestrini, P.; van Westing, E. P. M.; de Wit, J. H. W. Influence of Surface Preparation on Performance of Chromate Conversion Coatings on Alclad 2024 Aluminium Alloy: Part II: EIS Investigation. *Electrochimica Acta* **2001**, *46* (17), 2631-2647, DOI: [https://doi.org/10.1016/S0013-4686\(01\)00476-5](https://doi.org/10.1016/S0013-4686(01)00476-5).
- (21) Kumar, A.; Stephenson, L. D.; Murray, J. N. Self-healing Coatings for Steel. *Progress in Organic Coatings* **2006**, *55* (3), 244-253, DOI: 10.1016/j.porgcoat.2005.11.010.
- (22) White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. Autonomic Healing of Polymer Composites. *Nature* **2001**, *409* (6822), 794-797, DOI: 10.1038/35057232.
- (23) Meier, G. H.; Cheng, C.; Perkins, R. A.; Bakker, W. Diffusion Chromizing of Ferrous Alloys. *Surface and Coatings Technology* **1989**, *39-40*, 53-64, DOI: [https://doi.org/10.1016/0257-8972\(89\)90040-6](https://doi.org/10.1016/0257-8972(89)90040-6).
- (24) Bozza, F.; Bolelli, G.; Giolli, C.; Giorgetti, A.; Lusvardi, L.; Sassatelli, P.; Scrivani, A.; Candelì, A.; Thoma, M. Diffusion Mechanisms and Microstructure Development in Pack Aluminizing of Ni-based Alloys. *Surface and Coatings Technology* **2014**, *239*, 147-159, DOI: 10.1016/j.surfcoat.2013.11.034.
- (25) Shetty, P. P.; Zhang, R.; Angle, J. P.; Braun, P. V.; Krogstad, J. A. Pack Aluminization Assisted Enhancement of Thermo-mechanical Properties in Nickel Inverse Opal Structures. *Chemistry of Materials* **2018**, *30* (5), 1648-1654, DOI: 10.1021/acs.chemmater.7b04988.
- (26) Wang, Y. Q.; Zhang, Y.; Wilson, D. A. Formation of Aluminide Coatings on Ferritic–Martensitic Steels by a Low-Temperature Pack Cementation Process. *Surface and Coatings Technology* **2010**, *204* (16), 2737-2744, DOI: <https://doi.org/10.1016/j.surfcoat.2010.02.025>.
- (27) Xiang, Z. D.; Rose, S. R.; Datta, P. K. Low-temperature Formation and Oxidation Resistance of Nickel Aluminide/Nickel Hybrid Coatings on Alloy Steels. *Scripta Materialia* **2008**, *59* (1), 99-102, DOI: <https://doi.org/10.1016/j.scriptamat.2008.02.034>.
- (28) Oliver, W. C.; Pharr, G. M. Measurement of Hardness and Elastic Modulus by Instrumented Indentation: Advances in Understanding and Refinements to Methodology. *Journal of Materials Research* **2011**, *19* (1), 3-20, DOI: 10.1557/jmr.2004.19.1.3.
- (29) Standard Test Methods for Tension Testing of Metallic Materials.
- (30) Speich, G. R.; Leslie, W. C. Tempering of Steel. *Metallurgical Transactions* **1972**, *3* (5), 1043-1054, DOI: 10.1007/bf02642436.
- (31) Xiang, Z. D.; Datta, P. K. Pack Aluminisation of Low Alloy Steels at Temperatures below 700 °C. *Surface and Coatings Technology* **2004**, *184* (1), 108-115, DOI: 10.1016/j.surfcoat.2003.10.046.
- (32) Xiang, Z. D.; Datta, P. K. Kinetics of Low-temperature Pack Aluminide Coating Formation on Alloy Steels. *Metallurgical and Materials Transactions A* **2006**, *37* (11), 3359-3365, DOI: 10.1007/bf02586170.
- (33) Liu, Y.; Chong, X.; Jiang, Y.; Zhou, R.; Feng, J. Mechanical Properties and Electronic Structures of Fe-Al Intermetallic. *Physica B: Condensed Matter* **2017**, *506*, 1-11, DOI: 10.1016/j.physb.2016.10.032.
- (34) Kobayashi, S.; Yakou, T. Control of Intermetallic Compound Layers at Interface Between Steel and Aluminum by Diffusion-treatment. *Materials Science and Engineering: A* **2002**, *338* (1), 44-53, DOI: [https://doi.org/10.1016/S0921-5093\(02\)00053-9](https://doi.org/10.1016/S0921-5093(02)00053-9).
- (35) Liao, C. M.; Olive, J. M.; Gao, M.; Wei, R. P. In-Situ Monitoring of Pitting Corrosion in Aluminum Alloy 2024. *CORROSION* **1998**, *54* (6), 451-458, DOI: 10.5006/1.3284873.
- (36) Davoodi, A.; Pan, J.; Leygraf, C.; Norgren, S. In Situ Investigation of Localized Corrosion of Aluminum Alloys in Chloride Solution Using Integrated EC-AFM/SECM Techniques. *Electrochemical and Solid-State Letters* **2005**, *8* (6), B21-B24.

(37) Trunov, M. A.; Schoenitz, M.; Zhu, X.; Dreizin, E. L. Effect of Polymorphic Phase Transformations in Al_2O_3 Film on Oxidation Kinetics of Aluminum Powders. *Combustion and Flame* **2005**, *140* (4), 310-318, DOI: <https://doi.org/10.1016/j.combustflame.2004.10.010>.

(38) Ghosh, D.; Kay, D. A. R. Standard Free Energy of Formation of Alumina. *Journal of The Electrochemical Society* **1977**, *124* (12), 1836-1845.

(39) Fatoba, O.; Akid, R. Low Cycle Fatigue Behaviour of API 5L X65 Pipeline Steel at Room Temperature. *Procedia Engineering* **2014**, *74*, 279-286, DOI: 10.1016/j.proeng.2014.06.263.

(40) El-Danaf, E.; Baig, M.; Almajid, A.; Alshalfan, W.; Al-Mojil, M.; Al-Shahrani, S. Mechanical, Microstructure and Texture Characterization of API X65 Steel. *Materials & Design* **2013**, *47*, 529-538, DOI: 10.1016/j.matdes.2012.12.031.

(41) Kingklang, S.; Uthaisangsuk, V. Plastic Deformation and Fracture Behavior of X65 Pipeline Steel: Experiments and Modeling. *Engineering Fracture Mechanics* **2018**, *191*, 82-101, DOI: 10.1016/j.engfracmech.2018.01.026.

(42) Yürektürk, Y.; Baydoğan, M. Effect of Aluminizing and Austempering Processes on Structural, Mechanical and Wear Properties of a SSF Ductile Iron. *Materials Research Express* **2018**, *6* (1), 016550, DOI: 10.1088/2053-1591/aae804.

Figure 1. (a) Schematic of the crucible nesting technique used in the low-temperature pack aluminization process. The X65 coupons are embedded in a high activity aluminizing pack prior to the thermal activation in an inert environment. (b) Optical plan view micrograph of an as-aluminized X65 coupon showing the typical surface morphology. (c) and (d) SEM images of the cross-section of the aluminized surface at two different magnifications. The distinctive layers suggest the formation of an intermetallic region. (e) and (f) Detailed cross-sectional STEM micrographs of the aluminized layer showing a very thin native oxide layer formed because of air exposure.

Figure 2. (a) SEM micrograph of the indentation on the cross-section of the aluminide surface and (b) EDS analyses of the Al and Fe concentration profiles constituting the aluminized area. The downward arrow indicates the approximate position of the EDS Linescan. The concentration of Al is ~70 at.% in the top region (blue) and gradually decreases to zero within the interdiffusion zone (green). (c) GIXRD patterns corresponding to the Fe₂Al₅ phase attained from the as-aluminized surface. (d) Typical Load-depth plot obtained from nanoindentation on the cross-section of the aluminized and base X65. (e) Hardness distribution from the top surface to the base steel substrate. (f) The average hardness of aluminized and base X65 samples obtained from the nanoindentation test.

Figure 3. (a) Normalized mass gain of bare and aluminized X65 substrates after the high-temperature fouling test. No measurable mass gain was identified for the aluminized X65 coupon. The post-fouling optical micrographs of top surfaces show the drastic change in the (b) polished bare X65 coupons compared to almost no noticeable change in the (c) aluminized coupons. No foulant build-up was measured or seen on the surface of the aluminized substrate.

Figure 4. XPS spectra for Al 2p core levels from (a) an as-aluminized, (b) aluminized-annealed, and (c) aluminized-fouled X65 substrate. The Al oxide state is present in all conditions. The relative decrease of the peak intensity of the metallic Al in annealed and fouled samples reveals the growth of Al₂O₃ layer. (d) XPS spectrum of S 2p obtained from the aluminized-fouled sample. The peak at 169 eV signifies the presence of an aluminum sulfate deposit at the surface. No metal sulfide peak is identified after the fouling experiment. (e) and (f) Cross-sectional STEM micrographs of an aluminized-fouled X65 steel surface at two different magnifications showing a ~10 nm thick protective oxide layer formed during fouling tests. Other than a thicker oxide, the sample does not show any discernable deposit build-up at the top surface and resembles the as-aluminized samples.

Figure 5. (a) Cross-sectional STEM image of an aluminized sample after scratching the protective layer followed by annealing. High magnification STEM image of (b) tip and (c) side of the scratch showing the reformation of a thick and dense protective oxide layer.

Figure 6. Comparison of tensile yield strength of the bare and aluminized X65 samples.

TOC/Abstract graphic